

CHAPTER 12

INTERMOLECULAR FORCES: LIQUIDS AND SOLIDS

PRACTICE EXAMPLES

1A (E) 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 $-78.44^\circ C$ for CO_2 , $-42.1^\circ C$ for C_3H_8 , and $81.6^\circ C$ for CH_3CN .

1B (M) 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. $(CH_3)_3CH$ ($-11.6^\circ C$) < $CH_3CH_2CH_2CH_3$ ($-0.5^\circ C$) < SO_3 ($44.8^\circ C$) < C_8H_{18} ($125.7^\circ C$) < C_6H_5CHO ($178^\circ C$)

2A (E) Values of $\Delta_{\text{vap}}H$ 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 (M)

$$\Delta_{\text{overall}}H = \Delta_{\text{cond}}H + \Delta_{\text{cooling}}H$$

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

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

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

- 3A (E)** $d = 0.701 \text{ g/L}$ at $25 \text{ }^\circ\text{C}$ for C_6H_{14} (molar mass = $86.177 \text{ g mol}^{-1}$)
Consider a 1.00 L sample. This contains $0.701 \text{ g C}_6\text{H}_{14}$.

$$\text{moles C}_6\text{H}_{14} \text{ in } 1.00 \text{ L sample} = 0.701 \text{ g C}_6\text{H}_{14} \times \frac{1 \text{ mol C}_6\text{H}_{14}}{86.177 \text{ g C}_6\text{H}_{14}} = 8.13 \times 10^{-3} \text{ mol C}_6\text{H}_{14}$$

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

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

- 3B (M)** From Figure 12-9, the vapor pressure is $\approx 420 \text{ mmHg}$ or

$$420 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.553 \text{ atm}$$

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

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

- 4A (E)** We first calculate pressure created by the water at $80.0 \text{ }^\circ\text{C}$, assuming all $0.132 \text{ g H}_2\text{O}$ vaporizes.

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

$$= 307 \text{ mmHg}$$

At $80.0 \text{ }^\circ\text{C}$, the vapor pressure of water is 355.1 mmHg , thus, all the water exists as vapor.

- 4B (E)** The result of Example 12-3 is that $0.132 \text{ g H}_2\text{O}$ 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 (M)** From Table 12.4 we know that $\Delta_{\text{vap}}H = 37.4 \text{ kJ/mol}$ for methanol. We now can use the Clausius-Clapeyron equation to determine the vapor pressure at $25.0 \text{ }^\circ\text{C} = 298.2 \text{ K}$.

$$\ln \frac{P}{100 \text{ mmHg}} = -\frac{37.4 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{298.2 \text{ K}} - \frac{1}{(273.2 + 21.2) \text{ K}} \right) = +0.195$$

$$\frac{P}{100 \text{ mmHg}} = e^{+0.195} = 1.22 \quad P = 1.22 \times 100 \text{ mmHg} = 122 \text{ mmHg}$$

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

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

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

- 6A (M)** We first look to molar masses: Ne (20.2 g/mol), He (4.0 g/mol), Cl_2 (70.9 g/mol), $(\text{CH}_3)_2\text{CO}$ (58.1 g/mol), O_2 (32.0 g/mol), and O_3 (48.0 g/mol). Both $(\text{CH}_3)_2\text{CO}$ and O_3 are polar, O_3 weakly so (because of its uneven distribution of electrons). We expect $(\text{CH}_3)_2\text{CO}$ 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 ($-268.9 \text{ }^\circ\text{C}$), Ne ($-245.9 \text{ }^\circ\text{C}$), O_2 ($-183.0 \text{ }^\circ\text{C}$), O_3 ($-111.9 \text{ }^\circ\text{C}$), Cl_2 ($-34.6 \text{ }^\circ\text{C}$), and $(\text{CH}_3)_2\text{CO}$ ($56.2 \text{ }^\circ\text{C}$).

- 6B (M)** 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: $\text{H}_2 = 2.0 \text{ g/mol}$, $\text{CH}_4 = 16.0 \text{ g/mol}$, $\text{C}_6\text{H}_6 = 78.1 \text{ g/mol}$, 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 (M)** Moving from point R to P we begin with $\text{H}_2\text{O}(\text{g})$ at high temperature ($>100 \text{ }^\circ\text{C}$). When the temperature reaches the point on the vaporization curve, OC, water condenses at constant temperature ($100 \text{ }^\circ\text{C}$). 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 ($0 \text{ }^\circ\text{C}$). Once all of the water has been converted to $\text{H}_2\text{O}(\text{s})$, 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 ($\approx 10\%$) as ice is converted to liquid water. After melting, additional pressure produces very little change in volume because liquids are not very compressible.

7B (M)

1.00 mol H₂O. At point R, $T = 374.1\text{ }^\circ\text{C}$ 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 H₂O on P-R line, if 1/2 of water is vaporized, $T = 100\text{ }^\circ\text{C}$ (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

6A (M) We first look to molar masses: Ne (20.2 g/mol), He (4.0 g/mol), Cl₂ (70.9 g/mol), (CH₃)₂CO (58.1 g/mol), O₂ (32.0 g/mol), and O₃ (48.0 g/mol). Both (CH₃)₂CO and O₃ are polar, O₃ weakly so (because of its uneven distribution of electrons). We expect (CH₃)₂CO to have the highest boiling, followed by Cl₂, O₃, O₂, Ne, and He. In the following ranking, actual boiling points are given in parentheses. He ($-268.9\text{ }^\circ\text{C}$), Ne ($-245.9\text{ }^\circ\text{C}$), O₂ ($-183.0\text{ }^\circ\text{C}$), O₃ ($-111.9\text{ }^\circ\text{C}$), Cl₂ ($-34.6\text{ }^\circ\text{C}$), and (CH₃)₂CO ($56.2\text{ }^\circ\text{C}$)

6B (M) 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: H₂ = 2.0 g/mol , CH₄ = 16.0 g/mol , C₆H₆ = 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 C₆H₆ if CH₃NO₂ were nonpolar. But the molecule is definitely polar. Thus, the strong dipole-dipole forces developed between CH₃NO₂ molecules make the enthalpy of vaporization for CH₃NO₂ larger than that for C₆H₆, which is, of course, essentially non-polar.

8A (E) 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 Ga₂O₃ or Ca₃N₂, or both, such as AlN or Mg₃N₂.

8B (E) 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 (E) 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, $r = 227$ pm. Then $l = 4 \times 227 \text{ pm} / \sqrt{3} = 524$ pm

9B (M) 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 (M) 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:

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

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

The tabulated density of potassium at 20 °C is 0.86 g/cm³.

10B (M) 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 \times 8 corner atoms/unit cell) + (1/2 face atom \times 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.

$$\begin{aligned} \frac{\text{mass}}{\text{Al atom}} &= \frac{2.6984 \text{ g Al}}{1 \text{ cm}^3} \times \left(\frac{100 \text{ cm}}{1 \text{ m}} \times \frac{1 \text{ m}}{10^{12} \text{ pm}} \right)^3 \times \frac{6.628 \times 10^7 \text{ pm}^3}{1 \text{ unit cell}} \times \frac{1 \text{ unit cell}}{4 \text{ Al atoms}} \\ &= 4.471 \times 10^{-23} \text{ g/Al atom} \end{aligned}$$

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

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

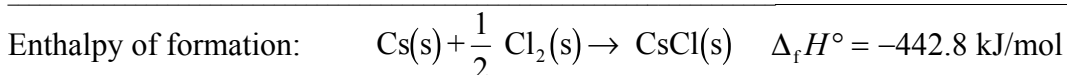
11B (M) Since NaCl is fcc, the Na^+ ions are in the same locations as were the Al atoms in Practice Example 12-10B, and there are 4 Na^+ ions per unit cell. For stoichiometric reasons, there must also be 4 Cl^- ions per unit cell. These are accounted for as follows: there is one Cl^- along each edge, 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 =

$$\left(\frac{1}{4} \text{Cl}^- \text{ on edge} \times 12 \text{ edges per unit cell} \right) + 1 \text{Cl}^- \text{ in body center} = 4 \text{Cl}^- / \text{unit cell.}$$

The volume of this cubic unit cell is the cube of its length. The density is:

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

12A (M) Sublimation of Cs:	$\text{Cs(s)} \rightarrow \text{Cs(g)}$	$\Delta_{\text{sub}}H = +78.2 \text{ kJ/mol}$
Ionization of Cs(g):	$\text{Cs(g)} \rightarrow \text{Cs}^+(\text{g}) + e^-$	$E_1 = +375.7 \text{ kJ/mol}$ (Table 9.3)
$\frac{1}{2}$ Dissociation of $\text{Cl}_2(\text{g})$:	$\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$	$DE = \frac{1}{2} \times 243 \text{ kJ} = 121.5 \text{ kJ/mol}$ (Table 10.3)
Cl(g) electron affinity:	$\text{Cl(g)} + e^- \rightarrow \text{Cl}^-(\text{g})$	$E_{\text{ea}1} = -349.0 \text{ kJ/mol}$ (Figure 9-12)
Lattice energy:	$\text{Cs}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{CsCl(s)}$	L.E.



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

$$\text{L.E.} = -442.8 \text{ kJ} - 226.4 \text{ kJ} = -669.2 \text{ kJ/mol}$$

12B (M) Sublimation:	$\text{Ca(s)} \rightarrow \text{Ca(g)}$	$\Delta_{\text{sub}}H = +178.2 \text{ kJ/mol}$
First ionization energy:	$\text{Ca(g)} \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$	$E_{i,1} = +590 \text{ kJ/mol}$
Second ionization energy:	$\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g}) + \text{e}^-$	$E_{i,2} = +1145 \text{ kJ/mol}$
Dissociation energy:	$\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl(g)}$	$\text{D.E.} = (2 \times 122) \text{ kJ/mol}$
Electron Affinity:	$2 \text{Cl(g)} + 2 \text{e}^- \rightarrow 2\text{Cl}^-(\text{g})$	$2 \times E_{\text{ea}} = 2(-349) \text{ kJ/mol}$
Lattice energy:	$\text{Ca}^{2+}(\text{g}) + 2 \text{Cl}^-(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$	$\text{L.E.} = -2223 \text{ kJ/mol}$
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Enthalpy of formation:	$\text{Ca(s)} + \text{Cl}_2(\text{s}) \rightarrow \text{CaCl}_2(\text{s})$	$\Delta_{\text{f}}H^\circ = ?$
$\Delta_{\text{f}}H^\circ = \Delta_{\text{sub}}H + E_{i,1} + E_{i,2} + \text{D.E.} + (2 \times E_{\text{ea}}) + \text{L.E.}$		
$= 178.2 \text{ kJ/mol} + 590 \text{ kJ/mol} + 1145 \text{ kJ/mol} + 244 \text{ kJ/mol} - 698 \text{ kJ/mol} - 2223 \text{ kJ/mol}$		
$= -764 \text{ kJ/mol}$		

INTEGRATIVE EXAMPLE

A. (M) 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.

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

$$P = e^{-2.87} \times 760 \text{ mmHg} = 43.1 \text{ mmHg} \text{ which is higher than H}_2\text{O's vapor pressure.}$$

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

Sublimation of Mg(s):	$\text{Mg(s)} \longrightarrow \text{Mg(g)}$	$\Delta_{\text{sub}}H = +146 \text{ kJ}$
First ionization of Mg(g):	$\text{Mg(g)} \longrightarrow \text{Mg}^+(\text{g}) + \text{e}^-$	$E_{i,1} = +737.7 \text{ kJ}$
Second ionization of Mg(g):	$\text{Mg}^+(\text{g}) \longrightarrow \text{Mg}^{2+}(\text{g}) + \text{e}^-$	$E_{i,2} = +1451 \text{ kJ}$
$\frac{1}{2}$ Dissociation of O ₂ (g):	$\frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{O(g)}$	$\Delta_{\text{dis}}H = +249 \text{ kJ}$
First electron affinity:	$\text{O(g)} + \text{e}^- \longrightarrow \text{O}^-(\text{g})$	$E_{\text{ea},1} = -141.0 \text{ kJ}$
Second electron affinity:	$\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	$E_{\text{ea},2}$
Lattice energy:	$\text{Mg}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \longrightarrow \text{MgO(s)}$	$\text{L.E.} = -3925 \text{ kJ}$
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Enthalpy of formation:	$\text{Mg(s)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{MgO(s)}$	$\Delta_{\text{f}}H^\circ = -601.7 \text{ kJ}$

$$-601.7 \text{ kJ} = +146 \text{ kJ} + 737.7 \text{ kJ} + 1451 \text{ kJ} + 249 \text{ kJ} - 141.0 \text{ kJ} + E_{\text{ea},2} - 3925 \text{ kJ}$$

$$E_{\text{ea},2} = +881 \text{ kJ}$$

EXERCISES

Intermolecular Forces

1. (M)

- (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 Br₂ 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 Br₂ than in HCl since Br₂ has more electrons (i.e., is more polarizable).
- (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 Br₂ 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 CH₄, 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 CH₄ has a very low critical temperature.

- 2. (M)** Substituting Cl for H makes the molecule heavier (and thus increases London forces) and polar, which results in the formation of dipole–dipole interactions. Both of these effects make it more difficult to disrupt the forces of attraction between molecules, increasing the boiling point. Substitution of Br for Cl increases the London forces, but makes the molecule less polar. Since London forces in this case are more important than dipole–dipole interactions, the boiling point increases yet again. Finally, substituting OH for Br decreases London forces but both increases the dipole-dipole interactions and creates opportunities for hydrogen bonding. Since hydrogen bonds are much stronger than London forces, the boiling point increases even further.

3. (E)

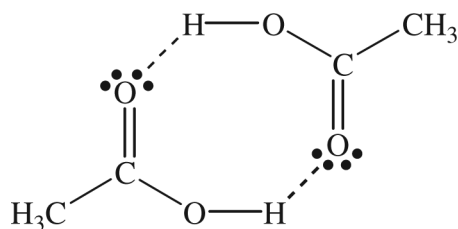
(c) < (b) < (d) < (a)
 (ethane thiol) (ethanol) (butanol) (acetic acid)

Viscosity will depend on the intermolecular forces. The stronger the intermolecular bonding, the more viscous the substance.

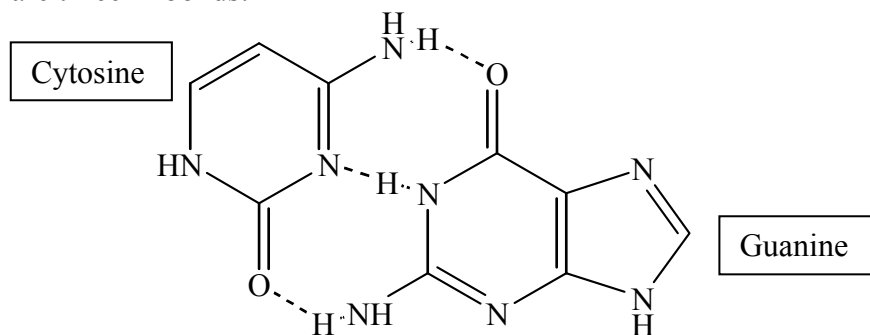
4. (E)
 (d) < (b) < (a) < (c)
 (butane) (carbon disulfide) (ethanol) (1,2-dihydroxyethane)

The boiling point is dependent on the intermolecular forces. Hence, hydrogen bonding produces the strongest interactions (highest boiling point) and non-polar molecules like butane and CS_2 have the lowest boiling point. We must also consider the effect of Van der Waals forces.

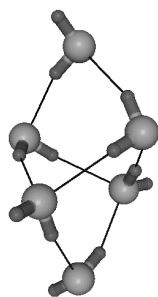
5. (E) We expect CH_3OH to be a liquid from among the four substances listed. Of these four molecules, C_3H_8 has the most electrons and should have the strongest London forces. However, only CH_3OH satisfies the conditions for hydrogen bonding (H bonded to and attracted to N, O, or F) and thus its intermolecular attractions should be much stronger than those of the other substances.
6. (E)
- (a) The conditions for hydrogen bonding are not satisfied in this molecule (i.e., hydrogen bonding requires an H atom covalently bonded to a N, an O, or an F atom, and that H atom is also attracted to another N, O, or F atom). Although there is an O in this molecule, none of the H atoms are bonded to it. The molecule forms neither intramolecular nor intermolecular hydrogen bonds.
- (b) Intramolecular hydrogen bonding is probably not important in CH_3NH_2 . The two H atoms will interact with the lone pair on the N atom in another molecule. Therefore, intermolecular hydrogen bonding will be more important than intramolecular hydrogen bonding.
- (c) Intramolecular hydrogen bonding is probably important in $\text{CH}_3\text{CH}_2\text{CHFCH}_2\text{OH}$. The H atom of the hydroxyl group can interact with the lone pairs on the nearby F atom.
- (d) In orthophthalic acid, intramolecular hydrogen bonds can occur. The H of one $-\text{COOH}$ group can be attracted to one of the O atoms of the other $-\text{COOH}$ group. The resulting ring is seven atoms around and thus should not cause substantial bond angle strain.
7. (M) 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.
8. (M) Two hydrogen bonds can occur between two acetic acid molecules. The interaction is shown below:



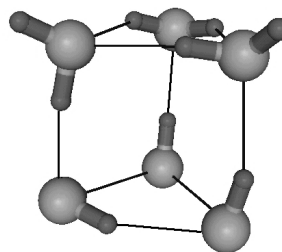
- 9. (M)** There are three H-bonds:



- 10. (D)** See the figures below:



Cage



Prism

Surface Tension and Viscosity

- 11. (E)** 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.
- 12. (E)** Both surface tension and viscosity deal with the work needed to overcome the attractions between molecules. Increasing the temperature of a liquid sample causes the molecules to move faster. Some of the work has been done by adding thermal energy (heat) and less work needs to be done by the experimenter, consequently, both surface tension and viscosity decrease. The vapor pressure is a measure of the concentration of molecules that have broken free of the surface. As thermal energy is added to the liquid sample, more and more molecules have enough energy to break free of the surface, and the vapor pressure increases.
- 13. (E)** 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.”

14. (E) The product can lower the surface tension of water. Then the water can more easily wet a solid substance, because a greater surface area of water can be created with the same energy. (Surface tension equals the work needed to create a given quantity of surface area.) This greater water surface area means a greater area of contact with a solid object, such as a piece of fabric. More of the fabric being in contact with the water means that the water is indeed wetter.
15. (E) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 < \text{CH}_3\text{OH} < \text{HOCH}_2\text{CH}_2\text{OH}$. Although all three substances are polar, the CH_3OH and $\text{HOCH}_2\text{CH}_2\text{OH}$ molecules form hydrogen bonds. The surface tension of $\text{HOCH}_2\text{CH}_2\text{OH}$ is higher than that of CH_3OH because the $\text{HOCH}_2\text{CH}_2\text{OH}$ molecule is not only larger (more polarizable) but also able to form a greater number of hydrogen bonds because of the OH groups at either end.
16. (E) One would expect the surface tension in *t*-butyl alcohol to be less than *n*-butyl alcohol, because *t*-butyl alcohol is a more compact/spherical molecule, it has less molecular “surface area” for interaction with other *t*-butyl alcohol molecules, and therefore its van der Waals forces are weaker than *n*-butyl alcohol’s.
17. (E) The intermolecular interactions in butanol are dominated by H-bonding, which is much stronger than the London dispersion forces dominant in pentane.
18. (E) Simply put, if two substances (in this case, CCl_4 and Hg) have the same viscosity, that means that the magnitudes of their intramolecular/atomic interactions have to be about the same, even though the nature of these interactions can be significantly different. The intermolecular interactions in CCl_4 are primarily London dispersion, for Hg mainly metallic.

Vaporization

19. (E) 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.
20. (E) Vapor cannot form throughout the liquid at temperatures below the boiling point because, for vapor to form, it must overcome the atmospheric pressure (≈ 1 atm) or slightly more due to the pressure of the liquid. Formation of a bubble of vapor in the liquid, requires that it must push the liquid out of the way. This is not true at the surface. The vapor molecules simply move into the gas phase at the surface, which is mostly empty space.
21. (E) We use the quantity of heat to determine the number of moles of benzene that vaporize.

$$V = \frac{nRT}{P} = \frac{\left(1.54 \text{ kJ} \times \frac{1 \text{ mol}}{33.9 \text{ kJ}}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}}{95.1 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 8.88 \text{ L C}_6\text{H}_6(\text{l})$$

$$22. \quad \text{(E)} \quad n_{\text{acetonitrile}} = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 1.17 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{K}^{-1} \times (273.2 + 81.6) \text{ K}} = 0.0402 \text{ mol acetonitrile}$$

$$\Delta_{\text{vap}}H = \frac{1.00 \text{ kJ}}{0.0402 \text{ mol}} = 24.9 \text{ kJ/mol acetonitrile}$$

23. (M)

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

$$n_{\text{N}_2\text{H}_4} = 25.09 \text{ g N}_2\text{H}_4 \times \frac{1 \text{ mol N}_2\text{H}_4}{32.0452 \text{ g N}_2\text{H}_4} = 0.7830 \text{ mol}$$

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

$$q_{\text{heating}} = (n)(C)(\Delta t) = (0.78295 \text{ mol N}_2\text{H}_4) \left(\frac{98.84 \text{ J}}{1 \text{ mol N}_2\text{H}_4 \text{ }^\circ\text{C}} \right) (88.5 \text{ }^\circ\text{C}) = 6848.7 \text{ J or } 6.85 \text{ kJ}$$

$$q_{\text{vap}} = (n_{\text{N}_2\text{H}_4})(\Delta_{\text{vap}}H) = (0.78295 \text{ mol N}_2\text{H}_4) \left(\frac{43.0 \text{ kJ}}{1 \text{ mol N}_2\text{H}_4} \right) = 33.7 \text{ kJ}$$

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

24. (M) $\Delta_{\text{vap}}H$ for $\text{CH}_3\text{OH}(\text{l}) = 38.0 \text{ kJ mol}^{-1}$ at 298 K (assumes ΔH does not depend on temperature)
 $\Delta t = 30.0 \text{ }^\circ\text{C} - 20.0 \text{ }^\circ\text{C} = 10.0 \text{ }^\circ\text{C}$

$$n_{\text{CH}_3\text{OH}} = 215 \text{ g CH}_3\text{OH} \times \left(\frac{1 \text{ mol CH}_3\text{OH}}{32.0422 \text{ g CH}_3\text{OH}} \right) = 6.71 \text{ mol CH}_3\text{OH}$$

Raise temperature of liquid from 20.0 °C to 30.0 °C

$$q = (n)(C)(\Delta t) = (6.71 \text{ mol CH}_3\text{OH}) \left(\frac{81.1 \text{ J}}{1 \text{ mol CH}_3\text{OH }^\circ\text{C}} \right) (10.0 \text{ }^\circ\text{C}) = 5441.8 \text{ J or } 5.44 \text{ kJ}$$

Vaporize liquid at 30 °C (Use $\Delta_{\text{vap}}H$ at 25 °C and assume value is the same at 30 °C)

$$q_{\text{vap}} = (n_{\text{CH}_3\text{OH}})(\Delta_{\text{vap}}H) = (6.71 \text{ mol CH}_3\text{OH}) \left(\frac{38.0 \text{ kJ}}{1 \text{ mol CH}_3\text{OH}} \right) = 255 \text{ kJ}$$

$$q_{\text{overall}} = q_{\text{heating}} + q_{\text{vap}} = 5.44 \text{ kJ} + 255 \text{ kJ} = 260. \text{ kJ}$$

25. (M)

$$\text{heat needed} = 3.78 \text{ L H}_2\text{O} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \frac{0.958 \text{ g H}_2\text{O}}{1 \text{ cm}^3} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = 8.18 \times 10^3 \text{ kJ}$$

$$\text{amount CH}_4 \text{ needed} = 8.18 \times 10^3 \text{ kJ} \times \frac{1 \text{ mol CH}_4}{890 \text{ kJ}} = 9.19 \text{ mol CH}_4$$

$$V = \frac{nRT}{P} = \frac{9.19 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{K}^{-1} \times 296.6 \text{ K}}{768 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 221 \text{ L methane}$$

26. (M) If not all of the water vaporizes, the final temperature of the system will be 100.00 °C. Let us proceed on that assumption and modify our final state if this is not true. First we determine the heat available from the iron in cooling down, and then the heat needed to warm the water to boiling, and finally the mass of water that vaporizes.

$$\text{heat from Fe} = \text{mass} \times \text{sp.ht.} \times \Delta t = 50.0 \text{ g} \times \frac{0.45 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (100.00 \text{ }^\circ\text{C} - 152 \text{ }^\circ\text{C}) = -1.17 \times 10^3 \text{ J}$$

$$\text{heat to warm water} = 20.0 \text{ g} \times \frac{4.21 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (100.00 \text{ }^\circ\text{C} - 89 \text{ }^\circ\text{C}) = 9.3 \times 10^2 \text{ J}$$

mass of water vaporized:

$$= (11.7 \times 10^2 \text{ J available} - 9.3 \times 10^2 \text{ J used}) \times \frac{1 \text{ mol H}_2\text{O vaporized}}{40.7 \times 10^3 \text{ J}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}$$

$$= 0.11 \text{ g of water vaporize}$$

Clearly, all of the water does not vaporize and our initial assumption was valid.

Vapor Pressure and Boiling Point

27. (E)

(a) We read up the 100 °C line until we arrive at C₆H₇N curve (e). This occurs at about 45 mmHg.

(b) We read across the 760 mmHg line until we arrive at the C₇H₈ curve (d). This occurs at about 110 °C.

28. (E)

(a) The normal boiling point occurs where the vapor pressure is 760 mmHg, and thus $\ln P = 6.63$. For aniline, this occurs at about the uppermost data point (open circle) on the aniline line. This corresponds to $1/T = 2.18 \times 10^{-3} \text{ K}^{-1}$. Thus,

$$T_{\text{nbp}} = \frac{1}{2.18 \times 10^{-3} \text{ K}^{-1}} = 459 \text{ K.}$$

(b) 25 °C = 298 K = T and thus $1/T = 3.36 \times 10^{-3} \text{ K}^{-1}$. This occurs at about $\ln P = 6.25$. Thus, $P = e^{6.25} = 518 \text{ mmHg}$.

29. (E) Use the ideal gas equation, $n = \text{moles Br}_2 = 0.486 \text{ g Br}_2 \times \frac{1 \text{ mol Br}_2}{159.8 \text{ g Br}_2} = 3.04 \times 10^{-3} \text{ mol Br}_2$.

$$P = \frac{nRT}{V} = \frac{3.04 \times 10^{-3} \text{ mol Br}_2 \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}}{0.2500 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}}$$

$$= 226 \text{ mmHg}$$

- 30. (M)** We can determine the vapor pressure by using the ideal gas law.

$$P = \frac{nRT}{V} = \frac{\left(0.876 \text{ g } (\text{CH}_3)_2\text{CO} \times \frac{1 \text{ mol } (\text{CH}_3)_2\text{CO}}{58.08 \text{ g } (\text{CH}_3)_2\text{CO}}\right) \times \left(\frac{0.08206 \text{ L atm}}{\text{K mol}}\right) \times (32 + 273.15) \text{ K}}{1 \text{ L}}$$

$$= 0.378 \text{ atm}$$

$$P = 0.378 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 38.3 \text{ kPa}$$

- 31. (E)**

(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 °C. This is the maximum temperature that can be realized without pressurizing the apparatus.

- 32. (E)** When the can is heated, the vapor pressure of water inside the can is ~ 760 mm Hg. As the can cools, most of the water vapor in the can condenses to liquid and the pressure inside the can drops sharply to the vapor pressure of water at room temperature (≈ 25 mmHg). The pressure on the outside of the can is still near 760 mmHg. It is this huge difference in pressure that is responsible for the can being crushed.

- 33. (M)** Use the Clausius-Clapeyron equation, and the vapor pressure of water at 100.0 °C (373.2 K) and 120.0 °C (393.2 K) to determine $\Delta_{\text{vap}}H$ 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.

$$\ln \frac{1489.1 \text{ mmHg}}{760.0 \text{ mmHg}} = \frac{\Delta_{\text{vap}}H}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{373.2 \text{ K}} - \frac{1}{393.2 \text{ K}} \right) = 0.6726 = 1.639 \times 10^{-5} \Delta_{\text{vap}}H$$

$$\Delta_{\text{vap}}H = 4.104 \times 10^4 \text{ J/mol} = 41.04 \text{ kJ/mol}$$

$$\ln \frac{2.00 \text{ atm}}{1.00 \text{ atm}} = 0.6931 = \frac{41.04 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{373.2 \text{ K}} - \frac{1}{T} \right)$$

$$\left(\frac{1}{373.2 \text{ K}} - \frac{1}{T_{bp}} \right) = 0.6931 \times \frac{8.1345 \text{ K}^{-1}}{41.03 \times 10^3} = 1.404 \times 10^{-4} \text{ K}^{-1}$$

$$\frac{1}{T_{bp}} = \frac{1}{373.2 \text{ K}} - 1.404 \times 10^{-4} \text{ K}^{-1} = 2.539 \times 10^{-3} \text{ K}^{-1} \quad T_{bp} = 393.9 \text{ K} = 120.7 \text{ }^\circ\text{C}$$

34. (E)
- (a) We need the temperature at which the vapor pressure of water is 640 mmHg. This is a temperature between 95.0 °C (633.9 mmHg) and 96.0 °C (657.6 mmHg). We estimate a boiling point of 95.3 °C.
- (b) If the observed boiling point is 94 °C, the atmospheric pressure must equal the vapor pressure of water at 94 °C, which is, 611 mmHg.
35. (M) The 25.0 L of He becomes saturated with aniline vapor, at a pressure equal to the vapor pressure of aniline.

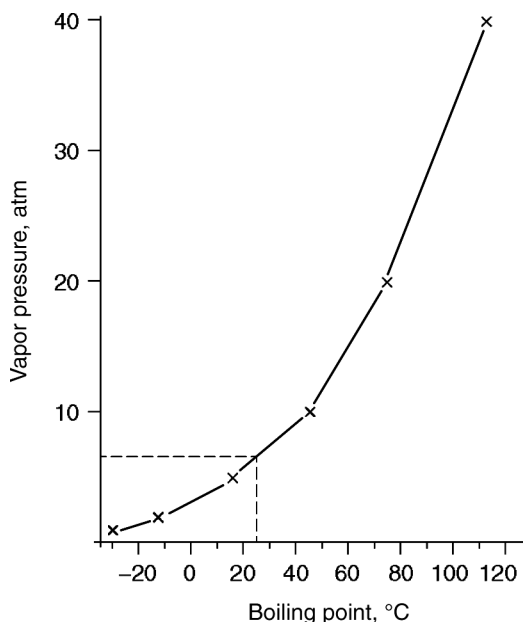
$$n_{\text{aniline}} = (6.220 \text{ g} - 6.108 \text{ g}) \times \frac{1 \text{ mole aniline}}{93.13 \text{ g aniline}} = 0.00120 \text{ mol aniline}$$

$$P = \frac{nRT}{V} = \frac{0.00120 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{K}^{-1} \times 303.2 \text{ K}}{25.0 \text{ L}} = 0.00119 \text{ atm} = 0.907 \text{ mmHg}$$

36. (M) The final pressure must be 742 mm Hg and the partial pressure of $\text{CCl}_4(\text{g})$ is constant at 261 mm Hg, thus, the partial pressure of N_2 must be 481 mm Hg. Using Dalton's law of partial pressures, $P_{\text{N}_2}/P_{\text{total}} = V_{\text{N}_2}/V_{\text{total}}$, the total and final pressures are known. Since the temperature does not change, the volume occupied by N_2 is constant at 7.53 L.

$$\text{Hence, } V_{\text{total}} = V_{\text{N}_2} \times \frac{P_{\text{total}}}{P_{\text{N}_2}} = 7.53 \text{ L} \times \frac{742 \text{ mmHg}}{481 \text{ mmHg}} = 11.6 \text{ L.}$$

37.
(M)



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

At a temperature of 25 °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.

- 38. (M)** At 27 °C, the vapor pressure of water is 26.7 mmHg. We use this value to determine the mass of water that can exist within the container as vapor.

$$\text{mass of water vapor} = \frac{\left(26.7 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times \left(1515 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right)}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (27 + 273) \text{ K}} = 0.00216 \text{ mol H}_2\text{O(g)}$$

$$\text{mass of water vapor} = 0.00216 \text{ mol H}_2\text{O(g)} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 0.0389 \text{ g H}_2\text{O(g)}$$

The Clausius-Clapeyron Equation

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

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

$$\ln \frac{10.0 \text{ mmHg}}{100.0 \text{ mmHg}} = \frac{\Delta_{\text{vap}}H}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{376.9 \text{ K}} - \frac{1}{329.2 \text{ K}} \right) = -2.30 = -4.624 \times 10^{-5} \Delta_{\text{vap}}H$$

$$\Delta_{\text{vap}}H = 4.97 \times 10^4 \text{ J/mol} = 49.7 \text{ kJ/mol}$$

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

$$T_1 = (5.0 + 273.2) \text{ K} = 278.2 \text{ K}$$

$$\ln \frac{760.0 \text{ mmHg}}{40.0 \text{ mmHg}} = 2.944 = \frac{38.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{278.2 \text{ K}} - \frac{1}{T_{\text{nbp}}} \right)$$

$$\left(\frac{1}{278.2 \text{ K}} - \frac{1}{T_{\text{nbp}}} \right) = 2.944 \times \frac{8.3145 \text{ K}^{-1}}{38.0 \times 10^3} = 6.44 \times 10^{-4} \text{ K}^{-1}$$

$$\frac{1}{T_{\text{nbp}}} = \frac{1}{278.2} - 6.44 \times 10^{-4} \text{ K}^{-1} = 2.95 \times 10^{-3} \text{ K}^{-1} \quad T_{\text{nbp}} = 339 \text{ K}$$

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

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

$$\ln \frac{760 \text{ mmHg}}{375 \text{ mmHg}} = \frac{25.5 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{T} - \frac{1}{329.4 \text{ K}} \right) = 0.706$$

$$\left(\frac{1}{T} - \frac{1}{329.4 \text{ K}} \right) = \frac{0.706 \times 8.3145}{25.5 \times 10^3} \text{ K}^{-1} = 2.30 \times 10^{-4} \text{ K}^{-1} = 1/T - 3.03_6 \times 10^{-3} \text{ K}^{-1}$$

$$1/T = (3.03_6 + 0.230) \times 10^{-3} \text{ K}^{-1} = 3.266 \times 10^{-3} \text{ K}^{-1} \quad T = 306 \text{ K} = 33 \text{ °C}$$

- 42. (M)** $P_1 = 40.0 \text{ Torr}$ $T_1 = -7.1 \text{ °C}$ (266 K) and $\Delta_{\text{vap}}H = 29.2 \text{ kJ mol}^{-1}$
 $P_2 = 760.0 \text{ Torr}$ $T_2 = ?$

$$\ln \left(\frac{760.0}{40.0} \right) = \frac{29,200 \text{ J}}{8.3145 \frac{\text{J}}{\text{K mol}}} \left(\frac{1}{266 \text{ K}} - \frac{1}{T_2} \right) \quad T_2 = 342.3 \text{ K or } \sim 69 \text{ °C}$$

(The literature boiling point for trichloromethane is 61 °C.)

- 43. (M)** Normal boiling point = 179 °C and critical point = 422 °C and 45.9 atm

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

$$\Delta_{\text{vap}}H = 41.2 \text{ kJ mol}^{-1}$$

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

- 44. (E)**

(a) The plot of $\ln P$ vs $1/T$ for benzene is located to the right of that for toluene. This tells us that, for a given temperature, the vapor pressure for toluene is lower than that for benzene, and thus benzene is a more volatile liquid than toluene.

(b) According to Figure 12-20, at 65 °C, the vapor pressure for benzene is ~ 450 mm Hg or 0.60 atm. We have been asked to estimate the temperature at which toluene has a vapor pressure of 0.60 atm. First, we find $\ln 450 = 6.11$ on the benzene curve of Figure 12-20. Then, we move horizontally to the left along $\ln P = 6.11$ until we reach the toluene curve. At this point on the toluene curve, the value of $1/T = 0.00273$. This corresponds to $T = 366 \text{ K}$.

Critical Point

- 45. (E)** Substances that can exist as a liquid at room temperature (about 20 °C) have critical temperature above 20 °C, 293 K. Of the substances listed in Table 12.6, $\text{CO}_2(T_c = 304.2 \text{ K})$, $\text{HCl}(T_c = 324.6 \text{ K})$, $\text{NH}_3(T_c = 405.7 \text{ K})$, $\text{SO}_2(T_c = 431.0 \text{ K})$, and $\text{H}_2\text{O}(T_c = 647.3 \text{ K})$ can exist in liquid form at 20 °C. In fact, CO_2 exists as a liquid in CO_2 fire extinguishers.
- 46. (E)** The critical temperature of SO_2 , 431.0 K, is above the temperature of 0 °C, 273 K. The critical pressure of SO_2 is 77.7 atm, which is below the pressure of 100 atm. Thus, SO_2 can be maintained as a liquid at 0 °C and 100 atm. The critical temperature of methane, CH_4 , is 191.1 K, which is below the temperature of 0 °C, 273 K. Thus, CH_4 cannot exist as a liquid at 0 °C, no matter what pressure is applied.

Melting and Freezing

- 47. (M)**

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

$$\Delta H = -776 \text{ kJ}$$

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

48. (M) The relevant reaction is $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$
 $\Delta_r H = \Delta_c H = [4(-285.8 \text{ kJ mol}^{-1}) + 3(-393.5 \text{ kJ mol}^{-1})] - (-103.8 \text{ kJ mol}^{-1})$
 $= -2219.9 \text{ kJ mol}^{-1} \text{ C}_3\text{H}_8(\text{g})$

$$n = \frac{PV}{RT} = \frac{\left(735 \text{ mmHg} \times \frac{1.013 \text{ bar}}{760 \text{ mm Hg}}\right)(1.60 \text{ L})}{(0.083145 \text{ L bar K}^{-1})(20 + 273.15 \text{ K})} = 0.0643 \text{ mol}$$

$$q_{\text{combustion}} = n \Delta_c H = 0.0643 \text{ mol C}_3\text{H}_8(\text{g}) \times (-2219.9 \text{ kJ mol}^{-1} \text{ C}_3\text{H}_8(\text{g}))$$

$$= -142.74 \text{ kJ}$$

From equation (12.3), the $\Delta_{\text{fus}}H$ of ice is 6.01 kJ mol^{-1} . Therefore, the moles of ice melted can be calculated from the available energy, and the mass of ice can be determined:

$$142.74 \text{ kJ} \times \frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \times \frac{18.02 \text{ g ice}}{1 \text{ mol ice}} = 428 \text{ g ice melted}$$

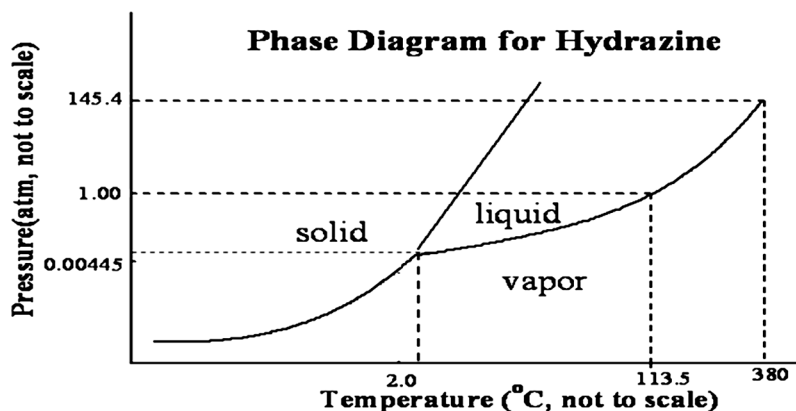
States of Matter and Phase Diagrams

49. (M) 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°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°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 $\sim 88.9 \text{ atm}$.

50. (M) The phase diagram for hydrazine is sketched below. The triple point is shown on the diagram at 0.00445 atm (3.4 mmHg) and 2°C . The normal boiling point is shown at 113.5°C and the critical point at 380°C and 145 atm . We are not certain of the slope and curvature of the lines in the diagram.



51. (M)

- (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 sublimates 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.

52. (D)

- (a) As heat is added initially, the temperature of the ice rises from $-20\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$. At (or just slightly below) $0\text{ }^{\circ}\text{C}$, ice begins to melt to liquid water. The temperature remains at $0\text{ }^{\circ}\text{C}$ until all of the ice has melted. Adding heat then warms the liquid until a temperature of about $93.5\text{ }^{\circ}\text{C}$ is reached, at which point the liquid begins to vaporize to steam. The temperature remains fixed until all the water is converted to steam. Adding heat then warms the steam to $200\text{ }^{\circ}\text{C}$. (Data for this part are taken from Figure 12-30 and Table 12.5.)
- (b) As the pressure is raised, initially gaseous iodine is just compressed. At $\sim 91\text{ mmHg}$, liquid iodine appears. As the pressure is pushed above 99 mmHg , more liquid condenses until eventually all the vapor is converted to a liquid. Increasing the pressure further simply compresses the liquid until a high pressure is reached, perhaps 50 atm , where solid iodine appears. Again the pressure remains fixed with further compression until all of the iodine is converted to its solid form. After this has occurred further compression raises the pressure on the solid until 100 atm is reached. (Data for this part are from Figure 12-27 and the surrounding text.)
- (c) Cooling of gaseous CO_2 simply lowers the temperature until a temperature of perhaps $20\text{ }^{\circ}\text{C}$ is reached. At this point, liquid CO_2 appears. The temperature remains constant as more heat is removed until all the gas is converted to liquid. Further cooling then lowers the temperature of the liquid until a temperature of slightly higher than $-56.7\text{ }^{\circ}\text{C}$ is reached, where solid CO_2 appears. At this point, further cooling simply converts liquid to solid at constant temperature, until all liquid has been converted to solid. From this point, further cooling lowers the temperature of the solid. (Data for this part are taken from Figure 12-28 and Table 12.6.)

53. (D) 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 °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-equilibrium condition, since not all the H_2O vaporizes.

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

(b) 50.0 °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 °C All the H_2O must vaporize, as this temperature is higher than that of part (b). Thus,

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

54. (M)

(a) If the pressure exerted by 2.50 g of H_2O (vapor) is less than the vapor pressure of water at 120 °C (393 K), then the water must exist entirely as a vapor.

$$P = \frac{nRT}{V} = \frac{\left(2.50 \text{ g} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}}\right) \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 393 \text{ K}}{5.00 \text{ L}} = 0.895 \text{ atm}$$

Since this is less than the 1.00 atm vapor pressure at 100 °C, it must be less than the vapor pressure of water at 120 °C. Thus, the water exists entirely as a vapor.

(b) 0.895 atm = 680 mmHg. From Table 12.3, we see that this corresponds to a temperature of 97.0 °C (at which temperature the vapor pressure of water is 682.1 mmHg). Thus, at temperatures slightly less than 97.0 °C the water will begin to condense to liquid. But we have forgotten that, in this constant-volume container, the pressure (of water) will decrease as the temperature decreases. Calculating the precise decrease in both involves linking the Clausius-Clapeyron equation with the expression $P = kT$, but we can estimate the final temperature. First, we determine the pressure if we lower the temperature from 393 K to 97.0 °C (370 K).

$$P_f = \frac{370 \text{ K}}{393 \text{ K}} \times 680 \text{ mmHg} = 640 \text{ mmHg}$$
 From Table 12.3, this pressure occurs at a temperature of about 95 °C (368 K). We now determine the final pressure at this temperature.

$$P_f = \frac{368 \text{ K}}{393 \text{ K}} \times 680 \text{ mmHg} = 637 \text{ mmHg}$$
 This is just slightly above the vapor pressure of water (633.9 mmHg) at 95 °C, which we conclude must be the temperature at which liquid water appears.

55. (M)

- (a) According to Figure 12-28, CO₂(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 CO₂(g) of 1 atm on the surface of Earth.
- (b) According to Table 12.6, the critical temperature of CH₄, the maximum temperature at which CH₄(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 12.6, the critical temperature of SO₂ is 431.0 K = 157.8 °C, SO₂(g) can be found on the surface of Earth.
- (d) According to Figure 12–27, I₂(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, I₂(l) is not found on the surface of Earth.
- (e) According to Table 12.6, the critical temperature – the maximum temperature at which O₂(l) exists – is 154.8 K = –118.4 °C. Temperatures this low do not exist on the surface of Earth.

56. (E) The final pressure specified (100. atm) is below the ice III-ice I-liquid water triple point, according to the text adjacent to Figure 12–30; no ice III is formed. The starting point is that of H₂O(g). When the pressure is increased to about 4.5 mmHg, the vapor condenses to ice I. As the pressure is raised, the melting point of ice I decreases–by 1 °C for every 125 atm increase in pressure. Thus, somewhere between 10 and 15 atm, the ice I melts to liquid water, and it remains in this state until the final pressure is reached.

57. (D)

- (a) heat lost by water = $q_{\text{water}} = (m)(C)(\Delta t)$

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

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

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

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

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

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

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

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

$$\text{mass of unmelted ice} = 1.65 \text{ kg} - 1.43 \text{ kg} = 0.22 \text{ kg}$$

(b) mass of unmelted ice = 0.22 kg (from above)

$$\text{heat required to melt ice} = n \Delta_{\text{fus}} H$$

$$\text{heat required} = (0.22 \text{ kg ice}) \left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) \left(\frac{6.01 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right) = 73.4 \text{ kJ}$$

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:

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

$$= -40.7 \text{ kJ} + -7.53 \text{ kJ} = -48.2 \text{ kJ per mole of H}_2\text{O(g) or per 18.015 g H}_2\text{O(g)}$$

$$\text{mass of steam required} = (73.4 \text{ kJ}) \left(\frac{1 \text{ mol H}_2\text{O(g)}}{48.2 \text{ kJ}} \right) \left(\frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 27 \text{ g steam}$$

58. (M) The heat gained by the ice equals the negative of the heat lost by the water. Let us use this fact in a step-by-step approach. We first compute the heat needed to raise the temperature of the ice to 0.0 °C and then the heat given off when the temperature of the water is lowered to 0.0 °C.

$$\text{to heat the ice} = 54 \text{ cm}^3 \times \frac{0.917 \text{ g}}{1 \text{ cm}^3} \times 2.01 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times (0 \text{ }^\circ\text{C} + 25.0 \text{ }^\circ\text{C}) = 2.5 \times 10^3 \text{ J}$$

$$\text{to cool the water} = -400.0 \text{ cm}^3 \times \frac{0.998 \text{ g}}{1 \text{ cm}^3} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times (0 \text{ }^\circ\text{C} - 32.0 \text{ }^\circ\text{C}) = 53.4 \times 10^3 \text{ J}$$

$$\text{Mass of ice} = 54 \text{ cm}^3 \times \frac{0.917 \text{ g}}{1 \text{ cm}^3} = 49.5 \text{ g} = 50. \text{ g ice}$$

$$\text{Mass of water} = 400.0 \text{ cm}^3 \times \frac{0.998 \text{ g}}{1 \text{ cm}^3} = 399 \text{ g water}$$

Thus, at 0 °C, we have 50. g ice, 399 g water, and $(53.4 - 2.5) \times 10^3 \text{ J} = 50.9 \text{ kJ}$ of heat available. Since 50.0 g of ice is a bit less than 3 moles of ice and 50.9 kJ is enough heat to melt at least 8 moles of ice, all of the ice will melt. The heat needed to melt the ice is

$$50. \text{ g ice} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \times \frac{6.01 \text{ kJ}}{1 \text{ mol ice}} = 17 \text{ kJ}$$

We now have $50.9 \text{ kJ} - 17 \text{ kJ} = 34 \text{ kJ}$ of heat, and $399 \text{ g} + 50. \text{ g} = 449 \text{ g}$ of water at 0 °C. We compute the temperature change that is produced by adding the heat to the water.

$$\Delta T = \frac{34 \times 10^3 \text{ J}}{449 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}} = 18 \text{ }^\circ\text{C}$$

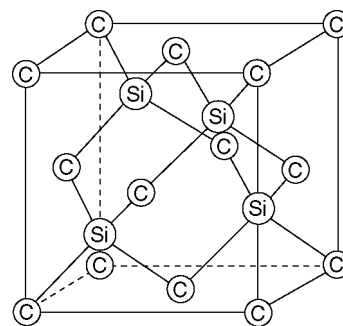
The final temperature is 18 °C.

- 59. (E)** 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 \rightarrow 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.
- 60. (E)** Both the melting point of ice and the boiling point of water are temperatures that vary as the pressure changes, and the boiling point changes more substantially than the melting point. The triple point, however, does not vary with pressure. Solid, liquid, and vapor coexist only at one fixed temperature and pressure.

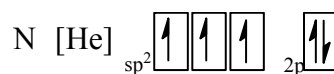
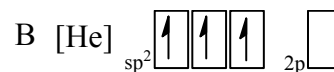
Network Covalent Solids

- 61. (E)** 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.
- 62. (E)** Diamond works well in glass cutters because of its extreme hardness. Its hardness is due to the crystal being held together entirely by covalent bonds. Graphite will not function effectively in a glass cutter, since it is quite soft, soft enough to flake off in microscopic pieces when used in pencils. The bonding in between layers of graphite is weak, which leads to it being a softer material. In fact, graphite is so soft that pure graphite is rarely used in common wooden pencils. Often clay or some other substance is mixed with the graphite to produce a mechanically strong pencil “lead.”

- 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 σ bonding structure, and a hexagonal array of atoms. The $2p_z$ orbitals then overlap to form the π bonding orbitals. Thus, there will be as many π electrons in a sample of BN as there are in a sample of graphite, assuming both samples have the same number of atoms.



- 64. (M)** Buckminsterfullerene is composed of C_{60} spheres. These molecules of carbon are rather like the N_2 , P_4 , and S_8 molecules in that they produce a nonpolar molecular solid. The chain of alternating single and triple bonds could be a network covalent solid, and hence another allotrope of carbon. The long carbon chain would be linear and these rods of carbon ($—C \equiv C — C \equiv C — C \equiv C — C \equiv C — C \equiv C — C \equiv C —$) could fit together rather like spaghetti in a box, with the π electrons of the triple bonds from adjacent rods attracting each other.

Ionic Bonding and Properties

- 65. (E)** 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.
- 66. (M)** Coulomb's law (Appendix B) states that the force between two particles of charges Q_1 and Q_2 that are separated by a distance r is given by $F = Q_1Q_2 / 4\pi\epsilon r^2$ where ϵ , the dielectric constant, equals 1 in a vacuum. Since we are comparing forces, we can use +1, -1, +2, and -2 for the charges on ions. The length r is equal to the sum of the cation and anion radii, which are taken from Figure 12-36.

$$\text{For NaCl, } r_+ = 99 \text{ pm, } r_- = 181 \text{ pm} \quad F = (+1)(-1) / (99 + 181)^2 = -1.3 \times 10^{-5}$$

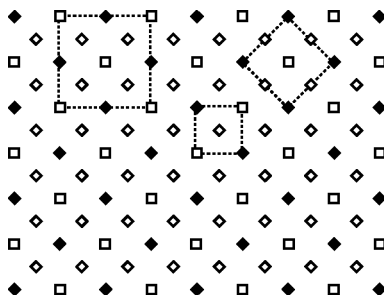
$$\text{For MgO, } r_+ = 72 \text{ pm, } r_- = 140 \text{ pm} \quad F = (+2)(-2) / (72 + 140)^2 = -8.9 \times 10^{-5}$$

Thus, it is clear that interionic forces are about seven times stronger in MgO than in NaCl.

- 67. (E)** 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.
- 68. (E)** MgO will have the higher Mohs constant, because the distance between Mg^{2+} and O^{2-} is the smallest (and hence the bond is strongest) because both the anion and cation are divalent.

Crystal Structures

- 69. (M)** 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).
- 70. (E)** Physical properties are determined by the type of bonding between atoms in a crystal or the types of interactions between ions or molecules in the crystal. Different types of interactions can produce the same geometrical relationships of unit cell components. In both Ar and CO_2 , London forces hold the particles in the crystal. In NaCl, the forces are interionic attractions, while metallic bonds hold Cu atoms in their crystals. It is the type of force, not the geometric arrangement of the components, that largely determines the physical properties of the crystalline material.
- 71. (M)**
- (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.

72. (M) This question reduces to asking what percentage of the area of a square remains uncovered by a circle inscribed within it. First, calculate the area that is covered by the circles, and then subtract from 100% to determine the area that is uncovered. The diameter of the circle equals the side of the square. Since diameter = $2 \times$ radius, we have

$$\frac{\text{area of circle}}{\text{area of square}} = \frac{\pi r^2}{(2r)^2} = \frac{\pi}{4} = \frac{3.14159}{4} = 0.7854 \quad \text{or} \quad 78.54\% \text{ covered}$$

$$100\% - 78.54\% = 21.46\% \text{ uncovered}$$

73. (M) 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 $\sqrt{3} = 1.732$.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{2 \text{ W atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol W}}{6.022 \times 10^{23} \text{ W atoms}} \times \frac{183.85 \text{ g W}}{1 \text{ mol W}} = 18.5 \text{ g/cm}^3$$

$$\left(\frac{4 \times 139 \text{ pm}}{1.732} \times \frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3$$

This compares well with a tabulated density of 19.25 g/cm^3 .

74. (M) One atom lies entirely within the hcp unit cell and there are eight corner atoms, each of which are shared among eight unit cells. Thus, there are a total of two atoms per unit cell. The volume of the unit cell is given by the product of its height and the area of its base. The base is a parallelogram, which can be subdivided along its shorter diagonal into two triangles. The height of either triangle, equivalent to the perpendicular distance between the parallel sides of the parallelogram, is given by $320. \text{ pm} \times \sin(60^\circ) = 277 \text{ pm}$.

$$\text{area of base} = 2 \times \text{area of triangle} = 2 \times (1/2 \times \text{base} \times \text{height})$$

$$= 277 \text{ pm} \times 320. \text{ pm} = 8.86 \times 10^4 \text{ pm}^2$$

$$\text{volume of unit cell} = 8.86 \times 10^4 \text{ pm}^2 \times 520. \text{ pm} = 4.61 \times 10^7 \text{ pm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{2 \text{ Mg atoms} \times \frac{1 \text{ mol Mg}}{6.022 \times 10^{23} \text{ Mg atoms}} \times \frac{24.305 \text{ g Mg}}{1 \text{ mol Mg}}}{4.61 \times 10^7 \text{ pm}^3 \times \left(\frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3} = 1.75 \text{ g/cm}^3$$

This is in reasonable agreement with the experimental value of 1.738 g/cm^3 .

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

$$\sin \theta = \frac{n\lambda}{2d} = \frac{(1)(1.785 \times 10^{-10})}{2(335 \times 10^{-12})} = 0.2664 \text{ or } \theta = 15.45^\circ$$

76. (M) Ge unit cell has a length of 565 pm. volume = $(\text{length})^3 = (565 \text{ pm})^3 = 1.80 \times 10^8 \text{ pm}^3$

$$\text{Next we convert to cm}^3: 1.80 \times 10^8 \text{ pm}^3 \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 1.804 \times 10^{-22} \text{ cm}^3$$

Now we determine the number of Ge atoms per unit cell.

Method: Find number of atoms of Ge per cm^3 , then using the unit cell volume (calculation above), determine number of Ge atoms in the unit cell.

$$\frac{\text{atoms Ge}}{\text{cm}^3} = \left(\frac{5.36 \text{ g Ge}}{\text{cm}^3} \right) \left(\frac{1 \text{ mol Ge}}{72.61 \text{ g Ge}} \right) \left(\frac{6.022 \times 10^{23}}{1 \text{ mol Ge}} \right) = 4.445 \times 10^{22} \frac{\text{atoms Ge}}{\text{cm}^3}$$

$$\frac{\text{atoms Ge}}{\text{unit cell}} = (1.804 \times 10^{-22} \text{ cm}^3) \left(4.445 \times 10^{22} \frac{\text{atoms Ge}}{\text{cm}^3} \right) = 8.02 \frac{\text{atoms Ge}}{\text{unit cell}}$$

There are 8 atoms of Ge per unit cell. Ge must adopt a face centered cubic structure with the 4 tetrahedral holes filled (diamond structure).

77. (E) 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 $8 \times 1/8 + 1 = 2$ Si atoms per unit cell.**78. (E)** 1.5 Ti atoms ($4 \times 1/8 + 1$) and 3 O atoms ($6 \times 1/2$) per unit cell**Ionic Crystal Structures****79. (M)** 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 .

- 80. (M)** The unit cell of CsCl is pictured in Figure 12–49. The length of the body diagonal equals $2r_+ + 2r_-$. For Cl^- , $r_- = 181$ pm. Thus, the length of the body diagonal equals $2(169 \text{ pm} + 181 \text{ pm}) = 700.$ pm. From Figure 12–45, the length of this body diagonal is $\sqrt{3}l = 700.$ pm. The volume of the unit cell is $V = l^3$. ($\sqrt{3} = 1.732$).

$$V = \left(\frac{700. \text{ pm}}{1.732} \times \frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 6.60 \times 10^{-23} \text{ cm}^3$$

Per unit cell, there is one Cs^+ and one Cl^- (8 corner ions \times 1/8 corner ion per unit cell).

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{\left(1 \text{ f.u. CsCl} \times \frac{1 \text{ mol CsCl}}{6.022 \times 10^{23} \text{ CsCl f.u.'s}} \times \frac{168.4 \text{ g CsCl}}{1 \text{ mol CsCl}} \right)}{6.60 \times 10^{-23} \text{ cm}^3} = 4.24 \text{ g/cm}^3$$

81. (D)

- (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.

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

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.

$$\begin{aligned} \text{total \# of Mg}^{2+} \text{ ions} &= 12 \text{ adjoining cells} \times \frac{1 \text{ magnesium ion}}{4 \text{ unit cells}} + 1 \text{ central Mg}^{2+} \text{ ion} \\ &= 4 \text{ Mg}^{2+} \text{ ions (Thus, there are four formula units per unit cell of MgO.)} \end{aligned}$$

- (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-} .

$$\text{edge length} = 2 \times \text{O}^{2-} \text{ radius} + 2 \times \text{Mg}^{2+} \text{ radius} = 2 \times 140 \text{ pm} + 2 \times 72 \text{ pm} = 424 \text{ pm}$$

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

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

- (d)
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4 \text{ MgO f.u.}}{7.62 \times 10^{-23} \text{ cm}^3} \times \frac{1 \text{ mol MgO}}{6.022 \times 10^{23} \text{ f.u.}} \times \frac{40.30 \text{ g MgO}}{1 \text{ mol MgO}} = 3.51 \text{ g/cm}^3$$

Thus, there are four formula units (f.u.) per unit cell of MgO.

- 82. (M)** According to Figure 12-48, there are four formula units of KCl in a unit cell and the length of the edge of that unit cell is twice the internuclear distance between K^+ and Cl^- ions. The unit cell is a cube; its volume is the cube of its length.

$$\text{length} = 2 \times 314.54 \text{ pm} = 629.08 \text{ pm}$$

$$\text{volume} = (629.08 \text{ pm})^3 = 2.4895 \times 10^8 \text{ pm}^3 \left(\frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 2.4895 \times 10^{-22} \text{ cm}^3$$

$$\begin{aligned} \text{unit cell mass} &= \text{volume} \times \text{density} = 2.4895 \times 10^{-22} \text{ cm}^3 \times 1.9893 \text{ g/cm}^3 = 4.9524 \times 10^{-22} \text{ g} \\ &= \text{mass of 4 KCl formula units} \end{aligned}$$

$$N_A = \frac{4 \text{ KCl formula unit}}{4.9524 \times 10^{-22} \text{ g KCl}} \times \frac{74.5513 \text{ g KCl}}{1 \text{ mol KCl}} = 6.0214 \times 10^{23} \text{ formula unit/mol}$$

- 83. (M)**

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

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

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

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

(c) $\text{LiO}_2 \rightarrow$ radius ratio $= \frac{r_{\text{Li}^+}}{r_{\text{O}_2^-}} = \frac{59 \text{ pm}}{128 \text{ pm}} = 0.461$

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

- 84. (M)** $\text{BaO} \rightarrow$ radius ratio $= \frac{r_{\text{Ba}^{2+}}}{r_{\text{O}^{2-}}} = \frac{135 \text{ pm}}{140 \text{ pm}} = 0.964$

Cations occupy cubic hole of a simple cubic array of anions.

$\text{CuI} \rightarrow$ radius ratio $= \frac{r_{\text{Cu}^+}}{r_{\text{I}^-}} = \frac{96 \text{ pm}}{220 \text{ pm}} = 0.436$

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

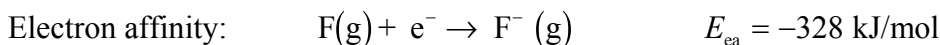
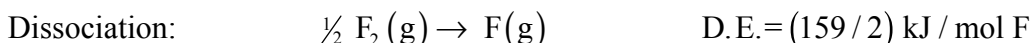
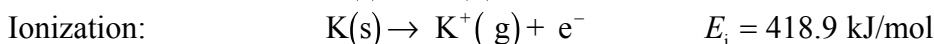
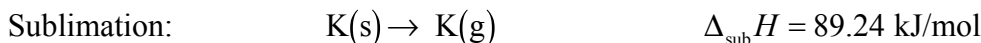
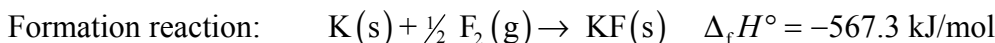
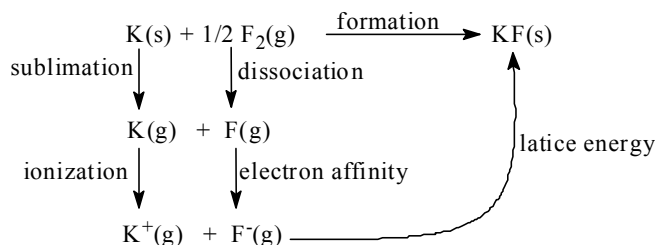
$\text{LiS}_2 \rightarrow$ radius ratio $= \frac{r_{\text{Li}^+}}{r_{\text{S}_2^-}} = \frac{59 \text{ pm}}{198 \text{ pm}} = 0.298$

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

Lattice Energy

- 85. (E)** 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.

86. (D) The cycle of reactions is shown. Recall that Hess's law (a state function), states that the enthalpy change is the same, whether a chemical change is produced by one reaction or several.

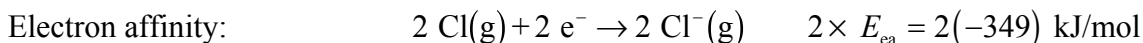
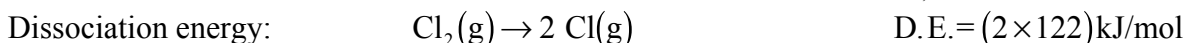
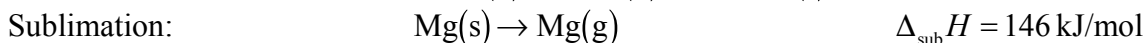


$$\Delta_f H^\circ = \Delta_{\text{sub}} H + E_i + \text{D.E.} + E_{\text{ea}} + \text{lattice energy (L.E.)}$$

$$-567.3 \text{ kJ/mol} = 89.24 \text{ kJ/mol} + 418.9 \text{ kJ/mol} + (159/2) \text{ kJ/mol} - 328 \text{ kJ/mol} + \text{L.E.}$$

$$\text{L.E.} = -827 \text{ kJ/mol}$$

87. (D)



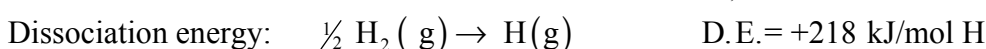
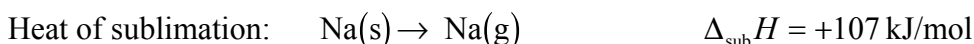
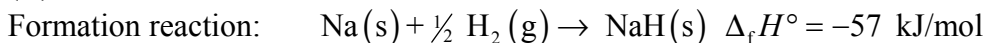
$$\Delta_f H^\circ = \Delta_{\text{sub}} H + E_{i,1} + E_{i,2} + \text{D.E.} + (2 \times E_{\text{ea}}) + \text{L.E.}$$

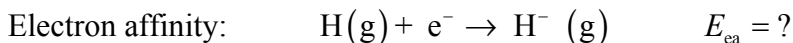
$$= 146 \frac{\text{kJ}}{\text{mol}} + 738 \frac{\text{kJ}}{\text{mol}} + 1451 \frac{\text{kJ}}{\text{mol}} + 244 \frac{\text{kJ}}{\text{mol}} - 698 \frac{\text{kJ}}{\text{mol}} - 2526 \frac{\text{kJ}}{\text{mol}} = -645 \frac{\text{kJ}}{\text{mol}}$$

In Example 12-12, the value of $\Delta_f H^\circ$ for MgCl is calculated as -19 kJ/mol . Therefore,

MgCl₂ is much more stable than MgCl, since considerably more energy is released when it forms. MgCl₂(s) is more stable than MgCl(s)

88. (D)





$$\Delta_{\text{f}}H^{\circ} = \Delta_{\text{sub}}H + E_{\text{i},1} + \text{D.E.} + E_{\text{ea}} + \text{lattice energy (L.E.)}$$

$$-57 \text{ kJ/mol} = 107 \text{ kJ/mol} + 496 \text{ kJ/mol} + E_{\text{ea}} + 218 \text{ kJ/mol} - 812 \text{ kJ/mol}$$

$$E_{\text{ea}} = -66 \text{ kJ/mol} \text{ (compares favorably to the literature value of } -72.8 \text{ kJ)}$$

INTEGRATIVE AND ADVANCED EXERCISES

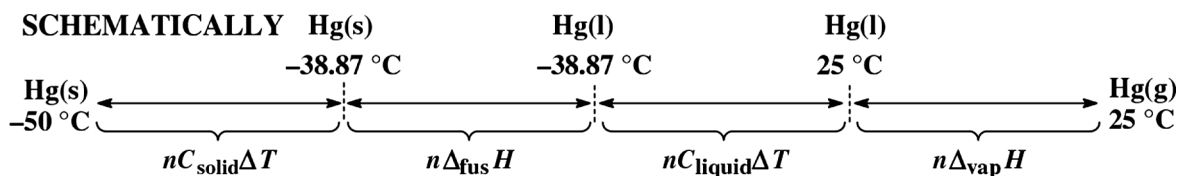
- 89. (E)** The heat of the flame melts the solid wax, converting it to a liquid. Still closer to the flame the temperature is higher, and the liquid wax vaporizes to the gaseous hydrocarbons, which are then burned. The liquid wax is drawn up the wick toward the flame by capillary action, where it is vaporized and burns, producing the heat needed to melt the solid wax, and the process continues until all the wax is burned.
- 90. (M)** We know that $1.00 \text{ atm} = 101,325 \text{ Pa}$ and $1 \text{ Bar} = 100,000 \text{ Pa}$. The enthalpy of vaporization is given as $40,657 \text{ J/mol}$ in the chapter. These numbers are substituted into the Clapeyron equation.

$$\ln \frac{101,325 \text{ Pa}}{100,000 \text{ Pa}} = \frac{40,657 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{T} - \frac{1}{373.15} \right)$$

$$T = 372.78 \text{ K}$$

- 91. (M)** 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 ($20 \text{ }^{\circ}\text{C}$ or 293 K). Thus, substances in Table 12.6 for which gas pressure does serve as a measure of the quantity of gas in the tank are H_2 ($T_{\text{c}} = 33.3 \text{ K}$), N_2 ($T_{\text{c}} = 126.2 \text{ K}$), O_2 ($T_{\text{c}} = 154.8 \text{ K}$), and CH_4 ($T_{\text{c}} = 191.1 \text{ K}$).

- 92. (D)** $m = 15.0 \text{ g Hg}(\text{s})$ or $n = 0.0748 \text{ mol Hg}(\text{s})$ $24.3 \text{ J K}^{-1} \text{ mol}^{-1} \text{ Hg}(\text{l})$ $28.0 \text{ J K}^{-1} \text{ mol}^{-1}$
(Hg melting point = $-38.87 \text{ }^{\circ}\text{C}$ and $\Delta_{\text{fusion}}H = 2.33 \text{ kJ mol}^{-1}$)



Here we need to calculate (using Appendix D), $\Delta_{\text{vap}}H$ at 25 °C. That is: $\text{Hg(l)} \rightarrow \text{Hg(g)}$ at 25 °C. Simply use $\Delta_f H^\circ$ values from Appendix D. $\Delta_{\text{vap}}H = \Delta_f H^\circ \text{Hg(g)} - \Delta_f H^\circ \text{Hg(l)}$

$$\Delta_{\text{vap}}H = 61.32 \text{ kJ/mol} - 0 \text{ kJ/mol} = 61.32 \text{ kJ/mol.}$$

Next we calculate each of the four quantities shown in the schematic.

$$nC_{\text{solid}}\Delta T + \Delta = 0.0748 \text{ mol}(24.3 \text{ J K}^{-1}\text{mol}^{-1})(-38.87 \text{ }^\circ\text{C} - -50.0 \text{ }^\circ\text{C})(1 \text{ kJ}/1000\text{J}) = 0.0202\bar{3} \text{ kJ}$$

$$n\Delta_{\text{fus}}H = 0.0748 \text{ mol}(2.33 \text{ kJ mol}^{-1}) = 0.174 \text{ kJ}$$

$$nC_{\text{liquid}}\Delta T = 0.0748 \text{ mol}(28.0 \text{ J K}^{-1}\text{mol}^{-1})(25.0 \text{ }^\circ\text{C} - -38.87 \text{ }^\circ\text{C})(1 \text{ kJ}/1000\text{J}) = 0.134 \text{ kJ}$$

$$n\Delta_{\text{vap}}H = 0.0748 \text{ mol}(61.32 \text{ kJ/mol}) = 4.58\bar{7} \text{ kJ}$$

$$q = nC_{\text{solid}}\Delta T + n\Delta_{\text{fus}}H + nC_{\text{solid}}\Delta T + n\Delta_{\text{vap}}H = 0.020\bar{2}\bar{3} \text{ kJ} + 0.174 \text{ kJ} + 0.134 \text{ kJ} + 4.58\bar{7} \text{ kJ}$$

$$q = 4.91\bar{5} \text{ kJ}$$

- 93. (M)** 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

$$\frac{10.00 \text{ kJ}}{4.430 \text{ g H}_2\text{O}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 2257 \text{ J/g H}_2\text{O}$$

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.

- 94. (M)** 1.00 g of Car Kooler (10 % $\text{C}_2\text{H}_5\text{OH}$) is used to cool 55 °C air which has a heat capacity of $29 \text{ J K}^{-1}\text{mol}^{-1}$. Hence, 0.100 g $\text{C}_2\text{H}_5\text{OH}$ is evaporated, (with $\Delta_{\text{vap}}H = 42.6 \text{ kJ}\cdot\text{mol}^{-1}$) and 0.900 g of H_2O (with $\Delta_{\text{vap}}H = 44.0 \text{ kJ}\cdot\text{mol}^{-1}$), is also evaporated.

Energy required to evaporate

$$0.100 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.068 \text{ g C}_2\text{H}_5\text{OH}} \times \frac{42.6 \text{ kJ}}{1 \text{ mol C}_2\text{H}_5\text{OH}} = 0.092\bar{5} \text{ kJ}$$

$$\text{Energy required to evaporate the water } 0.900 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{44.0 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = 2.20 \text{ kJ}$$

Thus, most of the energy (> 95%), absorbed by Car Kooler goes toward the evaporation of water. In fact, if one were to replace the $\text{C}_2\text{H}_5\text{OH}$ with water, it would be even more effective.

- 95. (M)** In this case, we use the Clausius-Clapeyron equation to determine the sublimation pressure at 25 °C. We also need the enthalpy of sublimation and the sublimation pressure at another temperature. We can closely estimate the sublimation pressure at the triple point with the following three step process. First, assume that the triple point temperature and the melting point temperature are the same (53.1 °C or 326.3 K). Second, realize that the vapor pressure and the sublimation pressure are the same at the triple point. Third, use the Clausius-Clapeyron equation to determine the vapor pressure at the triple point.

$$\ln \frac{P}{10.0 \text{ mmHg}} = \frac{72,220 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{328.0 \text{ K}} - \frac{1}{326.3 \text{ K}} \right) = -0.138 \quad P = 10.0e^{-0.138} = 8.71 \text{ mmHg}$$

$$\Delta_{\text{sub}}H \text{ is determined by: } \Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 17.88 \text{ kJ mol}^{-1} + 72.22 \text{ kJ mol}^{-1} \\ = 90.10 \text{ kJ mol}^{-1}$$

Use the Clausius-Clapeyron equation to determine the sublimation pressure at 25 °C.

$$\ln \frac{P}{8.71 \text{ mmHg}} = \frac{90,100 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{326.3 \text{ K}} - \frac{1}{298.0 \text{ K}} \right) = -3.15 \quad P = 8.71e^{-3.15} = 0.37 \text{ mmHg}$$

96. (E) 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.

97. (M) At the triple point, the sublimation pressure equals the vapor pressure. We need to also realize that Celsius temperature, t , is related to Kelvin temperature, T , by $t = T - 273.15$. Thus,

$$9.846 - 2309/T = 6.90565 - 1211.033/(220.790 + t) = 6.90565 - 1211.033/(220.790 + T - 273.15) \\ = 6.90565 - 1211.033/(T - 52.36)$$

$$9.846 - 6.90565 = 2.940 = \frac{2309}{T} - \frac{1211.033}{T - 52.36} = \frac{2309(T - 52.36) - 1211.033T}{T(T - 52.36)}$$

$$2.940T(T - 52.36) = 2.940T^2 - 153.9T = 2309T - 1.209 \times 10^5 - 1211.033T = 1098T - 1.209 \times 10^5$$

$$2.940T^2 - 153.9T - 1098T + 1.209 \times 10^5 = 0 = 2.940T^2 - 1252T + 1.209 \times 10^5$$

The quadratic formula is used to solve this equation.

$$T = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1252 \pm \sqrt{(1252)^2 - (4 \times 2.940 \times 1.209 \times 10^5)}}{2 \times 2.940}$$

$$T = 212.9 \pm 64.9 = 277.8 \text{ K} \quad \text{or} \quad 148.0 \text{ K} \quad \therefore T = 4.6 \text{ }^\circ\text{C} \quad \text{or} \quad -125.2 \text{ }^\circ\text{C}$$

The acceptable result from the quadratic equation is 4.6 °C; below this temperature liquid benzene can only exist as a metastable supercooled liquid, not as a stable liquid and thus -125.2 °C is not a reasonable value. The calculated value, 4.6 °C, compares favorably to the listed value of 5.5 °C.

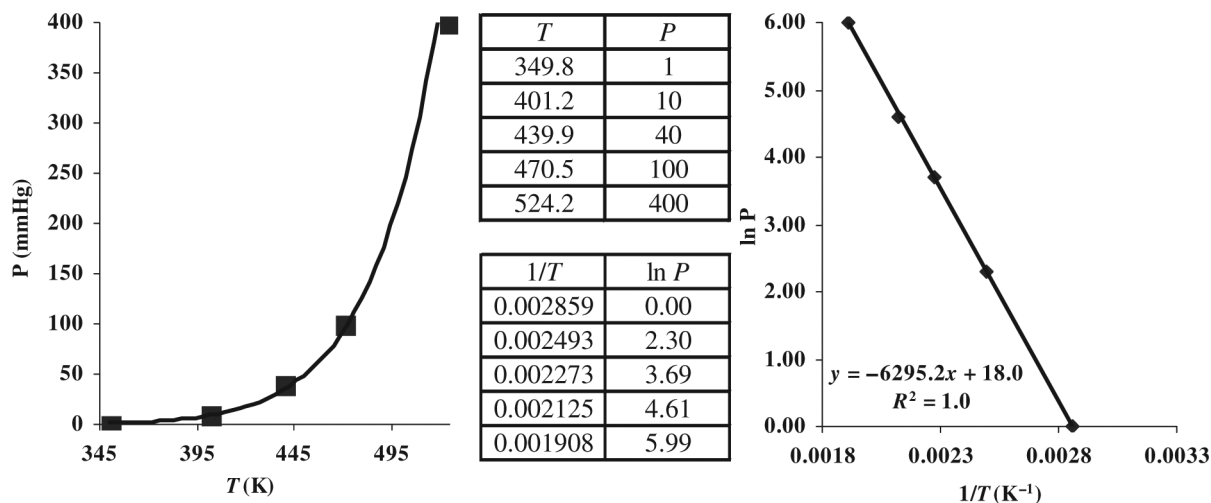
98. (D) First, we need to calculate $\ln P$ and $1/T$ for the given data points.

t , °C	76.6	128.0	166.7	197.3	251.0
P , mmHg	1	10	40	100	400
T , K	349.8	401.2	439.9	470.5	524.2
$1/T \times 10^3 \text{ K}^{-1}$	2.859	2.493	2.273	2.125	1.908
$\ln P$	0	2.303	3.689	4.605	5.991

NOTE: Graphs are given on the following page

(a) The normal boiling point of phosphorus occurs at a pressure of 760 mmHg, where $\ln P = 6.63$. Based on the graph below (left), this occurs when $1/T = 1.81 \times 10^{-3} \text{ K}^{-1}$, or $T = 552 \text{ K}$, 279 °C.

- (b) When $\ln P$ is plotted vs $1/T$, (see below), the slope of the line equals $-\Delta_{\text{vap}}H/R$.
 For the graph on the left, the slope (by linear regression) is $-6.30 \times 10^3 \text{ K}$.
 Thus, $\Delta_{\text{vap}}H = 6.30 \times 10^3 \text{ K} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 5.24 \times 10^4 \text{ J/mol}$.

**99. (M)**

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

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

The ice under the skates will melt at $-0.25 \text{ }^\circ\text{C}$.

100. (M) $P = P_0 \times 10^{-Mgh/2.303RT}$ Assume ambient temperature is $10.0 \text{ }^\circ\text{C} = 283.2 \text{ K}$

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

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

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

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

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

- 101. (M)** From the graphs in Figure 12-20, choose two points for benzene and two points for water. Set $\ln P_{\text{benzene}} = \ln P_{\text{water}}$. Hence: $-4.10 \times 10^3(1/T) + 18.3 = -5.35 \times 10^3(1/T) + 21.0$

Compound	$\ln P$	$1/T$ (K^{-1})	Equation of Line
Benzene	5.99	0.00300	$\ln P_{\text{benzene}} = -4.10 \times 10^3(1/T) + 18.3$
	4.35	0.00340	
Water	6.55	0.00270	$\ln P_{\text{water}} = -5.35 \times 10^3(1/T) + 21.0$
	4.41	0.00310	

$$1250(1/T) = 2.7(1/T) = 0.00216 \text{ or } T = 463 \text{ K.}$$

We can calculate the pressures for both benzene and water using this temperature.

Note: If the pressures for both benzene and water are close, this will serve as a double check.

$$\ln P_{\text{benzene}} = -4.10 \times 10^3(1/T) + 18.3 = -4.10 \times 10^3(0.00216) + 18.3 = 9.444$$

$$\ln P_{\text{water}} = -5.35 \times 10^3(1/T) + 21.0 = -5.35 \times 10^3(0.00216) + 21.0 = 9.444$$

$$\ln P = 9.444, \text{ hence } p = e^{9.444} = 12632 \text{ mmHg or } 16.6 \text{ atm.}$$

- 102. (M)** We first compute the volume of the cylinder, and then the mass of Cl_2 present as vapor.

$$V = \pi r^2 h = 3.1416 \times (5.0 \text{ in.})^2 \times 45 \text{ in.} \left(\frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 = 5.8 \times 10^4 \text{ cm}^3 = 58 \text{ L}$$

$$\text{amount } \text{Cl}_2 = \frac{PV}{RT} = \frac{100. \text{ psi} \times \frac{1 \text{ atm}}{14.7 \text{ psi}} \times 58 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}} = 16 \text{ mol } \text{Cl}_2$$

$$\text{mass } \text{Cl}_2 = 16 \text{ mol } \text{Cl}_2 \times \frac{70.9 \text{ g } \text{Cl}_2}{1 \text{ mol } \text{Cl}_2} \times \frac{1 \text{ lb}}{453.6 \text{ g}} = 2.5 \text{ lb } \text{Cl}_2(\text{g})$$

Thus, the mass of gas does not account for all of the 151 lb of chlorine in the cylinder. Since 20°C is below the critical temperature of Cl_2 , liquid chlorine can exist, provided that the pressure is high enough. That is the case in this instance. Both liquid and gaseous chlorine are present in the cylinder. There is almost certainly no solid present; 20°C is too far above chlorine's melting point of -103°C for any reasonable pressure to produce the solid.

- 103. (M)** 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: CH_3COOH .

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

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).



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.

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

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

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

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. (M) First we compute the mass and the amount of mercury.

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

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

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

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

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

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

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

105. (M) In the phase diagram on the left, the liquid-vapor curve dips down and then rises. This means that there can be a situation where raising the temperature will cause the vapor to condense to liquid – this is counterintuitive and does not correspond to the laws of thermodynamics as they operate in our universe. Also, a negative slope for the vapor pressure curve would correspond to a negative value of $\Delta_{\text{vap}}H$, but this quantity must always have a positive sign (vaporization is an endothermic process). In the diagram on the right, the liquid-vapor line has the same curvature as the solid-vapor line. This means that the heat of vaporization is the same as the heat of sublimation. This would mean that the heat of fusion is zero. Therefore no energy is needed to melt the solid, which is again counterintuitive and a physical impossibility.

- 106. (M)** The normal boiling point is that temperature at which the vapor pressure is 760 mmHg. We have been provided with the following expression to solve for T , the normal boiling point.

$$\text{Log}_{10}(760) = 2.88081 = 9.95028 - 0.003863T - 1473.17(T^{-1})$$

$$0 = 7.06947 - 0.003863T - 1473.17(T^{-1}) \text{ Multiply through by } T \text{ to get}$$

$$0 = 7.06947T - 0.003863T^2 - 1473.17$$

By solving the quadratic equation, we get the roots 239.8 K or 1590 K. The second of these temperatures makes no physical sense, since we know that NH_3 is a gas at room temperature. Thus the normal boiling point of $\text{NH}_3(\text{l})$ is 239.8 K.

- 107. (D)** 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 $T_2 = 1 \text{ mol Bi} \times \frac{10.9 \text{ kJ}}{\text{K mol}} \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 10.9 \text{ min}$

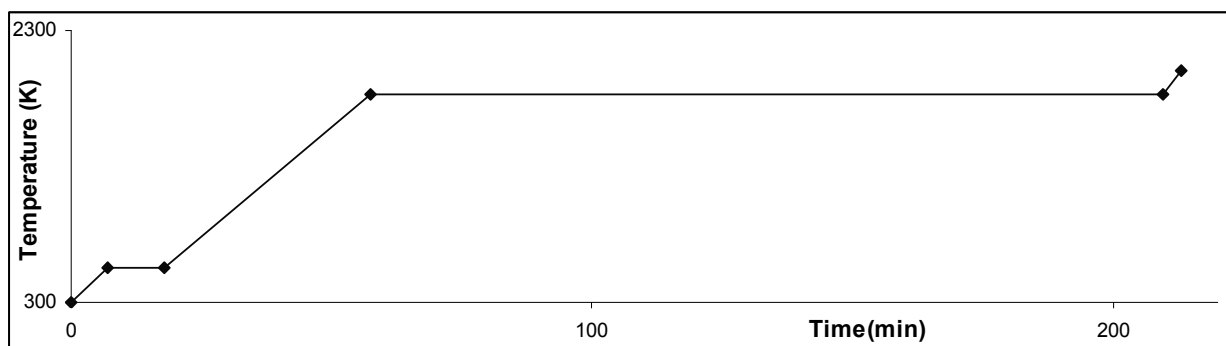
3. Heat the liquid to its boiling point $T_3 =$

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

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:



- 108. (M)**

(a) The coordination number for S^{2-} is 8, while for Li^+ it is 4 (tetrahedral holes).

(b) $8 \times \text{Li}^+$ within the unit cell (tetrahedral holes) and $4 \times \text{S}^{2-}$ (8 corners $\times 1/8$) + (6 faces $\times 1/2$) = 1 + 3 = 4 formula units per unit cell.

(c) Note: $1 \text{ pm}^3 = \frac{(1 \times 10^{-12} \text{ m})^3}{(1 \text{ pm})^3} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} = 1 \times 10^{-30} \text{ cm}^3$

$$V = \ell^3 = (5.88 \times 10^2 \text{ pm})^3 \times \frac{1 \times 10^{-30} \text{ cm}^3}{1 \text{ pm}^3} = 2.033 \times 10^{-22} \text{ cm}^3$$

In a unit cell there are 4 Li_2S formula units.

($\text{Li}_2\text{S} \rightarrow 45.948 \text{ g mol}^{-1}$ or $4 \text{ mol Li}_2\text{S} \rightarrow 183.792 \text{ g}$)

Consider one mole of unit cells. This contains 45.948 g of Li_2S and has a volume of $(2.03 \times 10^{-22} \text{ cm}^3) \times (6.022 \times 10^{23}) = 122.4 \text{ cm}^3$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{183.792 \text{ g}}{122.4 \text{ cm}^3} = 1.50 \text{ g cm}^3$$

- 109. (E)** 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 $560 \text{ pm} \div 2 = 280 \text{ pm}$. This is equal to the value of d in the Bragg equation (12.5). We first solve for $\sin \theta$ and then for θ .

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

- 110. (M)** In a bcc cell, there are two atoms per unit cell. The length of an edge of the unit cell is $4r \div \sqrt{3}$, where $\sqrt{3} = 1.732$. In a fcc cell, there are four particles per unit cell. The length of an edge of the unit cell is $4r \div \sqrt{2}$, where $\sqrt{2} = 1.414$. Now, the volume of a cube is $V = \ell^3$. Thus,

$$V_{\text{bcc}} = \left(\frac{4r}{1.732} \right)^3 = 12.32 r^3 \quad \text{and} \quad V_{\text{fcc}} = \left(\frac{4r}{1.414} \right)^3 = 22.63 r^3$$

The volume of an individual sphere is $\frac{4}{3}\pi r^3 = 4.189 r^3$

Then the fraction, F , of occupied volume in each unit cell can be computed.

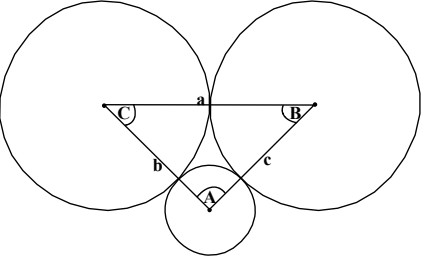
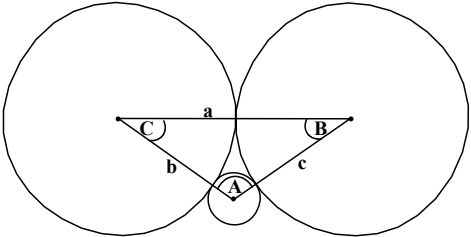
$$F_{\text{bcc}} = \frac{\text{volume of spheres}}{\text{volume of unit cell}} = \frac{2 \times 4.189 r^3}{12.317 r^3} = 0.6800 \text{ or } 68.00\% \text{ occupied, } 32.00\% \text{ void}$$

$$F_{\text{fcc}} = \frac{\text{volume of spheres}}{\text{volume of unit cell}} = \frac{4 \times 4.189 r^3}{22.627 r^3} = 0.7404 \text{ or } 74.04\% \text{ occupied, } 25.96\% \text{ void}$$

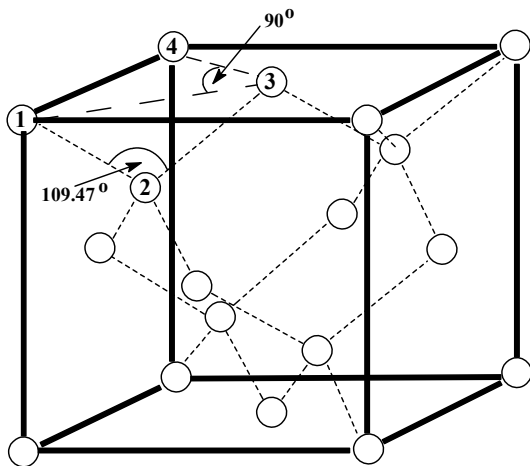
The volume of an individual sphere is $\frac{4}{3}\pi r^3 = 4.189 r^3$.

Then the fraction, F , of occupied volume in each unit cell can be computed.

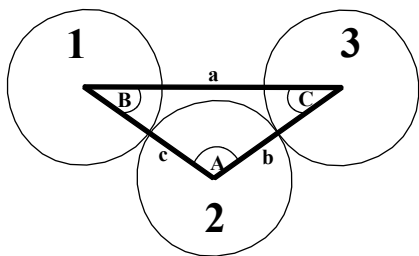
111. (D) Consider the two limits

<p style="text-align: center;">CASE I (Square planar arrangement of anions around a cation)</p>	<p style="text-align: center;">CASE II (Tetrahedral arrangement of anions around a cation)</p>
	
<p> $a = 2(r_{\text{anion}})$ $b = c = r_{\text{anion}} + r_{\text{cation}}$ $A = 90^\circ$ $a^2 = b^2 + c^2 = (2(r_{\text{anion}}))^2 = (r_{\text{anion}} + r_{\text{cation}})^2 + (r_{\text{anion}} + r_{\text{cation}})^2$ $(2(r_{\text{anion}}))^2 = 2(r_{\text{anion}} + r_{\text{cation}})^2$ (take root of both sides) $2(r_{\text{anion}}) = \sqrt{2} (r_{\text{anion}} + r_{\text{cation}})$ $2(r_{\text{anion}}) = \sqrt{2} r_{\text{anion}} + \sqrt{2} r_{\text{cation}}$ $2(r_{\text{anion}}) - \sqrt{2} r_{\text{anion}} = \sqrt{2} r_{\text{cation}}$ $(2 - \sqrt{2})r_{\text{anion}} = \sqrt{2} r_{\text{cation}}$ $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{2 - \sqrt{2}}{\sqrt{2}} = 0.414$ </p>	<p> $a = 2(r_{\text{anion}})$ $b = c = r_{\text{anion}} + r_{\text{cation}}$ $A = 109.47^\circ$ Use cosine law: $a^2 = b^2 + c^2 - 2bc(\cos A)$ & $\cos A = -1/3$ $2(r_{\text{anion}})^2 = (r_{\text{anion}} + r_{\text{cation}})^2 + (r_{\text{anion}} + r_{\text{cation}})^2 - 2((r_{\text{anion}} + r_{\text{cation}})^2)(-1/3)$ $(2(r_{\text{anion}}))^2 = 2(r_{\text{anion}} + r_{\text{cation}})^2 + (2/3)(r_{\text{anion}} + r_{\text{cation}})^2$ $(2(r_{\text{anion}}))^2 = (8/3)(r_{\text{anion}} + r_{\text{cation}})^2$ (take root of both sides) $2(r_{\text{anion}}) = \sqrt{8/3} (r_{\text{anion}} + r_{\text{cation}}) = \sqrt{8/3} r_{\text{anion}} + \sqrt{8/3} r_{\text{cation}}$ $2(r_{\text{anion}}) - \sqrt{8/3} r_{\text{anion}} = \sqrt{8/3} r_{\text{cation}} = (2 - \sqrt{8/3})r_{\text{anion}}$ $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{2 - \sqrt{8/3}}{\sqrt{8/3}} = 0.225$ </p>

112. (D) Diamond is a face centered cubic structure + $\frac{1}{2}$ filled tetrahedral holes. Therefore, in the unit cell there are $8 \times (1/8) + 6 \times (1/2) + 4 \times 1 = 8$ atoms. Need to find the length of the edge of the unit cell to determine the volume.



Structure of diamond is shown at the left. The carbon atoms of interest are numbered. Note that the tetrahedral angle (109.47°) around carbon 2 and right angle (90°) around carbon 3.



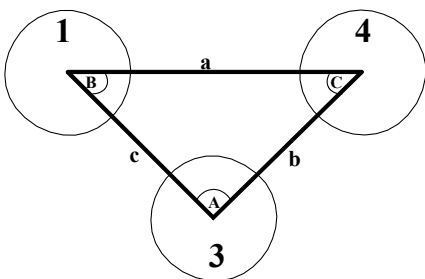
Close-up of carbons 1, 2 and 3.

angle $A = 109.47^\circ$, $c = b = 154.45$ pm

Use cosine law: $a^2 = b^2 + c^2 - 2bc(\cos A)$ &
 $\cos A = -1/3$

$a^2 = (154.45)^2 + (154.45)^2 - 2(154.45)^2(-1/3)$

$a^2 = 63,612.8$ pm². Take the square root of both sides $a = 252.2$ pm



Close-up of carbons 1, 3 and 4.

angle $A = 90.00^\circ$, $c = b = 252.2$ pm

$a^2 = b^2 + c^2 = (252.2 \text{ pm})^2 + (252.2 \text{ pm})^2$

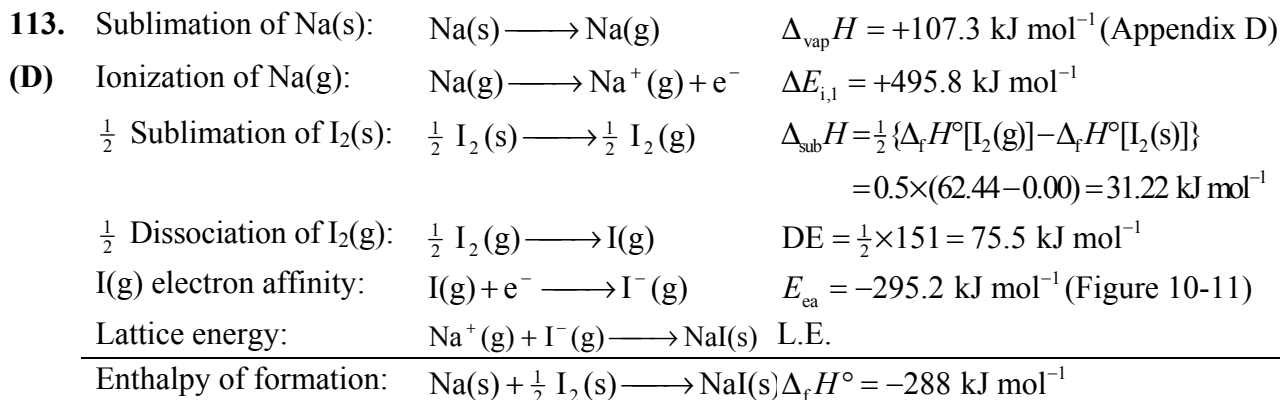
$a^2 = 127,209.7$ pm². Take the square root of both sides $a = 356.7$ pm = ℓ (length of unit cell)

$$V = \ell^3 = (356.7 \text{ pm})^3 = 4.538 \times 10^7 \text{ pm}^3 \quad (1 \text{ pm}^3 = 1 \times 10^{-30} \text{ cm}^3) \quad V = 4.538 \times 10^{-23} \text{ cm}^3$$

Consider one mol of unit cells. This contains 8 moles of carbon atoms or 96.088 g.

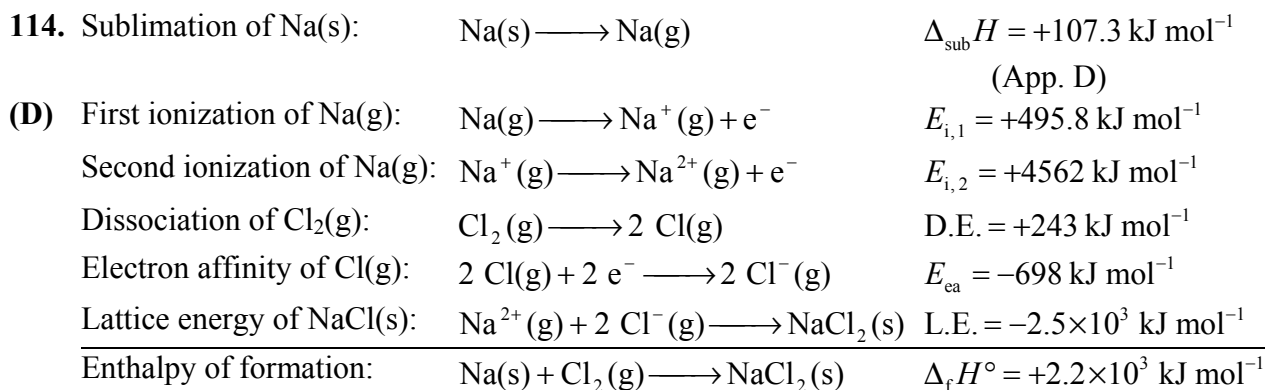
The volume of one mole of unit cells = $4.538 \times 10^{-23} \text{ cm}^3 (6.022 \times 10^{23}) = 27.33 \text{ cm}^3$.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{96.088 \text{ g}}{27.33 \text{ cm}^3} = 3.516 \text{ g cm}^{-3} \quad (\text{literature value} = 3.52 \text{ g cm}^{-3})$$



$$-288 \text{ kJ mol}^{-1} = (-107.3 + 495.8 + 31.22 + 75.5 - 295.2) \text{ kJ mol}^{-1} + \text{L.E.} = 415 \text{ kJ mol}^{-1} + \text{L.E.}$$

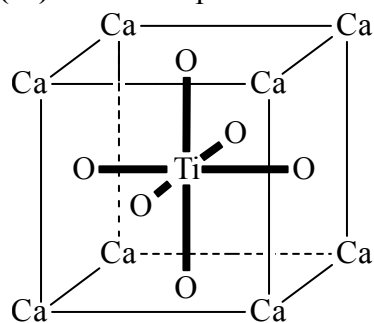
$$\text{L.E.} = (-288 - 415) \text{ kJ mol}^{-1} = -703 \text{ kJ mol}^{-1}$$



This highly endothermic process is quite unlikely. Thus NaCl_2 will not form under normal conditions.

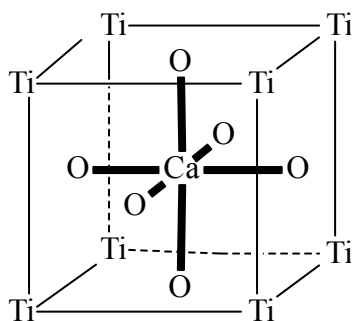
115. (M) The Na^+ ions on the 6 faces are shared by 2 cells; the O^{2-} ions on the 8 corners are shared by 8 cells; the Cl^- is unique to each cell. Thus, the formula is Na_3ClO . The coordination numbers of O^{2-} and Cl^- are both 6. The shortest distance from the center of Na^+ to the center of O^{2-} is half the length of a face diagonal, which is $\sqrt{2} \times (a/2)$. The shortest distance from the center of a Cl^- to the center of O^{2-} is half the length of a cell diagonal, namely, $\sqrt{3} \times (a/2)$.

116. (M) The two representations are shown below:



$$\begin{aligned} \text{Corner position Ca} &= 8 \times (1/8) = 1 \\ \text{Face center O} &= 6 \times (1/2) = 3 \\ \text{Body center Ti} &= 1 \times 1 = 1 \end{aligned}$$

Formula is CaTiO_3



$$\begin{aligned} \text{Corner position Ti} &= 8 \times (1/8) = 1 \\ \text{Face center O} &= 6 \times (1/2) = 3 \\ \text{Body center Ca} &= 1 \times 1 = 1 \end{aligned}$$

Formula is CaTiO_3

Note: In each representation, there are six oxygen atoms around each Ti atom and Ca atom.

117. (M) From Chapter 10, Ca^{2+} radius = 100 pm, F^- radius = 133 pm.

$$\text{radius ratio} = \frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{100 \text{ pm}}{133 \text{ pm}} = 0.752$$

This is a fairly large value suggesting a structure in which the anions adopt a simple cubic structure so that the cations can be accommodated in the cubic holes. For CaF_2 , the cations must occupy every other cubic hole so as to maintain the formula unit of CaF_2 . Essentially CaF_2 has the CsCl structure, however every second cell has the cation missing.

118. (M)

(a) Three ($6 \times 1/2$)

(b) One ($8 \times 1/8$)

(c) One (1×1)

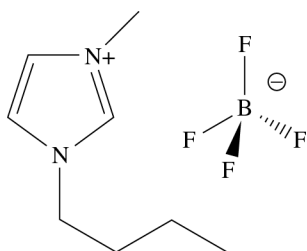
(d) Determine the volume of the unit cell and the mass of the atoms in each cell:

$$\text{volume} = (0.403 \times 0.398 \times 0.398) \text{ nm}^3 \times \frac{1 \text{ cm}^3}{(10^7 \text{ nm})^3} = 6.384 \times 10^{-23} \text{ cm}^3$$

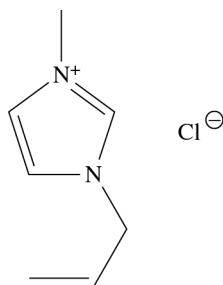
$$\text{mass of atoms} = \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \left(\begin{array}{l} 3 \text{ O atoms} \times 16.0 \text{ g} \cdot \text{mol}^{-1} \\ + 1 \text{ Pb atom} \times 207.19 \text{ g} \cdot \text{mol}^{-1} \\ + 1 \text{ Ti atom} \times 47.88 \text{ g} \cdot \text{mol}^{-1} \end{array} \right) = 5.0327 \times 10^{-22} \text{ g}$$

$$\text{density} = \frac{m}{V} = \frac{5.0327 \times 10^{-22} \text{ g}}{6.384 \times 10^{-23} \text{ cm}^3} = 7.87 \text{ g/cm}^3$$

119. (E)

(a) [Bmim][BF₄]

[Amim]Cl



(b) m.p.([Bmim][BF₄]) = -80 °C
 m.p.(Amim]Cl = 49 - 51 °C

(c) To a first approximation, the melting point of an ionic compound depends on the charges and sizes of the cations and anions involved. As suggested by Figure 12-36, the smaller the charges and the larger the ions, the weaker the interaction, the lower the lattice enthalpy, and the lower the melting temperature. Another factor may be that the interactions among the ions have a larger contribution from van der Waals forces (because of the large size of the cations). Since van der Waals forces are typically much weaker than “pure” ionic interactions, the lattice enthalpy of an IL is further reduced.

120. (M) In reality, a nanocrystal has many faces. However, for simplicity, this problem assumes the nanocrystal is spherical. The volume of a 2 nm diameter nanocrystal is

$$V_{\text{nc}} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \times \left(\frac{2 \text{ nm}}{2}\right)^3 = 4.189 \text{ nm}^3$$

Now, calculate the volume of the unit cell:

$$V_{\text{uc}} = a \times a \times a = (6.097 \times 10^{-1} \text{ nm})^3 = 0.2266 \text{ nm}^3/\text{unit cell}$$

Now determine how many unit cells fit into the nanocrystal:

$$\frac{V_{\text{nc}}}{V_{\text{uc}}} = \frac{4.189 \text{ nm}^3}{0.2266 \text{ nm}^3} = 18.48 \text{ unit cell}$$

Finally, determine the number of atoms: 20 atoms/unit cell \times 18.46 unit cells = 369 atoms

121. Sample calculations are shown below for the H₂O—H₂O interaction.

$$\begin{aligned} E(\text{dipole-dipole}) &= -\frac{1}{r^6} \cdot \frac{2\mu^4}{3k_5T} \cdot \frac{1}{(4\pi\epsilon_0)^2} \\ &= -\frac{1}{(4 \times 10^{-10} \text{ m})^6} \times \frac{2(1.8546 \text{ D} \times 3.33564 \times 10^{-30} \text{ C m D}^{-1})^4}{3(1.3807 \times 10^{-23} \text{ JK}^{-1})(298 \text{ K})} \\ &\quad \times \frac{1}{(4\pi(8.854 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}))^2} = -4.86 \times 10^{-21} \text{ J} \end{aligned}$$

(a) To express this result in kJ mol^{-1} , we multiply by the Avogadro constant and divide by 1000:

$$E(\text{dipole-dipole}) = -4.68 \times 10^{-21} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times \frac{\text{kJ}}{1000 \text{ J}} = -2.82 \text{ kJ mol}^{-1}$$

$$\begin{aligned} E(\text{dipole-induced dipole}) &= -\frac{1}{r^6} \cdot 2\mu^2 a' \cdot \frac{1}{4\pi\epsilon_0} \\ &= -\frac{1}{(4.00 \times 10^{-10} \text{ m})^6} \times 2(1.8546 \text{ D} \times 3.33564 \\ &\quad \times 10^{-30} \text{ C m D}^{-1})^2 (14.5 \times 10^{-25} \text{ cm}^3 \times 10^{-6} \text{ m}^3 \text{ cm}^3) \\ &\quad \times \frac{1}{4\pi(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} \\ &= -2.435 \times 10^{-22} \text{ J} \end{aligned}$$

$$E(\text{dipole-induced dipole}) = -2.435 \times 10^{-22} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times \frac{\text{kJ}}{1000 \text{ J}} = -0.15 \text{ kJ mol}^{-1}$$

$$\begin{aligned} E(\text{dispersion}) &= -\frac{1}{r^6} \cdot \frac{3}{4} \alpha^2 E_i \\ &= \frac{1}{(4.00 \times 10^{-10} \text{ m})^6} \times \frac{3}{4} (14.5 \times 10^{-25} \text{ cm}^3 \times 10^{-6} \text{ m}^3 \text{ cm}^{-3})^2 \times (1218 \text{ kJ mol}^{-1}) \\ &= -4.689 \times 10^{-2} \text{ kJ mol}^{-1} \end{aligned}$$

The sum of these contributions is

$$\begin{aligned} E &= E(\text{dipole-dipole}) + E(\text{dipole-induced dipole}) + E(\text{dispersion}) \\ &= -2.82 \text{ kJ mol}^{-1} + (-0.15 \text{ kJ mol}^{-1}) + (-0.47 \text{ kJ mol}^{-1}) \\ &= -3.44 \text{ kJ mol}^{-1} \end{aligned}$$

(b) The percent contributions are

$$\begin{aligned} \% \text{ dipole} &= \frac{E(\text{dipole-dipole})}{E} \times 100\% \\ &= \frac{-2.82 \text{ kJ mol}^{-1}}{-3.44 \text{ kJ mol}^{-1}} \times 100\% \\ &= 82.0\% \end{aligned}$$

$$\begin{aligned} \% \text{ induced} &= \frac{E(\text{dipole-induced dipole})}{E} \times 100\% \\ &= \frac{2(-0.15 \text{ kJ mol}^{-1})}{-3.44 \text{ kJ mol}^{-1}} \times 100\% \\ &= 4.3\% \end{aligned}$$

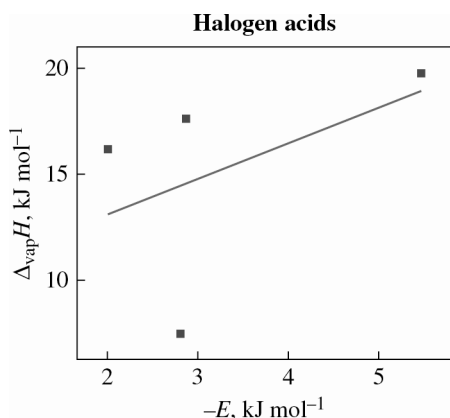
$$\begin{aligned} \% \text{ dispersion} &= \frac{E(\text{dispersion})}{E} \times 100\% \\ &= \frac{-0.47 \text{ kJ mol}^{-1}}{-3.44 \text{ kJ mol}^{-1}} \times 100\% \\ &= 13.6\% \end{aligned}$$

Results for the other substances are obtained in the same manner. The following table provides a summary:

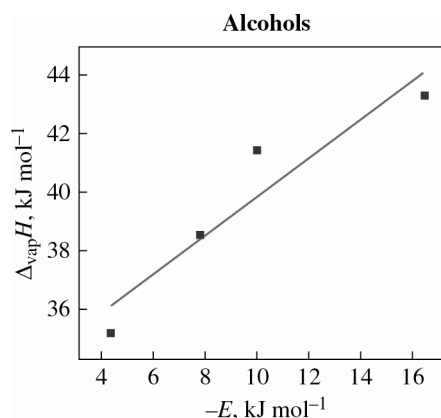
	$E(\text{dipole-dipole})$ (kJ mol ⁻¹)	$E(\text{dipole-induced dipole})$ (kJ mol ⁻¹)	$E(\text{dispersion})$ (kJ mol ⁻¹)	E (kJ mol ⁻¹)	Percent		
					Dipole-Dipole	Dipole-Induced Dipole	Dispersion
HF	-2.65	-0.08	-0.18	-2.91	91.1	2.7	6.2
HCl	-0.36	-0.10	-1.56	-2.01	17.9	4.7	77.4
HBr	-0.11	-0.07	-2.68	-2.87	3.9	2.5	93.6
HI	-0.01	-0.03	-5.43	-5.47	0.2	0.6	99.2
H ₂ O	-2.82	-0.15	-0.47	-3.44	82.1	4.3	13.6
CH ₃ OH	-1.99	-0.28	-2.08	-4.35	45.8	6.4	47.8
CH ₃ CH ₂ OH	-1.94	-0.45	-5.39	-7.79	25.0	5.8	69.2
CH ₃ (CH ₂) ₂ OH	-1.38	-0.48	-8.17	-10.02	3.7	4.8	81.5
CH ₃ (CH ₂) ₃ OH	-1.81	-0.72	-13.92	-16.45	11.0	4.4	84.6
CH ₄	0.00	0.00	-1.50	-1.50	0.0	0.0	100.0
CH ₃ CH ₃	0.00	0.00	-4.08	-4.08	0.0	0.0	100.0
CH ₃ CH ₂ CH ₃	0.00	0.00	-7.66	-7.66	0.0	0.0	100.0
(CH ₃) ₃ CH	0.00	0.00	-12.38	-12.38	0.0	0.0	100.0
CH ₃ (CH ₂) ₂ CH ₃	0.00	0.00	-12.51	-12.51	0.0	0.0	100.0
CH ₃ (CH ₂) ₃ CH ₃	0.00	0.00	-18.13	-18.13	0.0	0.0	100.0

(c) The values range from tenths of a kJ mol⁻¹ to approximately 12 kJ mol⁻¹. Intermolecular interaction energies are typically ten to a thousand times smaller than the energy of a covalent bond.

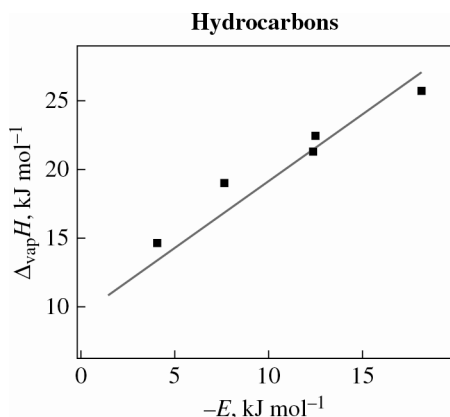
(d) The plot for the halogen acids



The plot for the alcohols



The plot for the alkanes



These plots show that as the magnitude of the intermolecular interaction energies increases, the enthalpy of vaporization increases.

- (e) For low temperatures, when thermal energies are small, the majority of molecules will have their dipoles aligned head-to-tail. However, at very high temperatures, the molecules will be able to “jiggle” out of alignment, with their dipoles more randomly oriented. Therefore, the attraction arising from a favorable alignment of dipole moments is less significant at higher temperatures.

FEATURE PROBLEMS

- 122. (E)** We obtain the surface tension by substituting the experimental values into the equation for surface tension.

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

- 123. (D)**

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

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}}H}{T\left(\frac{nRT}{P}\right)} = \frac{\Delta_{\text{vap}}H}{nRT^2} = \frac{P\Delta_{\text{vap}}H}{nRT^2} \quad \text{or} \quad \frac{dP}{P} = \frac{\Delta_{\text{vap}}H \times dT}{nRT^2}$$

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

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

Simplify and collect constants

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

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

- (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**124. (M)**

- (a) 1 NaCl unit missing from the NaCl unit cell \rightarrow overall stoichiometry is the same. The unit cell usually has 4 Na^+ and 4 Cl^- in the unit cell. Now the unit cell will have 3 Na^+ and 3 Cl^- . Accordingly, the density will decrease by a factor of 25% (1/4) if 1 Na^+ and 1 Cl^- are consistently absent throughout the structure. Thus, the density will be $0.75(d_{\text{NaCl, normal}})$.
- (b) No change in stoichiometry or density, as this is just a simple displacement of an ion within the unit cell.
- (c) Unit cell should contain 4 Ti^{2+} and 4 O^{2-} ions (same as in the NaCl unit cell). 4 TiO ions have a mass of:

$$4 \text{ formula units} \times \left(\frac{1 \text{ mol TiO}}{6.022 \times 10^{23} \text{ formula units}}\right) \left(\frac{63.88 \text{ g TiO}}{1 \text{ mol TiO}}\right) = 4.243 \times 10^{-22} \text{ g TiO}$$

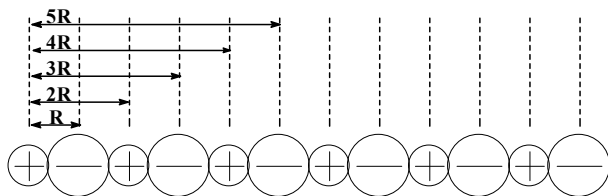
$$V = (418 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}}\right)^3 \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = 7.30 \times 10^{-23} \text{ cm}^3$$

$$\text{Calculated density} = \frac{m}{V} = \frac{4.243 \times 10^{-22} \text{ g}}{7.30 \times 10^{-23} \text{ cm}^3} = 5.81 \text{ g cm}^{-3} \text{ (actual density} = 4.92 \text{ g cm}^{-3}\text{)}$$

This indicates the presence of vacancies, and these could be Schottky-type defects.

125. (D)

- (a) For a uniformly spaced (separation = r) one dimensional linear “crystal” of alternating cations and anions (having the same unipositive charge $Q_1 = Q_2 = Q_3$ (see diagram below)), the interaction of one ion with all of the other ions is proportional to

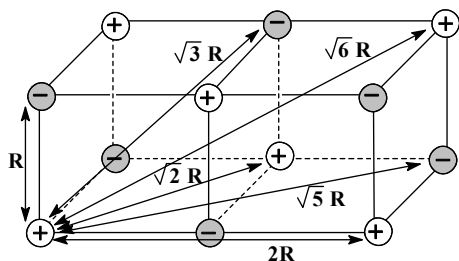


$$V = \frac{Q^2 e^2}{d_{12}} \quad \text{where} \quad \frac{1}{d_{12}} = \frac{2}{R} - \frac{2}{2R} + \frac{2}{3R} - \frac{2}{4R} + \frac{2}{5R} - \frac{2}{6R} \dots$$

Note: The factor of 2 comes from the fact that the same set of ions appears on both sides of the central ion and it does not matter if you start with a cation or an anion.

$$\frac{1}{d_{12}} = \frac{2}{R} \times \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} \dots \right) \quad \frac{1}{d_{12}} = \frac{1}{R} \times 2(\ln 2) \quad V = \frac{Q^2 e^2}{R} \times 2(\ln 2)$$

(b) Consider the crystal lattice for NaCl.



The 4 closest distances are marked to the reference Na^+ ion in the bottom left.

At a distance of R , there are 6 Cl^- ions which are attracted to the Na^+ ion.

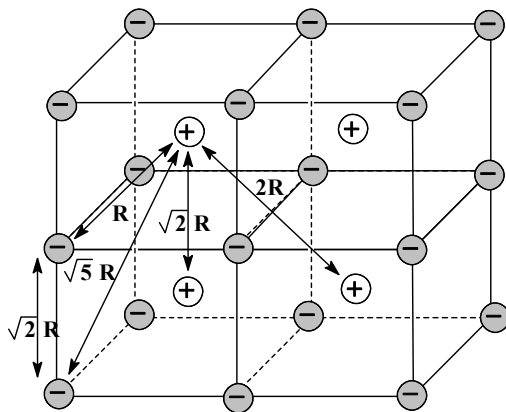
At a distance of $\sqrt{2}R$, there are 12 Na^+ ions which are repelled by the Na^+ ion.

At a distance of $\sqrt{3}R$, there are 8 Cl^- ions which are attracted to the Na^+ ion.

At a distance of $2R$ or $\sqrt{4}R$, there are 6 Na^+ ions which are repelled by the Na^+ ion.

The value of $k_M = \left(\frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right)$

(c) If we carry out the same calculation for the CsCl structure, we would see that the Madelung constant is not the same. This is because the crystal structure is not the same. Notable is the fact that there are 8 nearest neighbors in CsCl and only 6 in NaCl.



The 4 closest distances are marked to the reference Cs^+ ion in the top left cell.

At a distance of R , there are 8 Cl^- ions which are attracted to the Cs^+ ion.

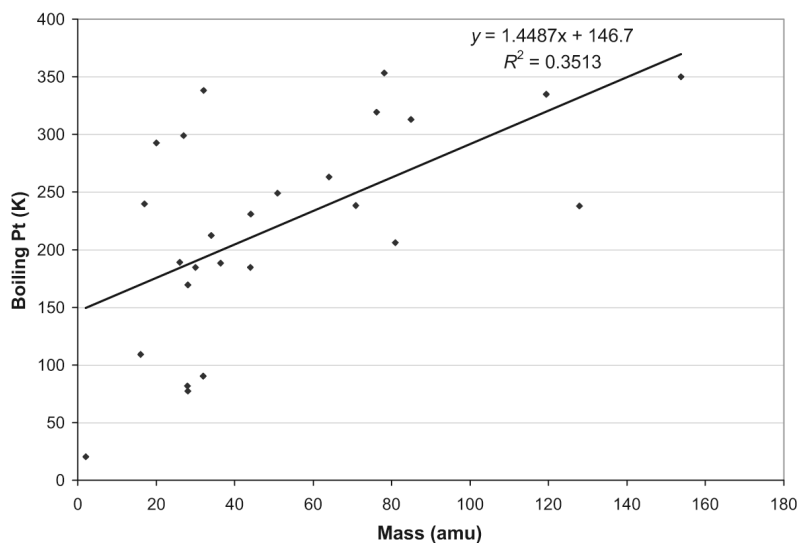
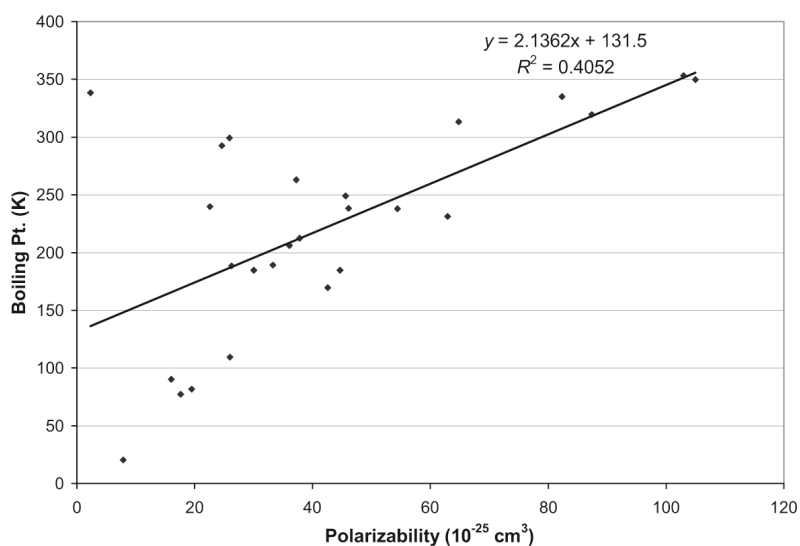
At a distance of $\sqrt{2}R$, there are 6 Cs^+ ions which are repelled by the Cs^+ ion.

At a distance of $\sqrt{5}R$, there are 24 Cl^- ions which are attracted to the Cs^+ ion.

At a distance of $2R$ or $\sqrt{4}R$, there are 8 Cs^+ ions which are repelled by the Cs^+ ion.

The value of $k_M = \left(\frac{8}{1} - \frac{6}{\sqrt{2}} + \frac{24}{\sqrt{5}} - \frac{8}{\sqrt{4}} + \dots \right)$

126. (M) There is a better linear correlation between polarizability and boiling point (as demonstrated by the linear regression fit) than between mass and boiling point. Therefore, interatomic/molecular interaction drive the boiling point, not mass.



127. (M) The first two entries are obtained by simple plugging in:

$$\text{NaCl} : \frac{(120,250 \text{ kJ pm mol}^{-1})(2)(+1 \times -1)}{(181+99) \text{ pm}} \times \left(1 - \frac{34.5 \text{ pm}}{(181+99) \text{ pm}}\right) = -753 \text{ kJ mol}^{-1}$$

$$\text{LaF}_3 : \frac{(120,250 \text{ kJ pm mol}^{-1})(4)(+3 \times -1)}{(133+117) \text{ pm}} \times \left(1 - \frac{34.5 \text{ pm}}{(133+117) \text{ pm}}\right) = -4975 \text{ kJ mol}^{-1}$$

The case of Na_2SO_4 is more difficult, and is approached as follows:

$$\text{Na}_2\text{SO}_4 : \frac{(120,250 \text{ kJ pm mol}^{-1})(3)(+1 \times -2)}{(r_0) \text{ pm}} \times \left(1 - \frac{34.5 \text{ pm}}{(r_0) \text{ pm}}\right) = -3389 \text{ kJ mol}^{-1}$$

Expanding the above term, we get the following expression:

$$\frac{-721500}{r_0} \left(\frac{r_0 - 34.5}{r_0} \right) = -3389$$

$$3389 \cdot r_0^2 - 721500r_0 + 24891750 = 0$$

Solving r_0 using the quadratic formula, we get $r_0 = 169$ pm

Since $r_0 = r_+ + r_-$, and $r_+ = 99$ pm, $r_- = 70$ pm.

This ionic radius for sulfate seems small. One would expect SO_4^{2-} to have a significantly higher radius than an Na^+ . What this suggests is that the Kapustinskii relationship does not do a good enough job for polyatomic anions, and thus would need to be modified.

SELF-ASSESSMENT EXERCISES

128. (E)

- (a) $\Delta_{\text{vap}}H$: Enthalpy of vaporization, the amount of heat needed to convert one mole of liquid to a gas
- (b) T_c : Critical temperature, the temperature at which the boundary between gas and liquid phase disappears (and beyond which, the gas cannot be compressed into a liquid no matter the pressure)
- (c) Instantaneous dipole: Purely based on chance at some point in time, electrons can be concentrated in one region of an atom or a molecule. This displacement of electrons causes a weak and instantaneous dipole in the molecule, making a normally non-polar species momentarily polar.
- (d) Coordination number: The number of atoms that are in contact with a central atom
- (e) Unit cell: In a crystalline substance, a unit cell is the smallest parallelepiped that can be used to represent the entire crystal by translation in the x , y and z directions.

129. (E)

- (a) Capillary action: See Figure 12-14. A thin film of water spreads up the inside walls of the capillary because of strong adhesive forces between water and glass (water wets glass). The pressure below the meniscus falls slightly. Atmospheric pressure then pushes a column of water up the tube to eliminate the pressure difference. The smaller the diameter of the capillary, the higher the liquid rises.
- (b) Polymorphism: The phenomenon of the pure solid of a substance existing in more than one form.
- (c) Sublimation: The phase transformation process involving the direct conversion of a solid to a gas.
- (d) Supercooling: If, during the cooling of a liquid, the temperature drops below the freezing point without any solid forming
- (e) Determining the freezing point of a liquid from a cooling curve: A cooling curve plots heat released by the system as a function of temperature. If, during the cooling of the system, the temperature of the liquid does not change, that is the freezing point. After the solid phase is formed and the liquid is frozen, the temperature will resume decreasing again.

- 130. (E)**
- (a) Adhesive and cohesive forces: Cohesive forces are forces between the molecules of a substance in a certain phase that holds the phase together (such as the forces holding together a droplet of water). Adhesive forces are the forces between molecules of a substance and another substance (such as a droplet of water sticking to glass).
 - (b) Vaporization and condensation: Vaporization is the process of converting a liquid into a gas. It is endothermic, because a net amount of energy has to be expended for this conversion. Condensation is the reverse process, where a gas forms a liquid.
 - (c) Triple point and critical point: Triple point is the temperature and pressure where all three phases of the matter exist simultaneously. Critical point is the temperature beyond which the gas cannot be condensed into a liquid no matter what the pressure (and also, the meniscus between the gas and liquid phase disappears).
 - (d) Face-centered and body-centered cubic unit cell: A face centered cubic unit cell has an atom at each corner of the cube, and an atom at each face. Body centered cubic has an atom at each corner, and one atom in the center of the cubic lattice.
 - (e) Tetrahedral and octahedral hole: tetrahedral holes are voids between packed layers of atoms where the void has 4 nearest atom neighbors. An octahedral hole is a void with 6 nearest neighbor atoms.

131. (E) The correct answer is (e) because all these properties depend on the strength of the intermolecular forces. Surface tension is the tendency of matter to resist an external force. The strength of the intermolecular attractions directly affects the ability of the surface of the liquid to resist this external force. Boiling point and vapor pressure are likewise affected. The stronger the intermolecular attractions, the lower the vapor pressure at a given temperature, and the higher the boiling temperature. Similarly, heat of vaporization of the substance also increases with increasing intermolecular attractions; more energy is required to take 1 mole of the substance from the liquid phase to the gas phase.

132. (E) The correct answer is (b). As the vapor escapes, there is less vapor over the liquid available for condensation, so the immediate effect is a lower condensation rate. More vapor will be produced because the vaporization rate will be greater than the condensation rate, until finally the two rates are again equal.

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

134. (E) The answer is (c). HF, CH₃OH, and N₂H₄ all participate in hydrogen bonding.

135. (E) The correct answer is (d). The normal boiling point is defined as the temperature where the vapor pressure of the liquid is the same as normal (sea level) atmospheric pressure of 760 Torr (1 atm).

- 136. (M)** The van't Hoff equation can be used to calculate the vapor pressure at a given temperature:

$$\ln \frac{p_2}{p_1} = -\frac{\Delta_{\text{vap}}H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Plugging in the values, we have

$$\ln \frac{50.0 \text{ mmHg}}{760 \text{ mmHg}} = -\frac{\Delta_{\text{vap}}H^\circ}{8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left[\frac{1}{T_2} - \frac{1}{329.4 \text{ K}} \right]$$

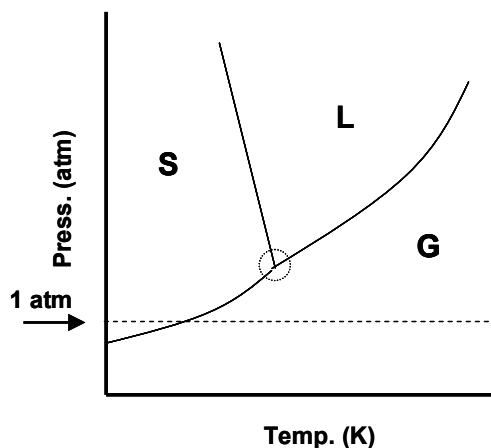
T_2 can be solved as follows:

$$T_2 = -\left[\ln \frac{50.0 \text{ mmHg}}{760 \text{ mmHg}} \times \left(\frac{8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{32.0 \times 10^3 \text{ J mol}^{-1}} \right) - \frac{1}{329.4 \text{ K}} \right]^{-1} = 267.17 \text{ K or } -6.0 \text{ }^\circ\text{C}$$

- 137. (E)** The answer is (b). Refer to Table 12.9.

- 138. (E)** The answer is (a).

- 139. (M)** The answers are (d) and (f).



- 140. (E)** The species with higher boiling points are underlined.

- (a) C_7H_{16} v. $\text{C}_{10}\text{H}_{22}$: The only interaction is London dispersion. $\text{C}_{10}\text{H}_{22}$ because it has the higher mass
- (b) C_3H_8 v. $(\text{CH}_3)_2\text{O}$: because dipole-dipole interactions are predominant, versus just London dispersion for C_3H_8 .
- (c) $\text{CH}_3\text{CH}_2\text{SH}$ v. $\text{CH}_3\text{CH}_2\text{OH}$: because H-bonding dominates the inter-molecular interactions. This interaction is much weaker for $\text{CH}_3\text{CH}_2\text{SH}$.

- 141. (E)** O_3 is the one that is out of place. The correct order of boiling points based on molar masses is: $\text{N}_2 < \text{F}_2 < \text{Ar} < \text{O}_3 < \text{Cl}_2$. 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).

142. (E) 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:
 $\text{Ne} < \text{C}_3\text{H}_8 < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_2\text{OHCHOHCH}_2\text{OH} < \text{KI} < \text{K}_2\text{SO}_4 < \text{MgO}$

143. (M) Refer to the photograph on page 538 of water boiling under a reduced pressure. If the vapor is evacuated fast enough, to supply the required $\Delta_{\text{vap}}H$, the water may cool to 0°C and ice may begin to form.

144. (M) 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.

145. (D)

(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.

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

Assuming a pressure of 110 Torr at 25°C :

$$\text{vol CCl}_4 = 3.50 \text{ g CCl}_4 / 1.59 \text{ g mol}^{-1} = 2.20 \text{ mL}$$

$$\text{vol inside the vessel} = 8.210 \text{ L} - 0.00220 \text{ L} = 8.208 \text{ L}$$

$$\text{pressure} = 110 \text{ Torr} / 760 \text{ Torr} = 0.145 \text{ atm.}$$

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

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

$0.0486 \text{ mol} > 0.0228 \text{ mol}$, 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 $\Delta_{\text{vap}}H$:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{760}{110}\right) = \frac{-\Delta_{\text{vap}}H}{8.3145 \text{ J mol}^{-1} \text{ K}}\left(\frac{1}{350 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\Delta_{\text{vap}}H = 32.2 \text{ kJ/mol}$$

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

$$\text{energy} = 2000 \text{ mL} \times \frac{1.59 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol CCl}_4}{153.80 \text{ g CCl}_4} \times \frac{32.2 \text{ kJ}}{\text{mol}} = 666 \text{ kJ}$$

146. (M)

- (a) Unit cell length: we note from the picture that the hypotenuse of the right triangle equals $4 \times r$.

$$L^2 + L^2 = (4r)^2 = 16 \cdot (128 \text{ pm})^2 = 2.621 \times 10^5$$

$$L = \sqrt{2.621 \times 10^5 / 2} = 362 \text{ pm}$$

- (b) volume = $(362 \text{ pm})^3 = 4.74 \times 10^7 \text{ pm}^3$

- (c) $8 \text{ corners} \times 1/8 + 6 \text{ faces} \times 1/2 = 4 \text{ atoms/unit cell}$.

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

$$\frac{\text{vol of atoms}}{\text{vol of cells}} = \frac{4 \times (4/3) \pi (128 \text{ pm})^3}{4.74 \times 10^7 \text{ pm}^3} \times 100 = 74\%$$

- (e)

$$\frac{\text{mass of Cu}}{\text{unit cell}} = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{1 \text{ mol Cu}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}} = 4.221 \times 10^{-22} \text{ g}$$

- (f) $D = m/V$

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

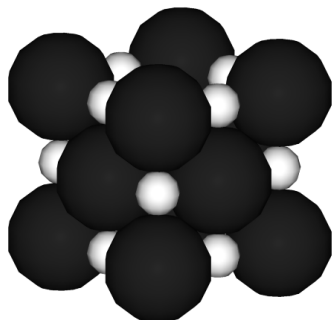
- 147. (E)** The answer is (a). All of these liquids participate in hydrogen-bonding. Therefore, higher van der Waals interactions translate to higher surface tensions. Methanol, CH_3OH , is the smallest molecule, therefore has the least amount of van der Waals forces, and the lowest surface tension.

- 148. (E)** 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.

- 149. (E)** 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.

- 150. (E)** MgO would have the highest melting point. Lattice energy increases as the magnitude of the charges on the ions increases and as the sizes (radii) of the ions decreases. Large lattice energies result from highly charged ions with the smallest radii.

- 151. (M)** 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 \AA , the length of the cube is $2 \times 3.02 \text{ \AA} = 6.04 \text{ \AA}$. Therefore, the face diagonal of the cube is:

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

Since there are 4 I^- radii in the face diagonal of the cube, radius of I^- is $8.54/4 = 2.13 \text{ \AA}$

- 152. (E)** The answer is (c), because of increased pressure, the transformation that causes the greatest packing efficiency change is likely to prevail.
- 153. (M)** The intermolecular forces can be broken down into two categories: dipole and induced dipole. The dipole interactions can be further subdivided to dipole–dipole, which originates from the attraction between two molecules that have a dipole moment, to the more specific case of hydrogen bonding, where the hydrogen in one molecule attached to F, O, and N interacts with the F, O, and N atom from another molecule. Induced dipole or van der Waals forces are between non-polar molecules, where the momentary changes in the electron cloud distribution in the molecule creates a temporary dipole, which interacts with other molecules for a weak interaction.
- 154. (M)** The concept of sphere packing can be described by the following packing types: hexagonal closed packing (HCP), cubic closed packing (CCP), body centered cubic (BCC) and simple cubic (SC). With the concepts of HCP and CCP come the concepts of interstitial sites, manifested in forms of octahedral and tetrahedral holes.
- 155. (M)** The phase diagram is the overarching concept (obviously), which needs to be broken down further. The major sub-topics are the three phases: gas, liquid, solid. Deriving from the three phases is phase transformation as a function of temperature and pressure. Phase transformations also give rise to two other topics: triple point and critical point.