Chapter 11. Intermolecular Forces, Liquids & Solids

The Kinetic Molecular Theory of Liquids and Solids (Section 11.1)
Intermolecular Forces (Section 11.2)
Properties of Liquids (Section 11.3)
The Solid State (Sections 11.4 – 11.7)
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SUMMARY
The Kinetic Molecular Theory of Liquids and Solids (11.1)

The Molecular View of Liquids and Solids. In this chapter, we examine the structure of liquids and solids, and discuss some of the fundamental properties of these two states of matter. Matter can exist in three phases: gas, liquid, and solid. Each phase can be described from a molecular viewpoint in terms of four characteristics: distance between molecules, attractive forces between molecules, the motion of molecules, and the orderliness of the arrangement of molecules. Figure 1.6 in the text gives a molecular representation of a solid, a liquid, and a gas.

In Chapter 5, we discussed the fact that a gas can be pictured as molecules that are far apart, in constant random motion, and exert almost no attractive forces on each other. The kinetic molecular theory was used to explain the behavior of gases.

Liquids and solids are quite different from gases. They are referred to as the condensed states because their molecules are very close together. Gases have low density, high compressibility, and completely fill a container. The condensed states have relatively high density, are almost incompressible, and have definite volumes. These properties indicate that the "molecules" of solids and liquids are close together and are held by strong intermolecular forces.

One difference between solids and liquids is that liquids, like gases, are fluids, but solids are not. In liquids, molecules can move past each other even though they cannot get very far from each other. In solids, molecules are fixed in position, and at most can only vibrate about that position. Many solids are characterized by the long-range order of their constituent molecules. This order gives rise to crystal structures. Table 11.1 summarizes some properties of the three states of matter.

<table>
<thead>
<tr>
<th>Table 11.1 Characteristic Properties of the States of Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
</tr>
<tr>
<td>Assumes the volume and shape of its container</td>
</tr>
<tr>
<td>Is a fluid (flows readily)</td>
</tr>
<tr>
<td>Very compressible</td>
</tr>
<tr>
<td>Low density</td>
</tr>
<tr>
<td>Molecules far apart</td>
</tr>
</tbody>
</table>

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van der Waals Forces. The forces that hold atoms together, such as covalent bonds, exist within molecules. In this chapter you will learn about the types of forces that act between individual molecules that hold them close together as in a solid or a liquid. Forces of attraction between molecules are called intermolecular forces (IMF). Intermolecular forces can be grouped for convenience into van der Waals forces, ion-dipole forces, and hydrogen bonds. The van der Waals forces cause a gas to deviate from ideal gas behavior and also are responsible for gases condensing to form liquids. They are attractive forces resulting from dipole-dipole forces, dipole-induced dipole forces, and dispersion forces. We shall discuss each of these interactions briefly.

Dipole-Dipole Forces. Some molecules have a dipole moment \( \mu \), and are referred to as polar molecules. In a polar substance, molecules tend to become aligned, with the positive end of one molecule directed toward the negative ends of neighboring dipoles. See Figure 11.1 in the text. The attraction is electrostatic. The larger the dipole moment, the stronger the force of attraction. Dipole-dipole forces are attractive forces between polar molecules.

Dipole-Induced Dipole Forces. The presence of a polar molecule in the vicinity of another molecule (usually nonpolar) has the effect of polarizing the second molecule. This means that a dipole moment has been induced in the previously nonpolar molecule. The induced dipole can then interact with the dipole moment of the first molecule, and the two molecules are attracted toward each other. The induced dipole is a temporary dipole. Its interaction with a permanent dipole such as that in a polar molecule is called a dipole-induced dipole force.

Dispersion Forces. Nonpolar molecules such as \( \text{O}_2 \), \( \text{SF}_6 \), and even the noble gases \( \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe} \) all show deviations from the ideal gas equation, and all condense at low temperatures to form liquids. We can ask: What kind of attractive forces exist between nonpolar molecules? In 1930, Fritz London proposed that although these molecules have no permanent dipole moments, their electron clouds are fluctuating. In a helium atom, for instance, the two electrons occupy a \( 1s \) orbital, which has a spherical shape. The electrons are in constant motion, and if for an instant they should both move to the same side of the nucleus, a short-lived dipole will exist. In an instant the electron will continue its motion and the dipole will be gone, but a new one will be formed. These short-lived dipoles are called instantaneous dipoles or temporary dipoles. An instantaneous dipole can polarize a neighboring molecule, thereby producing an induced dipole. The two dipoles will tend to stick together. The attractive interactions caused by instantaneous dipoles are known as dispersion forces.

The strength of dispersion forces depends on the polarizability of the molecule and can be as large as, or larger than, dipole-dipole forces. Polarizability is the tendency of an electron cloud to be distorted by the presence of an electrical charge such as that of an ion or the partial charge of a dipole. In general, the polarizability increases as the total number of electrons in a molecule increases. Since molecular mass and number of electrons are related, the polarizability of molecules and the strength of dispersion forces increases with increasing molecular mass.

Ion-Dipole Forces. The electrostatic attraction between an ion and a polar molecule is called an ion-dipole force. Hydration of ions, which was discussed in Section 6.6, is a good example of ion-dipole interactions. When an ionic compound such as NaBr dissolves, its
cations and anions are attracted to water molecules. Water molecules are polar and, as so, have a negative end and a positive end. The Na\(^+\) ions attract the negative end of the water molecule, and the Br\(^-\) ions attract the positive end of the water molecule. As the charge of an ion increases, it attracts polar molecules more strongly. Thus Mg\(^{2+}\) ions attract water molecules more strongly than Na\(^+\) ions, and S\(^2-\) ions attract water molecules more strongly than Br\(^-\) ions.

**Hydrogen Bonding.** An additional type of intermolecular force is necessary to explain certain properties of ammonia, water, and hydrogen fluoride. A hydrogen bond is a special type of dipole-dipole interaction between the hydrogen atom in a polar bond and an O, N, or F atom. In water, for instance, the attractions are stronger than just the attractions of one dipole for another. Each hydrogen atom, with its partial positive charge, is attracted to one of the lone electron pairs of an oxygen atom of a neighboring molecule. This interaction is called a hydrogen bond, and is usually represented by the three dots in the following:

```
H
\text{..} \delta^+ \quad \delta^- \quad \text{..}
H-O : .. H-O : ..
\vert
H
```

Hydrogen bonding is limited to compounds containing hydrogen bonded to nitrogen, oxygen, and fluorine. Hydrogen bonds are the strongest of the intermolecular forces, with energies of the order 10–40 kJ/mol. The energies of van der Waals interactions are between 2 and 20 kJ/mol.

**The requirements for hydrogen bond formation are:**

1. The element that is covalently linked to hydrogen must be sufficiently electronegative to attract bonding electrons and leave the hydrogen atom with a significant \(\delta^+\) charge. Only N, O, and F are sufficiently electronegative.
2. The electronegative atom, bound to hydrogen by the hydrogen bond, must have a lone pair of electrons.
3. The small size of the hydrogen atom allows it to approach N, O, and F atoms in neighboring molecules very closely. It is significant that hydrogen bonding is limited to these three elements of the second period. Both sulfur and chlorine are highly electronegative, but do not form hydrogen bonds. These third period atoms are apparently too large and do not present a highly localized nonbonding electron pair for the H atom to be attracted to.

**Properties of Liquids (11.3)**

**Surface Tension.** The surface tension of a liquid is a property that has no direct counterpart in solids or gases. Surface tension is what makes water bead up on a freshly waxed surface and what makes soap bubbles round. Surface tension is a force that tends to minimize the surface area of a drop of liquid. Energy is required to expand the surface of a liquid, and the surface tension is the amount of energy required to increase the surface area.
of a liquid by a unit area. Liquids in which strong intermolecular forces exist exhibit high surface tensions.

Water beads up on a freshly waxed surface because its cohesive forces are stronger than its adhesive forces. Cohesion is the intermolecular attraction between like molecules in the drop. Adhesion is the intermolecular attractions between unlike molecules, such as between water and wax. Since there is very little attraction between water and wax (adhesion), the strong cohesive forces tend to maintain the drop. The drop adopts a spherical shape because a sphere has the least surface area.

When water comes in contact with glass, adhesion is stronger than cohesion. Water is pulled against the glass surface, and we say that water "wets" the surface. Wetting results in the spreading of a thin film of water on the glass surface. The strength of the cohesive forces overcomes the ability of the surface tension to make a spherical drop.

**Viscosity.** One characteristic of liquids that we have all observed is related to how freely they flow. For example, water pours much more freely than motor oil, and motor oil more readily than glycerol. The unique pouring characteristics of each liquid are the result of its viscosity. Viscosity is a measure of a fluid's resistance to flow. Liquids whose molecules have strong intermolecular forces have greater viscosities than liquids that have weaker intermolecular forces. Table 11.3 (in the text) lists viscosities of some common liquids.

The viscosity of water and glycerol is the result of strong hydrogen bonds. The viscosity of motor oil results from strong London dispersion forces.

**Properties of Water.** Given its abundance and familiarity, we often fail to realize just how unusual water actually is. Some of the unusual properties of water are:

1. Water has a considerably greater surface tension than most other liquids.
2. At 4.184 J/g °C, the specific heat of water is one of the highest of all substances.
3. The heats of fusion and vaporization are 6.0 and 40.8 kJ/mol, respectively. H₂O is unusual because 40.8 kJ is a huge vaporization energy. Compare values in Table 11.6 (text).
4. The boiling point of water is about 200 °C higher than might be reasonably expected. Boiling point tends to be related to the molar mass. Compare the boiling point of water with that of other low molar mass liquids in Table 11.2.

<table>
<thead>
<tr>
<th>Table 11.2 Boiling Points of Some Small Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>CH₄</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
</tbody>
</table>

5. Density versus temperature. As liquids cool they become more and more dense. As water is cooled from 100 °C down to 4 °C it does indeed get more dense. But from 4 °C (actually 3.98 °C) down to 0 °C just the opposite happens: it gets less dense (see Table 11.3).
Table 11.3 Density of H₂O Near 0 °C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.9997</td>
</tr>
<tr>
<td>5.0</td>
<td>0.99999</td>
</tr>
<tr>
<td>3.98</td>
<td>1.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>0.99997</td>
</tr>
<tr>
<td>0</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

6. Density of liquid versus density of solid. There are over eight million known chemical compounds. All, except a dozen or so, have a solid state that is more dense than the liquid. Water, of course, is one of the exceptions. The density of solid water at 0 °C is 0.917 g/cm³, which compares with 0.9998 g/cm³ for the liquid. Because of its lower density, ice floats on water.

The Solid State (11.4 – 11.7)

Crystal Structure. The atoms, molecules, or ions of a crystalline solid occupy specific positions in the solid, and possess long-range order. The unit cell is the smallest unit that when repeated over and over again, generates the entire crystal. Three types of unit cell are the simple cubic cell (scc), the body-centered cubic cell (bcc), and the face-centered cubic cell (fcc). These types are illustrated in Figure 11.17 of the text.

In a simple cubic cell, particles are located only at the corners of each unit cell. In a body-centered cubic cell, particles are located at the center of the cell as well as at the corners. In a face-centered cubic cell, particles are found at the center of each of the six faces of the cell as well as at the corners. In many calculations involving properties of a crystal, it is important to know how many atoms or ions are contained in each unit cell. Atoms at the corners of unit cells are shared by neighboring unit cells. For a cubic cell, each corner atom is shared by eight unit cells and is counted as 1/8 particle for each unit cell. A face-centered atom is shared by two unit cells and is counted as 1/2 of an atom for each unit cell. An atom located at the center belongs wholly to that unit cell.

The packing efficiency is the percentage of the cell space occupied by spheres. The empty space is the interstices or "holes" between spheres. There are many substances whose atomic arrangement can be pictured as a result of packing together identical spheres so as to achieve maximum density. Many metallic elements and many molecular crystals display these "closest packed" structures. The text describes these two "closest packed" structures in Section 11.4. Alternating layers of spheres in ABABAB... fashion yields a hexagonal close-packed (hcp) structure, while alternating layers of spheres in the ABCABC... fashion generates the cubic close-packed (ccp) structure. In both, structures each sphere has a coordination number of 12 which is the maximum coordination number. For both structures the packing efficiency is 74%.

X-Ray Diffraction of Crystals. Crystal structures are analyzed experimentally by the technique of X-ray diffraction. Diffraction is a wave property. When an X-ray beam encounters a single crystal, the beam is scattered from the crystal at only a few angles, rather than randomly. The scattering angle, $\theta$, depends on the spacing, $d$, between layers or...
planes of atoms in the crystal, the wavelength of the X rays, and the reflection order \( (n = 1, 2, 3, \ldots) \). These quantities are related by the Bragg equation:

\[ n\lambda = 2d \sin \theta \]

The spacing \( (d) \) between atomic planes in crystals can be determined by using X rays of known wavelength \( (\lambda) \) and by experimental measurement of the angle \( \theta \).

**Types of Crystals.** In a solid, atoms, molecules, or ions occupy specific positions called lattice points. Crystalline solids are characterized by a regular three-dimensional arrangement of lattice points. In ionic solids the lattice points are occupied by positive and negative ions. In all ionic compounds there are continuous three-dimensional networks of alternating positive and negative ions held together by strong electrostatic forces (ionic bonds). Most ionic crystals possess high lattice energies, high melting points, and high boiling points. In ionic solids there are no discrete molecules as are found in molecular or covalent substances.

In covalent crystals the lattice points are occupied by atoms that are held by a network of covalent bonds. Diamond, graphite, and quartz are well known examples. Materials of this type have high melting points and are extremely hard because of the large number of covalent bonds that have to be broken to melt or break up the crystal. The entire crystal can be thought of as one giant molecule.

Covalent compounds form crystals in which the lattice positions are occupied by molecules. Such solids are called molecular crystals. Covalent crystals are soft and have low melting points. These properties are the result of the relatively weak intermolecular forces (van der Waals forces and hydrogen bonding) that hold the molecules in the crystal.

Crystals of polar compounds are held together by dipole-dipole forces and dispersion forces. Only dispersion forces occur in the lattices of nonpolar compounds. As a rule polar compounds melt at higher temperatures than nonpolar compounds of comparable molecular mass.

Metallic crystals are quite strong. Most transition metals have high melting points and densities. In metals the array of lattice points is occupied by positive ions. The outer electrons of the metal atoms are loosely held and move freely from ion to ion throughout the metallic crystal. This mobility of electrons in metals accounts for one of the characteristic properties of metals, namely the ability to conduct electricity.

Amorphous solids lack a well-defined arrangement and long range order. Glass is considered an amorphous solid because it lacks a regular three dimensional arrangement of atoms.

**Phase Changes and Phase Diagrams (11.8 – 11.9)**

**Liquid-Vapor Equilibrium.** The different physical states of a substance that are present in a system are referred to as phases. A phase is a homogeneous part of the system that is in contact with other parts of the system, but is separated by a noticeable boundary. Ice, liquid water, and water vapor can exist together in a suitable container. Each of these is a phase. When a liquid substance is placed in a closed container, it will not be long before molecules of this substance can be found in the gas phase above the liquid. Vaporization is the process in which liquids become gases. When a portion of a liquid evaporates, the gaseous molecules exert a pressure called the vapor pressure. The term vapor is often applied to the gaseous state of a substance that is normally a liquid or solid at the temperature of interest.
In a closed container the vapor pressure does not just continually increase, rather a state of equilibrium is reached in which the vapor pressure becomes constant and the amount of liquid remains constant. This equilibrium vapor pressure results from two opposing processes. The opposing process to vaporization is condensation. As the concentration of the molecules in the vapor phase increases, some will strike the liquid surface and condense.

\[
\text{vaporization} \quad \underset{\text{condensation}}{\xrightarrow{\text{liquid}}} \quad \text{vapor}
\]

When the rates of the opposing processes become equal, the vapor pressure remains constant and is called the equilibrium vapor pressure, or just vapor pressure. Note that in the state of equilibrium, even though the amounts of vapor and liquid do not change, there is considerable activity on the molecular level. Vaporization and condensation are constantly occurring, but at the same rates. Such an equilibrium state is referred to as a dynamic equilibrium.

Vapor pressure is a function of the temperature. As temperature increases the rate of vaporization increases, but the rate of condensation remains the same. Therefore, more molecules exist in the vapor phase at higher temperatures than at lower temperatures.

**Table 11.4 Vapor Pressure of Water**

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>17.54</td>
</tr>
<tr>
<td>30</td>
<td>31.82</td>
</tr>
<tr>
<td>40</td>
<td>55.32</td>
</tr>
<tr>
<td>50</td>
<td>92.51</td>
</tr>
<tr>
<td>80</td>
<td>355.1</td>
</tr>
<tr>
<td>86.5</td>
<td>460.0</td>
</tr>
<tr>
<td>100</td>
<td>760.0</td>
</tr>
</tbody>
</table>

Boiling of a liquid is marked by bubble formation. In a container open to the atmosphere, boiling of a liquid will occur when the temperature is raised high enough. In order for a bubble to form, the vapor inside the bubble must be able to push back the atmosphere. This will not occur until a temperature is reached at which the vapor pressure is greater than the atmospheric pressure. Therefore, the boiling point of a liquid is the temperature at which the vapor pressure is equal to the atmospheric pressure. Since the boiling point of a liquid depends on the atmospheric pressure, and the atmospheric pressure varies daily, the boiling point is not a constant. A normal boiling point is defined for purposes of comparing liquid substances. The normal boiling point is the boiling temperature when the external pressure is 1 atm. Figure 11.1 shows the vapor pressures and normal boiling points of three liquids.
The energy required to vaporize one mole of a liquid is called the molar heat of vaporization ($\Delta H_{vap}$). The value of $\Delta H_{vap}$ is directly proportional to the strength of intermolecular forces. Liquids with relatively high heats of vaporization have low vapor pressures and high normal boiling points.

The quantity $\Delta H_{vap}$ can be determined experimentally. The vapor pressure of a liquid is proportional to the temperature. The quantitative relationship between the vapor pressure ($P$) and the absolute temperature ($T$) is given by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

where $\ln P$ is the natural logarithm of $P$, $R$ is the ideal gas constant (8.314 J/K·mol), and $C$ is a constant.

A useful form of this equation is

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

The $\Delta H_{vap}$ can be calculated if the vapor pressures $P_1$ and $P_2$ are measured at two temperatures $T_1$ and $T_2$. Alternatively if $\Delta H_{vap}$ is already known and one vapor pressure $P_1$ is known at temperature $T_1$, you can calculate the vapor pressure $P_2$ at some new temperature $T_2$. See Example 11.10.

**Boiling Point as a Measure of IMF.** The boiling point and the heat of vaporization are convenient measures of the strength of intermolecular forces. In the liquid phase, molecules are very close together and are strongly influenced by intermolecular forces. In the gas phase, molecules are widely spaced, move rapidly, and have enough energy to overcome intermolecular forces. During vaporization, molecules are completely separated from one another. The heat of vaporization is the energy necessary to overcome intermolecular forces. The boiling point reflects the amount of kinetic energy that liquid molecules must achieve in order to overcome intermolecular forces and escape into the gas phase.
comparing molecules, as the strength of IMFs increase, the $\Delta H_{\text{vap}}$ and the normal boiling points increase.

**Critical Temperature and Pressure.** When a liquid is heated in a closed container the vapor pressure increases, but boiling does not occur. The vapor cannot escape, and the vapor pressure continually rises. Eventually a temperature is reached at which the meniscus between liquid and vapor disappears. This temperature is called the critical temperature. The critical temperature is the highest temperature at which the substance can exist as a liquid. The critical pressure is the lowest pressure that will liquefy a gas at the critical temperature. Critical temperatures and pressures are listed in Table 11.7 (in the text).

As we saw previously, intermolecular forces are dominant in liquids and effectively determine many of their properties. The critical temperature and pressure are no exceptions. Substances with high critical temperatures have strong intermolecular forces of attraction.

**Liquid-Solid Equilibrium.** The temperature at which the solid and liquid are in dynamic equilibrium at 1 atm pressure is called the normal melting point or freezing point. Melting is also called fusion. During melting the average distance between molecules is increased slightly as evidenced by the approximately 10% decrease in density for most substances.

$$\text{fusion} \quad \text{solid} \rightarrow \text{liquid} \quad \text{freezing}$$

The energy required to melt one mole of a solid is called the molar heat of fusion, $\Delta H_{\text{fus}}$. Upon freezing, the substance will release the same amount of energy. If this heat is removed from the system very quickly, the substance can be supercooled, that is cooled without solidifying. The $\Delta H_{\text{fus}}$ is always much less than $\Delta H_{\text{vap}}$ because during vaporization molecules are completely separated from each other, while melting only separates molecules to a small extent.

**Heating Curves.** A heating curve is a convenient way to summarize the solid-liquid-gas transitions for a compound. The heating curve of water is shown in Figure 11.2. It is the result of an experiment in which a given amount of ice, 1 mole for instance, at some initial temperature below 0 °C is slowly heated at a constant rate.

The curve shows that the temperature of ice increases on heating (line 1) until the melting point is reached. No rise in temperature occurs while ice is melting (line 2); as long as some ice remains, the temperature stays at 0 °C. The length of line 2 is a measure of the heat necessary to melt 1 mole of ice, which is $\Delta H_{\text{fus}}$. Along line 3 the temperature of liquid water increases from 0 °C to 100 °C. The slope of the line $\Delta t$ per joule of heat depends inversely on the specific heat of liquid water. The greater slope for line 1 than for line 3 means that less heat is required to raise the temperature of ice than of water. This is evidenced by the difference in specific heats of ice and liquid water. The specific heat of ice is 2.09 J/g·°C versus 4.18 J/g·°C for liquid H$_2$O.
At 100 °C the liquid begins to boil, and the heat added is used to bring about vaporization. The temperature does not rise until all the liquid has been transformed to gas. The length of line 4 is the heat required to vaporize 1 mole of liquid. Line 4 will always be longer than line 2 because $\Delta H_{vap} > \Delta H_{fus}$. Line 5 corresponds to the heating of steam. Again the slope of line 5 depends on the specific heat of steam, which is about 1.98 J/g °C.

**Solid-Vapor Equilibrium.** Sublimation is the transition of a solid directly into the vapor phase. Dry ice and iodine are substances that sublime readily. Ice also sublimes to some extent. As with liquids, the vapor pressure of a solid increases as the temperature increases. The direct conversion of solid to vapor is equivalent to melting the solid first and then vaporizing the liquid. From Hess's law we obtain:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

**Phase Diagrams.** From discussions in preceding sections we can see that the phase in which a substance exists depends on its temperature and pressure. In addition, two phases may exist in equilibrium at certain temperatures and pressures. Information about the stable phases for a specific compound is summarized by a phase diagram such as that shown in Figure 11.3.
A phase diagram is a graph of pressure versus temperature. The lines represent $P$ and $T$ at which two phases can coexist. The regions between lines represent $P$ and $T$ at which only one phase can exist. The line between the solid and liquid regions is made up of points of $P$ and $T$ at which the solid and liquid phases are in equilibrium. The line between the solid and gas regions is made up of points of $P$ and $T$ at which solid and gas are in equilibrium. And the line between the liquid and gas regions gives temperatures and pressures at which liquid and gas are in equilibrium. All three lines intersect at the triple point. This one point describes the conditions under which gas, liquid, and solid are all in equilibrium.

The phase diagram shows at a glance several properties of a substance: melting point, boiling point, and triple point. If a point ($P$ and $T$) describing a system falls in the solid region, the substance exists as a solid. If the point falls on a line such as that between liquid and gas regions, the substance exists as liquid and vapor in equilibrium.

Examples
11.10 – 11.13
Exercises
11.14 – 11.24
WORKED EXAMPLES

EXAMPLE 11.1 Types of Intermolecular Forces

Which of the following substances should have the strongest intermolecular attractive forces: N₂, Ar, F₂, or Cl₂?

* Solution

Note that none of these molecules is polar and that there is no chance for H bonding to occur. The only intermolecular forces existing in these molecules then are dispersion forces. Dispersion forces increase as the polarizability of the molecule increases, while polarizability increases with molecular mass. The most polarizable molecule will be Cl₂ (70.9 amu).

EXAMPLE 11.2 Types of Intermolecular Forces

Indicate all the different types of intermolecular forces that exist in each of the following substances.

a. CCl₄(t)
b. HBr(t)
c. CH₃OH(t)

* Solution

The types of IMF depend primarily on the polarity of the molecule and the electronegativity of atoms.

a. CCl₄ is nonpolar. The only type of IMF between nonpolar molecules are dispersion forces.
b. HBr is a polar molecule. The types of IMF are dipole-dipole and dispersion forces. There is no hydrogen bonding in HBr. The Br atom is not electronegative enough.
c. CH₃OH is polar and has a hydrogen atom bound to an oxygen atom. Dipole-dipole attractions, dispersion forces, and H bonds exist in liquid methanol.

EXAMPLE 11.3 Intermolecular Forces

The dipole moment \( \mu \) in HCl is 1.03 D, and in HCN it is 2.99 D. Which one should have the higher boiling point?

* Solution

The larger the dipole moment, the stronger the IMF. The stronger the IMF, the higher the temperature needed to provide molecules of the liquid with enough kinetic energy to overcome these attractive forces. The boiling point of HCN should be greater than that of HCl. Observed values are b.p. (HCl) = -85 °C, and b.p. (HCN) = 26 °C.
EXAMPLE 11.4 Intermolecular Forces in Liquids

The viscosities of ether and water are 0.000233 and 0.00101 N s/m². Discuss their relative values in terms of the following molecular structures.

\[
\text{water} \quad \begin{array}{c}
\text{O} \\
/ \\
\text{H} \quad \text{H}
\end{array} \quad \text{ethyl ether} \quad \begin{array}{c}
\text{CH}_3 \\
/ \\
/ \\
\text{CH}_2 \quad \text{CH}_2
\end{array}
\]

- Solution

Molecules with strong intermolecular forces have greater viscosities than those that have weak intermolecular forces. Here both molecules are polar: water because of the O–H bonds, and ether because of the polar C–O bond. However, water has a higher viscosity than ether because of its ability to form hydrogen bonds between molecules.

EXAMPLE 11.5 Number of Atoms Per Unit Cell

If atoms of a solid occupy a face-centered cubic lattice, how many atoms are there per unit cell?

- Solution

In a face-centered cubic cell there are atoms at each of the eight corners, and one in each of the six faces.

\[
8 \text{ corners (1/8 atom per corner)} + 6 \text{ faces (1/2 atom per face)} = 4 \text{ atoms per unit cell}
\]

EXAMPLE 11.6 Dimensions of a Unit Cell

Potassium crystallizes in a body-centered cubic lattice, and has a density of 0.856 g/cm³ at 25 °C.

a. How many atoms are there per unit cell?
b. What is the length of the side of the cell?

- Solution

a. A body-centered cubic structure has one K atom in the center, and eight other K atoms, one at each corner of the cube. The corner atoms, however, are shared by 8 adjoining cells. Each corner atom contributes 1/8 of an atom to the unit cell. The total number of K atoms per unit cell is

\[
1 + \frac{1}{8} (8) = 2 \text{ atoms}
\]
b. Ideally the crystal of potassium is made up of a large number of unit cells repeated over and over again. Thus, the density of the unit cell will be the same as the density of metallic K. Recall that density is an intensive property.

\[
\text{density} = \frac{\text{mass}}{\text{volume}}
\]

\[
\text{density (unit cell)} = \frac{\text{mass of 2 K atoms}}{a^3}
\]

where \(a\) is the length of the side of the unit cell.

The mass of a K atom is:

\[
\frac{39.1 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} = 6.50 \times 10^{-23} \text{ g/atom}
\]

Substituting into the density equation yields:

\[
0.856 \text{ g/cm}^3 = \frac{2(6.50 \times 10^{-23} \text{ g/atom})}{a^3}
\]

Rearranging yields:

\[
a^3 = 1.52 \times 10^{-22} \text{ cm}^3
\]

\[
a = 5.34 \times 10^{-8} \text{ cm} = 534 \text{ pm}
\]

EXAMPLE 11.7 Atomic Radius of a Potassium Atom

Determine the radius of a K atom for the metallic potassium crystal in Example 11.8.

• Solution

From Figure 11.22 in the text, it is clear that we need the diagonal distance of the body-centered cubic cell because only along the diagonal do the atoms actually touch. The diagonal \(c\) will equal \(4r\) where \(r\) is the atomic radius. From the figure we see that

\[
c = 4r \quad \text{and} \quad c = \sqrt{3} \, a
\]

Therefore

\[
4r = \sqrt{3} \, a
\]

where \(a\) is the length of an edge. Solving for \(r\), we get

\[
r = \frac{\sqrt{3}}{4} \times 534 \text{ pm} \times \frac{\sqrt{3}}{4}
\]

\[
r = 231 \text{ pm}
\]
EXAMPLE 11.8 Using the Bragg Equation

When X rays with a wavelength of 0.154 nm are diffracted by a crystal of metallic copper, the angle corresponding to the first order diffraction \((n = 1)\) is found to be \(37.06^\circ\). What is the spacing between planes of Cu atoms that gives rise to this diffraction angle?

**Solution**

The spacing between Cu atoms corresponds to \(d\) in the Bragg equation, which we rearrange to solve for \(d\).

\[
d = \frac{n\lambda}{2 \sin \theta}
\]

For a first-order diffraction \(n = 1\). The sine of \(37.06^\circ\) can be determined with your calculator.

\[
d = \frac{0.154 \text{ nm}}{2 \sin 37.06^\circ} = \frac{0.154 \text{ nm}}{2(0.603)}
\]

\[= 0.128 \text{ nm (128 pm)}
\]

EXAMPLE 11.9 Types of Crystals

What type of force must be overcome in order to melt crystals of the following substances?

a. Mg  b. Cl\(_2\)  c. MgCl\(_2\)  d. SO\(_2\)  e. Si

**Solution**

a. Magnesium is a metal and so it forms metallic crystals. Since the mobile electrons are shared between positive ions, the forces between Mg atoms could be described as covalent bonds, in this case called metallic bonds. The melting point is 1105 °C.

b. Cl\(_2\) forms molecular crystals that are held together by intermolecular forces, more specifically dispersion forces. The melting point is -101 °C.

c. MgCl\(_2\) is an ionic compound. When it melts, Mg\(^{2+}\) ions and Cl\(^-\) ions break away from their lattice positions. To melt magnesium chloride, ionic bonds must be broken. The melting point is 1412 °C.

d. SO\(_2\) is a polar molecule. Thus, dipole-dipole attractions and dispersion forces must be overcome. The melting point is -73 °C.

e. Si crystallizes in a diamond structure with each silicon atom bound to four others by covalent bonds. It is a covalent crystal, and covalent bonds must be broken in order for it to melt. The melting point is 1410 °C.
EXAMPLE 11.10 Clausius-Clapeyron Equation

The vapor pressure of water is 55.32 mmHg at 40.0 °C, and 92.51 mmHg at 50.0 °C. (See Table 5.3 in the text.) Calculate the molar heat of vaporization of water.

- Solution

The Clausius-Clapeyron equation relates the vapor pressure of a liquid to its molar heat of vaporization.

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

Substituting the values given above

\[
\ln \left( \frac{55.32 \text{ mmHg}}{92.51 \text{ mmHg}} \right) = \frac{\Delta H_{vap}}{8.314 \text{ J/K·mol}} \left( \frac{313 \text{ K} - 323 \text{ K}}{313 \text{ K} \times 323 \text{ K}} \right)
\]

\[
\ln 0.5980 = \frac{\Delta H_{vap}}{8.314 \text{ J/K·mol}} \left( \frac{-10 \text{ K}}{1.01 \times 10^5 \text{ K}^2} \right)
\]

Taking the logarithm and rearranging yields:

\[
\Delta H_{vap} = \frac{0.5142(8.314 \text{ J/K·mol})(1.01 \times 10^5 \text{ K})}{-10 \text{ K}}
\]

\[
\Delta H_{vap} = 43,000 \text{ J/mol}
\]

- Comment

Compare this result to the \( \Delta H_{vap} \) listed in Table 11.6 of the text, 40,790 J/mol. The observed difference is real. The \( \Delta H_{vap} \) is less at the boiling point than it is at a lower temperature. Over the entire temperature range of a liquid, \( \Delta H_{vap} \) is close to, but not really, a constant.

EXAMPLE 11.11 Vapor Pressure and Boiling Point

Using Figure 11.35 in the text estimate the boiling point of water in a pressure cooker at 2.0 atm pressure.

- Solution

The boiling point of water at 2.0 atm pressure is the temperature at which the vapor pressure of water is 2.0 atm. According to the figure this should be approximately 120 °C.
EXAMPLE 11.12 Heat of Vaporization

How much heat is given off when 1.0 g of steam condenses at 100 °C?

- Solution

The heat of vaporization of water at 100 °C is 40.8 kJ/mol. Condensation is the reverse of vaporization so it releases the same amount of heat.

\[
H_2O(g) \rightarrow H_2O(l) \quad \Delta H_{\text{cond}} = -40.8 \text{ kJ/mol}
\]

Since \(\Delta H_{\text{cond}}\) is in molar units, first convert 1.0 g \(H_2O\) into moles. The heat evolved when 1.0 g of water vapor condenses is:

\[
q = \text{mol } H_2O \times \Delta H_{\text{cond}}
\]

\[
= 1.0 \text{ g } H_2O \times \frac{1 \text{ mol}}{18.0 \text{ g } H_2O} \times \frac{40.8 \text{ kJ}}{1 \text{ mol}}
\]

\[
= -2.27 \text{ kJ}
\]

- Comment

This is a lot of heat and shows us why burns from steam can be very serious.

EXAMPLE 11.13 Heat of Fusion

The heat of fusion of aluminum is 10.7 kJ/mol. How much energy is required to melt one ton of Al at the melting point, 660 °C?

- Solution

The heat of fusion is the energy required to melt 1 mole of a substance. Therefore, first we need to convert 2000 lb of Al to moles.

\[
q = \text{mol } Al \times \Delta H_{\text{fus}}
\]

\[
= 2000 \text{ lb } Al \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol } Al}{27.0 \text{ g } Al} \times \frac{10.7 \text{ kJ}}{1 \text{ mol } Al} = 3.60 \times 10^5 \text{ kJ (360 MJ)}
\]
EXAMPLE 11.14 The Critical Temperature

Discuss the possibilities of liquefying oxygen and carbon dioxide at 25 °C by increasing the pressure.

Solution

Above its critical temperature a substance cannot be liquefied by increasing the pressure. Substances having critical temperatures above 25 °C can be liquefied at 25 °C by application of sufficient pressure. With a critical temperature of 31 °C, CO₂ can be liquefied at 25 °C with application of enough pressure. The pressure required can be read off the phase diagram for CO₂ (Figure 11.41 in the text). Reading straight up from 25 °C you will cross the liquid-vapor equilibrium point at a pressure of 67 atm. This is the pressure required to liquefy CO₂ at 25 °C. Oxygen has a critical temperature of −119 °C; therefore, at any temperature above −119 °C oxygen cannot be liquefied, no matter how much pressure is applied. To liquefy O₂, its temperature must first be lowered below −119 °C and pressure applied.