CHAPTER 7 – STATES OF MATTER AND CHANGES IN STATE

Introduction

The materials we deal with every day exist in one of three states of matter: solid, liquid, or gas. The molecules in the liquid and solid phase are much closer to one another than are the molecules in the gas state. Consequently, the solid and liquid states are often called the *condensed states.* Some substances, such as water, are found in all three states under normal conditions (ice, water, and steam). However, most other substances are found in only one state under normal conditions. Thus, most of us have only encountered elemental iron as a solid, helium as a gas, and table salt as a solid. In this chapter, we examine the properties of the states of matter.

7.1 Gases

Introduction

Gases are characterized by their volume (V), pressure (P), temperature (T), and the number of moles of particles (n). In this section, we discuss how the volume of a gas is affected by changes in its pressure, temperature, and number of moles. Finally, we consider mixtures of gases.

Objectives

- Explain how a barometer is used to determine atmospheric pressure.
- Determine the pressure of a gas with a manometer reading and atmospheric pressure.
- Explain how the volume of a gas varies with its pressure (sketch V vs. P for an amount of gas at constant T).
- State Boyle's Law and use it to determine the volume of a gas at one pressure from its volume at a different pressure but at the same temperature.
- Explain how the volume of a gas varies with its temperature (sketch V vs. T for an amount of gas at constant pressure).
- Convert a temperature from the Celsius scale to the Kelvin scale and vice versa.
- State Charles's Law and use it to determine a volume of a gas at one temperature given its volume at a different temperature.
- State the Ideal Gas Law.
- Use the Ideal Gas Law.
- Define *partial pressure.*
- Determine the pressure of a mixture of gases from the partial pressures of the component gases.
- Define *molarity* and determine the molarity of a gas from its pressure and temperature or the number of moles of gas and its volume.

Boyle's Law and Pressure

7.1-1. Boyle's Law and Pressure

Barometric pressure is usually given by the height of a mercury column that the atmosphere will support.

As shown in Figure 7.1, a ***barometer*** is a glass tube, which is closed at one end and open at the other, that is filled with mercury and immersed with the open end down into a pool of mercury. Only part of the mercury drains from the tube, and the resulting column has a height that depends upon the atmospheric pressure. The column, which is supported by the molecules in the atmosphere, has a height of 760 mm at sea level at normal conditions. Gas pressures can be determined by measuring the height of the mercury column that they support. The height is usually given in mm, and the pressure is given in mm of Hg or ***torr*** (1 torr = 1 mm Hg). The following are common ways of expressing the normal pressure at sea level.

$$1 \text{ atm} = 14.7 \text{ lb/in}^2 = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01 \times 10^5 \text{ Pa} \qquad (7.1)$$

Pa is the ***pascal***, the SI unit of pressure.

$$1\ \mathrm{Pa} = 1\ \mathrm{kg \cdot m^{-1} \cdot s^{-2}}$$

Note that the barometric pressures given in weather reports are given in inches of Hg. The median barometric pressure at sea level is 760 mm = 29.9 in. Some extreme barometric pressures observed in the U.S. are given below.

- High: 809 mm = 31.9 in = 1.06 atm (Alaska, 1969)
- Low: 670 mm = 26.3 in = 0.88 atm (Florida, 1935)

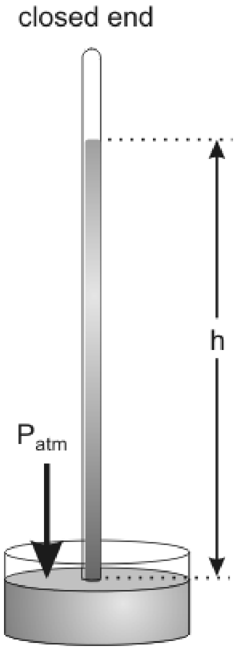


Figure 7.1: A Barometer The pressure exerted by the weight of the mercury column of height h equals the pressure exerted by the weight of the atmosphere.

7.1-2. Measuring Pressure with a Manometer

The pressure of a gas in the laboratory is often found as the difference in heights of two columns of a liquid (most often mercury) in a manometer.

The device used to measure the pressure of a gas in the laboratory is called a ***manometer***. One side of the manometer shown in Figure 7.2 is open to the atmosphere, while the other is attached to the gas whose pressure is to be measured. Consequently, the atmospheric pressure (P_{atm}) is pushing on the right side, and the unknown gas pressure (P) is pushing on the left. When the two pressures are the same, the two mercury columns in the manometer are at the same height, and $h = 0$. However, when the two pressures are not the same, the side with the greater pressure exerts the greater force, which causes the mercury column on that side to drop, and the column on the other side to rise. The difference in the pressures of the two sides is given by the difference in the two mercury levels, h, as described below.

- $P_{\text{gas}} = P_{\text{atm}} + h$ if mercury level is higher on atmosphere side
- $P_{\text{gas}} = P_{\text{atm}} - h$ if mercury level is higher on gas side

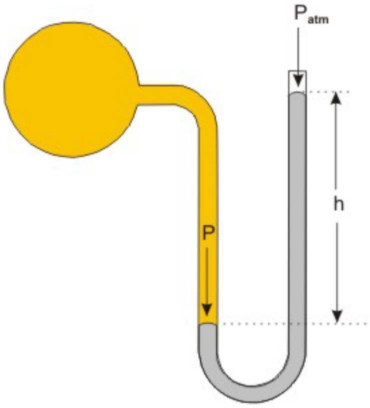
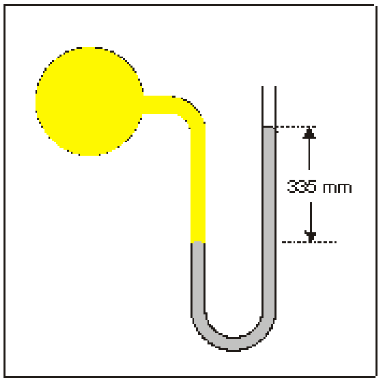


Figure 7.2: Determining Pressure with a Manometer A manometer, which is used to measure the pressure of a gas: In the above experiment, the pressure of the gas (P) is greater than barometric pressure (P_{atm}) by h mm of Hg, i.e., $P = P_{\text{atm}} + h$.

7.1-3. Barometer Exercise

EXERCISE 7.1:



What is the pressure of the yellow gas in torr (mm Hg) if barometric pressure is 762 torr?

_______________ torr

What is the pressure of the yellow gas in atmospheres?

_______________ atm

7.1-4. Boyle's Law

$PV = k$, where k is a constant that depends only upon the amount and temperature of the gas.

The volume of a given amount of gas at a constant temperature varies with its pressure. The graph in Figure 7.3 shows the volume of one mole of gas as a function of its pressure at 0 °C. The relationship between pressure and volume

$$PV = k(n, T) \qquad \text{Boyle's Law} \tag{7.2}$$

is known as ***Boyle's Law***. The constant, $k(n, T)$, is a function of the number of moles of gas (n) and its temperature (T). Boyle found that the product of the pressure of a gas and its volume is constant as long as the number of moles of the gas and the temperature of the gas are held constant. The following equation is often used for Boyle's Law.

It indicates that the PV product is unchanged in processes that involve no change in temperature or amount of gas. Thus, the following form of Boyle's Law is also commonly used.

$$P_\mathrm{f}V_\mathrm{f} = P_\mathrm{i}V_\mathrm{i}$$

where $P_\mathrm{f}V_\mathrm{f}$ is the final PV product and $P_\mathrm{i}V_\mathrm{i}$ is the initial product.

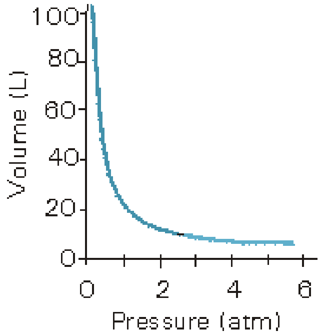


Figure 7.3: Volume of Gas vs. Pressure of Gas The volume of one mole of a gas at 0 °C vs. the pressure of the gas is shown.

7.1-5 Boyle's Law Exercise

EXERCISE 7.2:

The pressure on 5.2 L of a gas is decreased from 1.0 to 0.75 atm at constant temperature. What is the new volume?

initial volume in liters ______________ L

initial pressure in atmospheres ______________ atm

final pressure in atmospheres ______________ atm

final volume in liters ______________ L

Temperature and Charles's Law

7.1-6. Charles's Law

$V = kT$, where k is a constant that depends on the amount and pressure of the gas, and T is the temperature in kelvins.

Experiments with gases in the late 1700s and early 1800s determined the relationship between the volume of a gas and its temperature. As shown in Figure 7.4, the volume of a given amount of gas at constant pressure increases linearly with its temperature. Although the slope of the straight line varies with the number of moles and pressure of the gas, extrapolation of all lines to the temperature of zero volume yields the same temperature, −273.15 °C (degrees Celsius). At lower temperatures, the volume of the gas would be negative, which is not possible, so we conclude that temperatures can be no lower than −273.15 °C. The absolute temperature, or Kelvin, scale was defined based on this absolute minimum in temperature.

$$\mathrm{K} = {}^\circ\mathrm{C} + 273.15 \tag{7.3}$$

Note that the word "degrees" is not used with Kelvin temperatures, so 273 K is said "273 kelvins." Equation 7.3 shows that you add 273.15 to a temperature in degrees Celsius to convert it to the absolute scale. For example, water freezes at 0 °C, which is 273 K, and boils at 100 °C, which is 373 K. Room temperature is usually assumed to be 25 °C, which is 298 K. The absolute temperature must be used in all equations involving the temperature of a chemical system. However, either the Celsius or absolute scales can be used in equations involving a change in the temperature of a system because the unit size is the same in both scales. Once the new temperature scale was defined, the volume of a gas was found to be directly proportional to its temperature expressed in kelvins, which is known as **Charles's Law**.

$$V = k(n, P)T \qquad \text{Charles's Law} \qquad (7.4)$$

Charles's Law indicates that the V/T ratio of a gas is constant as long as n and P are unchanged, so Charles's Law can also be given as follows.

$$\frac{V_\mathrm{f}}{T_\mathrm{f}} = \frac{V_\mathrm{i}}{T_\mathrm{i}}$$

The above shows that the final V/T ratio equals the initial V/T ratio as long as the amount of gas and its pressure are unchanged.

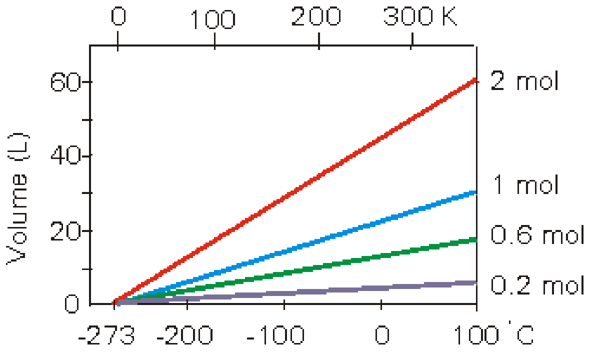


Figure 7.4: Charles's Law The volume of the specified number of moles of gas as a funtion of temperature: The bottom scale is in degrees Celsius, and the top scale is the Kelvin scale.

7.1-7. Charles's Law Exercise

EXERCISE 7.3:

What is the volume of gas at 0 °C if the volume is 250 mL at 100 °C?

initial volume in milliliters ______________ mL

initial temperature in kelvins ______________ K

final temperature in kelvins ______________ K

final volume in milliliters ______________ mL

The Ideal Gas Law

7.1-8. Ideal Gas Law

$PV = nRT$ is the ideal gas law.

Avogadro's Law states that equal volumes of gases measured under the same conditions of temperature and pressure contain equal numbers of molecules. The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of gas,

$$V = k(P, T)n \qquad \text{Avogadro's Law} \tag{7.5}$$

where n is the number of moles of gas, and $k(P,\ T)$ is a proportionality constant that depends upon the pressure and the temperature of the gas.

We now have three equations that relate the volume of a gas to its pressure, its temperature, and to the number of moles of the gas. These three relationships can be combined into the ***ideal gas law***.

$$PV = nRT \qquad \text{Ideal Gas Law} \tag{7.6}$$

P	***V***	=	***n***	***R***	***T***
Pressure expressed in **atmospheres**: It can be expressed in other units, but that would change the value of R.	Volume of the gas expressed in **liters**: It can be expressed in other units, but that would change the value of R.		**Number of moles of gas**	$R = 0.0821\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$: It is the **gas law constant**.	T is the absolute temperature in **kelvins**.

Table 7.1

7.1-9. Ideal Gas Law Exercise

<u>EXERCISE 7.4</u>:

The ideal gas law can be used to solve for any one of the variables (P, V, n, or T) if the others are known. Things to remember when using $R = 0.0821\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$:

- T is in kelvins.
- P is in atmospheres.
- V is in liters.

What is the pressure in a 280-mL container that contains 1.8 g He at 330 °C?

$n =$ ______________ mol

$R =$ ______________ $\text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$T =$ ______________ K

$V =$ ______________ L

$P =$ ______________ atm

Mixtures of Gases

7.1-10. Molarity

The molar concentration, or molarity, of a gas is the number of moles of gas present in 1 L.

Mixtures of gases are the same throughout, i.e., they are *homogeneous mixtures*, and homogeneous mixtures are called solutions. The molecules in a mixture (solution) of ideal gases do not interact, so they can be treated independently. This means that we can apply the ideal gas law to each component of a mixture as if the other components were not present. Each gas in a mixture is at the same temperature, and each has the same volume (the volume of the container). Thus, only the number of moles and the pressure of each component differ. The pressure exerted by gas A in a mixture is called the ***partial pressure*** of A and given the symbol P_A. If A is an ideal gas, we can express its pressure with the ideal gas law as follows.

$$P_\mathrm{A} = \frac{n_\mathrm{A}RT}{V} \qquad \text{Partial Pressure} \qquad (7.7)$$

(n_A/V) is the number of moles of A per unit volume. The amount of substance per unit volume is called the ***concentration*** of the substance. When the amount is expressed in moles and the volume in liters, it is called the molar concentration, or ***molarity***, of the substance, so n_A/V is the molarity of A in the solution. Molarity is the most common unit of concentration in a chemistry laboratory (and the only one used in this course). The molarity of A is represented as [A] and is defined as follows.

$$[\mathrm{A}] = \frac{\text{moles of A}}{\text{total volume in liters}} \qquad \text{Definition of Molarity} \qquad (7.8)$$

[A] = 1 M is read as "the concentration of A is one molar, or one mole per liter." Substituting $[\mathrm{A}] = n/V$ into the expression for the partial pressure of A, we obtain the relationship between the pressure of a gas and its concentration.

$$P_\mathrm{A} = [\mathrm{A}]RT \qquad \text{Pressure and Molarity} \qquad (7.9)$$

Thus, the pressure of a gas is directly proportional to its molar concentration.

EXAMPLE:

If a mixture of gases in a 9.6-L flask at 300 K contains 0.53 moles of A, we would determine that $[\mathrm{A}] = 0.53/9.6 = 0.055$ M, i.e., the solution of gases is 0.055 molar in A. In addition, the partial pressure of A would be:

$$\begin{aligned} P_\mathrm{A} &= (0.055\ \mathrm{mol/L})(0.0821\ \mathrm{L\cdot atm\cdot mol^{-1}\cdot K^{-1}})(300\mathrm{K}) \\ &= 1.36\ \mathrm{atm} \end{aligned}$$

7.1-11. Molarity Exercise

EXERCISE 7.5:

What is the concentration of fluorine (F_2) in a 4.0-L flask that contains 4.2 g of fluorine?

1. Determine the number of moles of F_2 ($M_m = 38.00$ g/mol).

$n =$ ______________ mol F_2

2. Calculate the molarity.

$[F_2] =$ ______________ M

7.1-12. Partial Pressures

The pressure of a mixture of gases equals the sum of the partial pressures of the component gases.

The total pressure in a container filled with a mixture of gases is equal to the sum of the partial pressures of the component gases.

$$P_{\text{tot}} = \sum_{\text{all gases}} P_i \qquad \text{Dalton's Law of Partial Pressures} \tag{7.10}$$

where P_i is the partial pressure of the i^{th} component of the gas.

Thus, the total pressure in a container that contains two gases, A and B, can be expressed as follows.

$$P = P_{\text{A}} + P_{\text{B}}$$

Using Equation 7.7 to evaluate P_{A} and P_{B}, we obtain the following.

$$P = \frac{n_{\text{A}}RT}{V} + \frac{n_{\text{B}}RT}{V} = \frac{(n_{\text{A}} + n_{\text{B}})RT}{V}$$

The total pressure of a mixture of gases equals the total number of moles of gas times RT/V.

7.1-13. Partial Pressure Exercise

EXERCISE 7.6:

What are the partial pressures of Ne and He in a 6.0-L flask that contains 0.12 mol Ne and 0.19 mol He at 55 °C?

$P_{\text{Ne}} =$ ______________ atm

$P_{\text{He}} =$ ______________ atm

What is the total pressure in the flask?

______________ atm

7.1-14. Gas Law Exercise

EXERCISE 7.7:

A mixture contains 15 g Ne (AW = 20) and 10 g Ar (AW = 40) in a 5.0-L container at 30 °C.

Neon:
number of moles ____________ mol Ne

molar concentration ____________ M Ne

partial pressure in atm ____________ atm Ne

Argon:
number of moles ____________ mol Ar

molar concentration ____________ M Ar

partial pressure in atm ____________ atm Ar

What is the total pressure in the container?

____________ atm

7.2 Kinetic-Molecular Theory and Thermal Energy

Introduction

The ideal gas law applies only to gases that exhibit ideal gas behavior, which can deviate from real gas behavior. In this section, we examine the properties of ideal gases.

Objectives

- Explain the meaning of *temperature* at the molecular level.
- Explain the meaning of *thermal energy* and determine the relative thermal energies of several gases.

7.2-1. Postulates

The behavior of gases is explained by kinetic-molecular theory, which is based on the four postulates provided below. Gases that obey all four postulates are called ideal gases.

1 The volume of the particles is negligible compared to the volume of the container. On average, the distances between gas particles are large compared to the size of the particles.

2 The particles are in constant, random motion. Collisions are elastic, i.e., no kinetic energy is converted into potential energy.

3 Particles in the gas phase do not interact with one another, i.e., there are no attractive forces between the particles, which is why the collisions are elastic (Postulate 2).

4 The average kinetic energy of the molecules in a gas depends only on the absolute temperature of the gas. The kinetic energy of a particle is $\frac{1}{2}mv^2$, so hot molecules move faster than cold ones. This postulate provides the molecular definition of the absolute ***temperature***:

  - The ***absolute temperature*** of a system is a measure of the *average* kinetic energy of the molecules in the system.

7.2-2. Thermal Energy

Thermal energy, which is approximated as RT, is a measure of the average kinetic energy of the molecules.

The average kinetic energy of the molecules in a system is often referred to as the ***thermal energy*** of the system. Thermal energy is an average energy because the molecules in a system do not all move at the same speed—some are moving faster and have more energy than others. All of the energies related to molecules or ions that we have encountered to this point have been potential energies arising from Coulombic interactions. The thermal energy of the molecules is energy that can be used to overcome Coulombic interactions. Thus, thermal energy can be used to break a bond or to melt a solid. Thermal energy is also required to make reactions occur. As we will see in Chapter 9, rates of reaction increase when the temperature is increased. Thus, thermal energy plays an important role in chemistry, but the thermal energy of a solid or a liquid is not easily determined. However, thermal energy is usually approximated as follows:

$$E_{\text{thermal}} \sim RT \qquad \text{Thermal Energy Approximation} \qquad (7.11)$$

where

- $R = 8.31451\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ or
- $R = 0.00831451\ \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

is the ideal gas law constant in J rather than L · atm.

7.2-3. Thermal Energy Exercise

EXERCISE 7.8:

What is thermal energy at room temperature (25 °C)?

____________ kJ/mol

What is thermal energy at 100 °C?

____________ kJ/mol

What is the approximate temperature at which $E_{\text{thermal}} \sim 100$ kJ/mol?

____________ K

7.3 Intermolecular Interactions

Introduction

Why are some molecules gases, while others are liquids and solids at room conditions? Why does water expand upon freezing? The answers to both questions lie in the nature of the interaction between molecules, the topic of this section.

Prerequisites

- 1.7 Energy (Distinguish between kinetic and potential energy.)
- 1.8 Electromagnetism and Coulomb's Law (Explain how the force of attraction of two opposite charges varies with their charge and the distance between them.)
- 5.2 Bond Polarity (Represent the bond dipole with an arrow.)
- 5.6 Determining Lewis Structures

Objectives

- Distinguish between intermolecular and intramolecular forces.
- Explain a temporary dipole and how it leads to dispersion forces.
- Describe a molecular dipole and represent it with an arrow.
- Use bond dipoles in a molecule to determine if there is a molecular dipole.
- Describe the hydrogen bond and state the requirements for it.
- Describe the structure of ice, explain why it has the structure it does, and use the structure to explain some physical properties of water.

7.3-1. Intermolecular Forces

Particles in the gas phase are relatively far apart, so their attractive forces are negligible compared to their thermal energy. However, the attractive forces between particles in the condensed states are strong enough to hold the particles in contact with one another. Ionic compounds are always solids at room temperature because their cations and anions are held in the solid network by strong electrostatic attractions called ionic bonds. However, molecular substances can occur as gases (O_2), liquids (H_2O), or solids (sugar) at room conditions. This diversity in states arises from a diversity in the strengths of the forces between the molecules. Whereas the strength of ionic bonds determines the physical properties of a salt crystal, the physical properties of molecular substances are not related to the strength of their covalent bonds. In molecular substances, we must distinguish between two different kinds of forces:

1 ***Intramolecular forces*** exist **within** a molecule. They are the bonds between atoms that hold the atoms together in the molecule.

2 ***Intermolecular forces*** exist **between** molecules. They are the forces between different molecules that keep the molecules in the liquid and solid states.

The N≡N bond is a very strong bond, so the intramolecular force between the nitrogen atoms in an N_2 molecule is very strong. However, N_2 is a gas at room conditions because the intermolecular forces between different N_2 molecules are very weak. Intermolecular forces, like all interactions in chemistry, are electrostatic. Thus, condensed phases in molecular substances result because there is an attraction between regions of opposite charge on the molecules. However, these charges are smaller, more diffuse, and farther apart than those in bonds, so the force of attraction between different molecules is much less than that between the atoms in a bond. Bond energies lie between 100 and 1000 kJ/mol, but the strengths of most intermolecular interactions are less than 10 kJ/mol. Consider that the bond formed with Super Glue is an intramolecular (bonding) interaction, while static cling is an intermolecular interaction.

Although molecules are electrically neutral, many have regions of nonzero charge due to asymmetric distributions of their valence electrons that produce regions with above normal electron density that are slightly negative ($\delta-$) and regions of depleted electron density that are slightly positive ($\delta+$). Such molecules contain two poles, one positive ($\delta+$) and one negative ($\delta-$). The presence of two poles in the molecule results in a molecular dipole, much like the bond dipole discussed in Chapter 5.2 Bond Polarity. In the remainder of this section, we discuss the origin of these dipoles and the forces they create.

Dispersion Forces

7.3-2. Dispersion Forces

Dispersion forces, which result from the interaction of induced dipoles, increase with molar mass.

Electrical charge in molecules is derived from asymmetrical electron distributions within the molecules, i.e., there are regions within the molecule that are electron rich and other regions that are electron deficient. These regions of excess and deficient electron density result in negatively and positively charged regions in the molecule. The center of the positive regions and the center of the negative regions form two **poles**. If the two poles do not coincide, the molecule is said to have a ***dipole***. Dipoles can be permanent or temporary.

Temporary dipoles result from random electron motion, which can create a dipole in a molecule. The resulting dipole then *induces* dipoles in surrounding molecules as the electrons in surrounding molecules move toward the positive pole and away from the negative pole. Thus, temporary dipoles are also called **induced dipoles**. The force of attraction of the opposite charges of the temporary dipoles is called a ***dispersion force***.

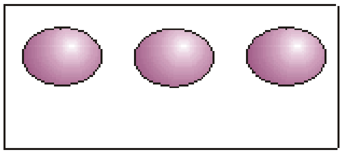


Figure 7.5a: The Dispersion Force Three molecules with no regions of charge have no way to interact.

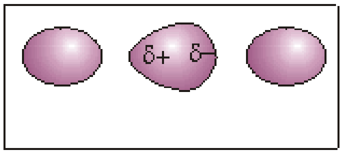


Figure 7.5b: The Dispersion Force Random electron movement in the central molecule causes more electrons to be on one side and fewer on the other, which results in two charged regions.

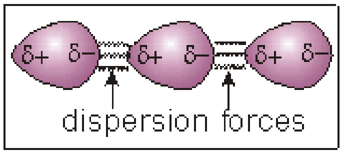


Figure 7.5c: The Dispersion Force The charged regions on the central molecule induce charged regions on the adjacent molecules. The result is that the adjacent molecules have ***induced dipoles***. The interaction of the opposite charges of the induced dipoles is called a **dispersion force**.

Dispersion forces are present in all molecular substances, but they are most important in large molecules where the electron clouds are more easily deformed. Thus, **dispersion forces increase with molar mass**.

Molecular Dipoles

7.3-3. Dipolar Interactions

Dipolar forces act in addition to dispersion forces to increase the strength of the intermolecular interaction.

Most molecules contain atoms with partial positive charge and atoms with partial negative charge as a result of the electronegativity differences that produce polar bonds. If the centers of positive and negative charge do not coincide, two poles are produced and the molecule has a permanent dipole. The magnitude of the dipole depends upon both the size and the separation of the two centers of charge; if the centers of charge coincide, their separation is zero and they have no permanent dipole. Molecules with permanent dipoles are said to be ***polar molecules***, or simply polar, while those that do not have permanent dipoles are said to be nonpolar. Interactions between the centers of opposite charge of the permanent dipoles of different molecules are called ***dipolar forces*** or dipole-dipole forces. Dipolar forces act in addition to dispersion forces. For example, the dispersion forces in HCl and F_2 are expected to be nearly the same because they have similar molar masses (38 and 37 g/mol, respectively). However, HCl is polar, and as shown in Figure 7.6, the partial positive charge on the hydrogen atom of one HCl molecule interacts with the partial negative charge on the chlorine atom of an adjacent molecule to produce a dipolar force between the molecules. This force is in addition to the dispersion forces, so the intermolecular forces are greater in HCl than in F_2, which makes HCl gas much easier to liquefy.

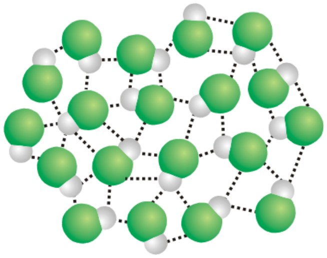


Figure 7.6: Dipolar interactions in HCl Dipolar interactions (dotted lines) are between the chlorine atom (negative end of dipole) of one molecule and the hydrogen atom (positive end of dipole) on an adjacent molecule.

7.3-4. Charge Distribution

Molecules with a permanent asymmetric charge distribution are said to be polar or to have a molecular dipole.

Recall from Chapter 5.2 Bond Polarity that bond dipoles arise in bonds due to electronegativity differences between the bound atoms. Although the total charge on a molecule is zero, some of the atoms in a molecule with polar bonds can carry some charge. The charge on an atom lies somewhere between its formal charge and its oxidation state, depending upon bond polarities.

The centers of positive and negative charge in a molecule are called poles, and a ***molecular dipole*** is defined as the product of the charge on the two poles of a molecule and the distance between them. If the centers of positive and negative charge coincide, their separation is zero, and there is no molecular dipole. Molecules with permanent dipoles are said to be ***polar***, while those without molecular dipoles are said to be nonpolar. We now compare the charge distributions in SO_3 and H_2O. In Figures 7.7a and 7.7b, regions of negative charge are shown in red and regions of positive charge are shown in blue, with a deeper color used to depict more charge.

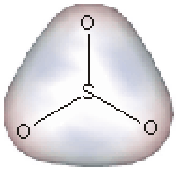


Figure 7.7a: Charge Distribution in SO_3

O is more electronegative than S, so the three S–O bonds in SO_3 are polar. As a result, negative charge resides on the O atoms (red regions in Figure 7.7a), while positive charge is found around the S atom (blue regions in Figure 7.7a). The geometric centers of the negative and positive charge both lie on the sulfur atom. Although SO_3 has regions of charge, the centers of positive and negative charge coincide, so SO_3 does not contain a molecular dipole and is a nonpolar molecule.

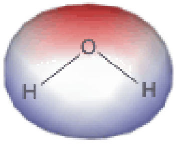


Figure 7.7b: Charge Distribution in H_2O

O is more electronegative than H, so the two O–H bonds in H_2O are polar. Increased electron density on the oxygen produces a partial negative charge there (red region in Figure 7.7b), while decreased electron density on the hydrogens results in positive charge on both hydrogen atoms (blue regions in Figure 7.7b). The coloring is more intense in H_2O than in SO_3 because O–H bonds are more polar than S–O bonds. The center of negative charge (near the O atom) does not coincide with the center of positive charge (between H atoms), so water is a polar molecule (has a molecular dipole).

7.3-5. Representing Molecular Dipoles

A molecular dipole is represented by an arrow that points from the positive pole toward the negative pole. A line is drawn through the arrow at the positive end to make "+" sign.

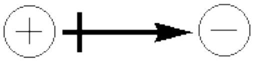


Figure 7.8 A molecule's permanent dipole is indicated by an arrow pointing from the center of positive charge toward the center of negative charge. A short line crosses the arrow forming a "+" at the positive end.

7.3-6. Effect of Geometry on Molecular Polarity

Molecular dipoles also depend upon molecular shape.

The strength of the dipole depends on both the charge on the poles and their separation.

- **Charge**: The charge depends upon the electronegativity differences (strengths of the bond dipoles).
- **Structure**: The separation between dipoles depends upon the structure of the molecule. If the structure is such that the centers of negative and positive charge coincide, i.e., the separation is zero, the molecule is not polar.

Consider the examples of CO_2 and SO_2.

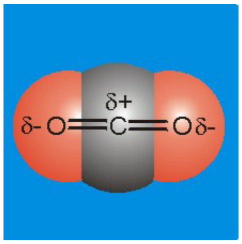


Figure 7.9a: Charge Distribution in CO_2

CO_2

- **Charge**: Oxygen ($\chi = 3.5$) is more electronegative than carbon ($\chi = 2.5$), so the oxygen atoms will carry some negative charge, while the carbon carries some positive charge.
- **Structure**: CO_2 is linear, so the centers of positive and negative charge both reside on the carbon atom.
- **Polarity**: Since the centers of charge coincide, CO_2 is not polar.

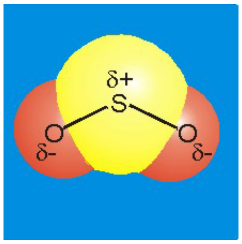


Figure 7.9b: Charge Distribution in SO_2

SO_2

- **Charge**: The electronegativity of sulfur is identical to that of carbon, so the charges carried by S and O in SO_2 are identical to those carried by C and O in CO_2.
- **Structure**: There is a lone pair on the sulfur atom, so sulfur dioxide is bent with an O–S–O bond angle of about 120°.

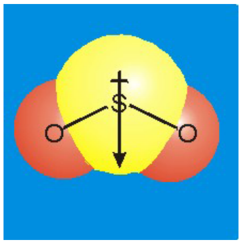


Figure 7.9c: Polarity in SO_2

- **Polarity**: The center of positive charge is on the sulfur atom, but the center of negative charge lies at the midpoint of the line connecting the two oxygen atoms. Thus, the centers of positive and negative charge do not coincide, so SO_2 is a polar molecule. The dipole points from the positive sulfur toward the center of negative charge between the two oxygen atoms.

7.3-7. Molecular Dipole of H_2O

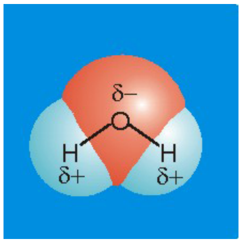


Figure 7.10a

- **Charge:** Oxygen is more electronegative than hydrogen, so it carries a partial negative charge, and the hydrogen atoms each carry a partial positive charge.
- **Structure:** There are two lone pairs on the oxygen atom, so water is bent with an H–O–H bond angle of about 109° (actually it is 104° due to a strong lp-lp interaction).

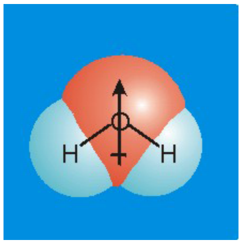


Figure 7.10b

- **Polarity**: The center of negative charge resides on the oxygen, while the center of positive charge resides on the line between the two hydrogen atoms. The two centers do not coincide, so water is a polar molecule (it contains a dipole). In fact, water is a very polar molecule. Its strong dipole plays an important role in its ability to dissolve ionic substances such as table salt.

7.3-8. Molecular Dipoles from Bond Dipoles

Molecular dipoles are the vector sum of the bond dipoles in a molecule.

Recall that the bond dipole (5.2 Bond Polarity) points from the less electronegative atom to the more electronegative atom in the bond. It is a vector that indicates the charge distribution in the bond. The molecular dipole can be determined as the vector sum of the bond dipole vectors.

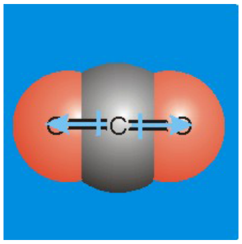


Figure 7.11a: Molecular dipoles are the sums of bond dipoles. The bond dipole of each CO bond points from the carbon toward the oxygen. Because they point in opposite directions, they cancel one another, and CO_2 does not have a molecular dipole, i.e., it is a nonpolar molecule.

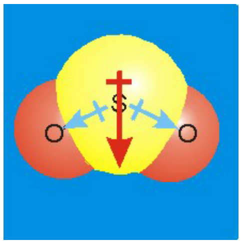


Figure 7.11b: Molecular dipoles are the sums of bond dipoles. Each SO bond has a bond dipole pointing from the sulfur toward the more electronegative oxygen. The sum of the two bond dipoles results in the molecular dipole represented by the red arrow.

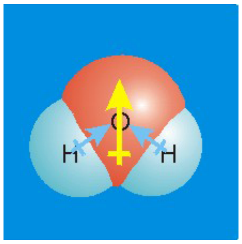
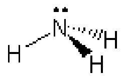


Figure 7.11c: Molecular dipoles are the sums of bond dipoles. The OH bond dipoles (blue arrows) are at 104° angles. The resultant molecular dipole (yellow arrow) points from the center of the line connecting the hydrogens toward the oxygen.

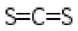
7.3-9. Predicting Dipoles Exercise

<u>EXERCISE 7.9</u>:

Predict whether each of the following molecules is polar or nonpolar.

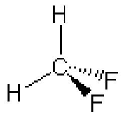


polar
nonpolar

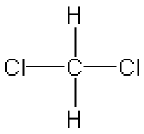


polar
nonpolar

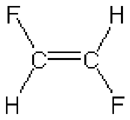
polar
nonpolar



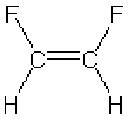
polar
nonpolar



polar
nonpolar



polar
nonpolar



polar
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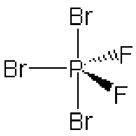

polar
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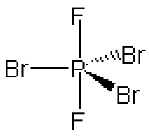


polar
nonpolar

Hydrogen Bonding

7.3-10. Hydrogen Bonding

Hydrogen bonding is a strong dipolar force that can occur between a hydrogen atom and either a nitrogen, oxygen, or fluorine atom.

The strength of a dipole-dipole interaction depends upon the distance between the two interacting poles (the positive pole of one molecule and the negative pole of a different molecule) and the magnitude of the charge on the poles. Consequently, dipole-dipole interactions can be quite strong in molecules that contain small atoms of very different electronegativities.

- Small size allows the interacting poles to get closer.
- Large electronegativity differences produce more charge on the poles.

Hydrogen is the smallest and one of the least electronegative nonmetals, so when it is bound to another small, highly electronegative element (N, O, or F), a very strong dipole-dipole interaction, the ***hydrogen bond***, is established. However, a molecule must contain one of the following bonds to participate in a hydrogen bond.

- H–F bond: HF is the only molecule that contains an H–F bond.
- H–O bond: Water is a strong H-bonder, but there are many other molecules with O–H bonds.
- H–N bond: Ammonia is a strong hydrogen bonder, but there are many other compounds with H–N bonds.

7.3-11. H-bonding in Water

An oxygen atom in water can hydrogen bond to two hydrogen atoms on different water molecules.

Hydrogen bonding in water is especially strong because each oxygen atom can bond to two different water molecules through its two lone pairs. Note that the oxygen is tetrahedral with two O–H covalent bonds that are responsible for H_2O molecules and two longer O–H hydrogen bonds that hold water molecules close to one another and are responsible for water being a liquid at room temperature.

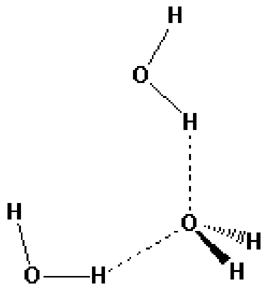


Figure 7.12

7.3-12. Ice

In order to maximize the hydrogen bonding interactions, water molecules in ice orient relative to one another so that the two lone pairs on an oxygen interact with hydrogen atoms of two different water molecules. As a result, water crystallizes in a structure containing hexagonal channels (see Figure 7.13). These channels, which are created when water freezes, result in void space. The presence of the large amount of void space makes the solid less dense than the liquid. The following properties of ice are due to these channels.

- Ice floats because the solid is less dense than the liquid.
- Pipes and radiators burst when water freezes in them because the water expands to create the channels.
- Ice crystallizes around the six-sided channels, so snowflakes are six-sided.
- Ice melts when pressure is applied because the pressure collapses the channels. One theory holds that ice skating is possible because the high pressure exerted by the skates melts the ice under them. The layer of liquid on top of the ice is what is actually slippery.

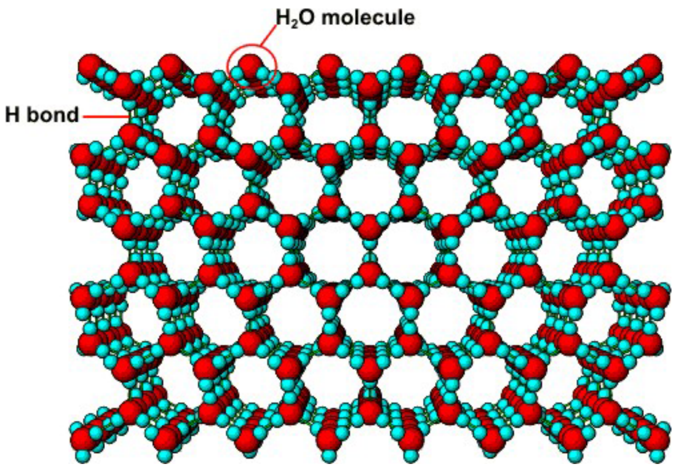


Figure 7.13: Structure of Ice

Predicting Relative Forces

7.3-13. Summary

As shown in Table 7.2, the relative strengths of the various interactions we have discussed overlap, so it is difficult to predict whether the interactions in a large nonpolar molecule are stronger or weaker than in a small polar molecule that hydrogen bonds. For example, I_2 is a solid at room condition, while H_2O is a liquid. Remember that dispersion forces are always present, so the interactions in a large polar molecule are probably stronger than in a small one. In the examples in Exercise 7.10, you will be asked to select the molecule in each pair that is expected to have the stronger interactions and the force responsible for the difference. Only one is responsible for the difference because the molecules have been chosen so that the other forces are comparable, not because they do not exist.

Type of Interaction	Energy of Interaction (kJ/mol)
Covalent Bond	100–1000
Hydrogen Bond	10–50
Dipolar Force	5–25
Dispersion	1–50

Table 7.2: Relative Strengths of Interaction

7.3-14. Predicting Relative Strengths of Interaction Exercise

EXERCISE 7.10:

Predict the compound with the stronger interaction in each pair. Then indicate the force that is most responsible for the difference.

Compound:
CH_3–O–CH_3
C_2H_5–O–H

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
CH_3–O–CH_3
C_6H_{13}–O–C_6H_{13}

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
NH_4Cl
PCl_5

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
PH_3
NH_3

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

7.4 Solids

Introduction

Molecules in the solid and liquid states are much closer to one another than they are in the gas phase, so the solid and liquid states are referred to as the condensed states. Since the molecules are much closer, they interact much more strongly, and the strengths of those interactions dictate the properties of the substance.

7.4-1. Introduction to Solids

The energy of interaction between particles in the solid state is much greater than thermal energy, so the particles in a solid sit in fixed positions relative to one another that maximize their interactions. Figure 7.14 shows the structure of NaCl, which has ions in each position. Each ion interacts with six ions of opposite charge, and the arrangement that is shown is the one that maximizes those interactions. Each particle has a fixed position, so solids have their own shape and volume, which are independent of the container. The kinetic (thermal) energy of each particle is in the form of oscillations about these positions. Thus, solids are characterized by an ordered array of particles, and that order allows us to understand their structures and properties. The structure/property relationships of solids are discussed in much more detail in the next chapter.

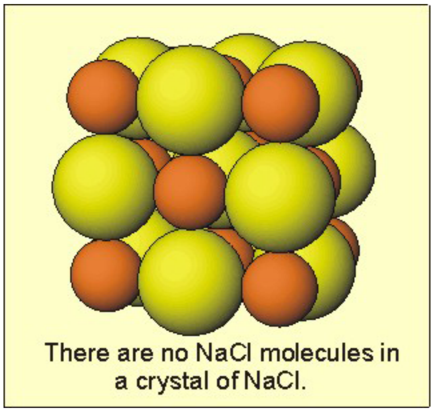


Figure 7.14

7.5 Liquids

Introduction

The intermolecular interactions in the liquid state are comparable to thermal energy, so the molecules remain relatively close to one another while undergoing random, but restricted, motion. This combination of hindered motion without fixed positions makes understanding liquids much more difficult than gases or solids. Liquids adopt the shape of the bottom of the container but maintain their own volume, which depends only slightly on the temperature. In this section, we introduce a few properties of liquids and relate them to the strengths of the intermolecular interactions.

Objectives

- Describe the differences between solids, liquids, and gases.

7.5-1. Viscosity

Viscosity, which is the resistance of liquids to flow, depends upon the energy of interaction relative to thermal energy. In order for a liquid to flow, molecules must slide past one another, breaking and forming intermolecular interactions. If thermal energy is relatively low compared to the energy of interaction, flow is retarded and the liquid is viscous because the molecules cannot readily break the interactions. Thus, viscosity decreases as the liquid is heated. Viscosity also depends upon the shape of the molecule: viscosity increases as the ease with which molecules become entangled increases.

7.5-2. Surface Tension

Molecules in a liquid minimize their energy by minimizing their surface area, and the surface tension is the energy required to increase the surface area of a liquid by a fixed amount.

Intermolecular interactions lower the energy of a molecule, so the more interactions that a molecule experiences, the lower is its energy. Molecules on the surface of a liquid cannot interact with as many other molecules as those within the bulk, which causes the liquid to "bead."

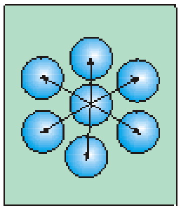


Figure 7.15a: Surface Tension Molecules in bulk of a liquid experience forces in all directions, which cancel one another. Thus, there is no net force acting on the molecule.

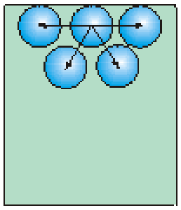


Figure 7.15b: Surface Tension There are no molecules above one at the surface so there is no upward force to cancel the downward force. Thus, there is a net inward force exerted on molecules at the surface that causes liquid to minimize its surface area.

Alternatively, molecules on the surface are at a higher potential energy (fewer interactions to lower it). Consequently, liquids minimize the number of high-energy molecules on the surface by minimizing their surface, which is why water "beads" into distorted spheres when it is placed on a surface with which it does not interact. Energy is required to increase the surface area of a liquid, and the ***surface tension*** is the energy that is required to increase the surface area of a liquid by a fixed amount. Surface tension increases with increasing intermolecular forces. Surface tension is the reason that some insects can walk on water.

7.5-3. Meniscus

A meniscus is concave when the adhesive forces between a liquid and its container are strong, but it is convex when they are weak.

Forces between like molecules are called ***cohesive forces***, while those between unlike molecules are said to be ***adhesive***. Viscosity and surface tension both result from cohesive forces. However, when a liquid is placed in a container, there may also be adhesive forces between the liquid and the walls of the container, and the balance between the cohesive forces that tend to "bead" the liquid and the cohesive forces that tend to "wet" the walls of the container dictates the curved shape of the top of the liquid, which is known as the ***meniscus***.

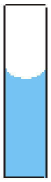


Figure 7.16a: Meniscus Glass contains many Si–O bonds, and water can hydrogen bond to the oxygens on the surface of the wall. The strong adhesive forces between water and glass tend to draw the liquid up the walls of the glass and produce the concave shape of the meniscus.

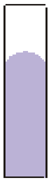


Figure 7.16b: Meniscus Mercury atoms do not interact well with glass, so the adhesive forces are very weak. Consequently, mercury forms a convex meniscus to maximize Hg-Hg interactions and minimize interactions with the walls of the container.

7.5-4. Summary of Properties

It is the interplay between thermal energy and the energy of interaction that dictates the state of a substance.

The strength of a dipole does not change with temperature, so two polar molecules do interact when they collide. However, if they are moving fast enough, their kinetic energy is sufficient to overcome the potential energy of their interaction and they do not "stick" to one another. As they are cooled, however, their kinetic energy is decreased, and, when they are cold enough, they no longer have sufficient kinetic energy to escape their interaction. Thus, it is the interplay between temperature and the strength of the intermolecular interaction that dictates the state of a substance. Table 7.3 summarizes some of the differences between the three states of matter. Note that solids are taken up in some detail in the next chapter.

	Gas	**Liquid**	**Solid**
Shape	shape and volume of the container	shape of the bottom of container, but have own volume	own shape and volume
Intermolecular Distance	great enough that intermolecular forces can be neglected	much smaller in a liquid than in a gas	similar to those in a liquid, but the molecules are oriented so as to optimize their interactions
Thermal vs. Interaction Energy	thermal >> interaction	thermal ~ interaction	thermal << interaction
Molecular Motion	straight line until a collision	random but restricted	oscillations about fixed positions

Table 7.3: A Comparison of the Gas, Liquid, and Solid States

7.6 Changes in State

Introduction

We have all seen ice melt and liquid water boil as a result of increasing the temperature, but ice can also be melted by applying pressure, and liquid water can be made to boil by reducing the pressure. Thus, ice melts under a skater's weight, and water that boils in Denver will not boil at the same temperature at sea level. In this section, we discuss the various changes in state at a molecular level.

Prerequisites

- 1.7 Energy (Distinguish between kinetic and potential energy.)
- 7.3 Intermolecular Interactions (Distinguish between intermolecular and intramolecular forces.)

Objectives

- Order the three states of matter in terms of their potential energies.
- Distinguish between the thermal energy and potential energy of interaction of a molecule.
- Define heat of fusion, heat of vaporization, and heat of sublimation.
- Define *fusion*.

- Describe melting and freezing at a molecular level.
- Define *melting point.*
- Predict whether the solid or liquid state is more dense from the slope of the solid $\rightleftharpoons$ line in a plot of P vs. T for the substance.
- Define *vapor pressure.*
- Define *boiling point* and explain what is meant by the normal boiling point.
- Use a plot of vapor pressure versus temperature to determine whether a substance is a liquid or a vapor at a given set of conditions of T and P.
- Determine which of two substances has the stronger intermolecular forces based on their vapor pressures at some temperature or their boiling points at some pressure.
- Predict which of two compounds is expected to show stronger dispersion forces.
- Predict relative boiling points based on the relative strengths of the dispersion forces of the molecules.
- Explain the effect of permanent dipoles on boiling points.
- Explain the effect of hydrogen bonding on boiling points.
- Explain why bubbles form at the boiling point.
- Define *sublimation* and *deposition.*
- Use a phase diagram to determine which state of matter a substance is in at given conditions of temperature and pressure.
- Use a phase diagram to determine the melting point, the normal boiling point, and the triple point of a substance.
- Use a phase diagram to determine the vapor pressure at a given temperature or the temperature at which the vapor pressure has a given value.

Introductory Overview

7.6-1. Video on the Molecular View of Changes in State

View a video describing **changes in state using kinetic molecular theory**.

A video or simulation is available online.

Energy Considerations

7.6-2. Heats of Change

The potential energy of a particle varies as solid < liquid << gas.

The potential energies of the particles in each of the three states are different because the strength of the intermolecular forces is different. Thus, particles in the solid are at the lowest (most negative) energy because the strength of the intermolecular forces is the strongest in the solid. There are no intermolecular interactions in an ideal gas because the particles are far apart and do not interact. In the liquid, the particles are close together, but interactions are not optimized as they are in the solid. Consequently, the potential energy of a particle varies as solid < liquid << gas. Note that, due to these relative energies,

- the interactions in a solid are so strong that the solid has its own shape;
- the interactions in the liquid are not strong enough to retain a unique shape, but they are strong enough to keep the liquid in the bottom of the container and adopting that shape; and
- the interactions in gases are so weak that the molecules fill the container.

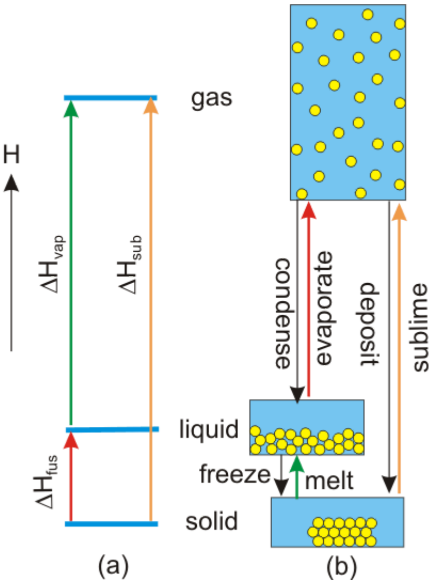


Figure 7.17: Relative Energies of the Vapor, Liquid, and Solid States The solid and liquid states have similar energies, but the energy of the vapor is much higher.

7.6-3. Heats of State Changes Defined

The heats of fusion, vaporization, and sublimation are always positive.

The energy required to melt a solid at its melting point is called its ***heat of fusion***, ΔH_{fus}. The heat of fusion is simply the difference in the potential energies of the liquid and solid states. Heats of fusion are always positive because the liquid is always at higher energy (less negative) than the solid.

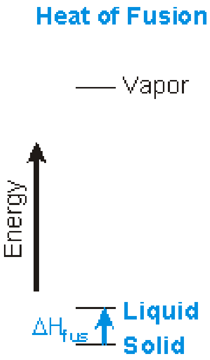


Figure 7.18a: Heat of Fusion

The energy required to vaporize a liquid at a given temperature is called the liquid's ***heat of vaporization***, ΔH_{vap}, at that temperature. The heat of vaporization is the potential energy difference between the liquid and gas. Since the potential energy of the gas is much greater than that of the liquid, a substance's heat of vaporization is always positive and greater than its heat of fusion.

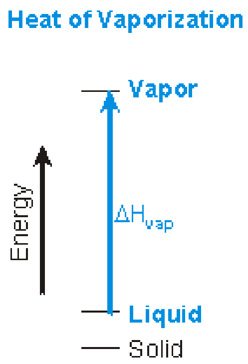


Figure 7.18b: Heat of Vaporization

The energy required to convert the solid directly to the vapor at a given temperature is called the ***heat of sublimation***, ΔH_{sub}. It is the sum of the heats of fusion and vaporization.

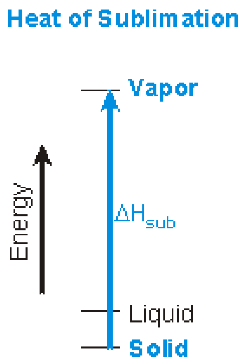


Figure 7.18c: Heat of Sublimation

Solid-Liquid Equilibria

7.6-4. Solid-Liquid Equilibria

The melting point is the temperature at which the solid and liquid are in equilibrium.

When the temperature is such that the kinetic energy of the molecules is low compared to the potential energy of interaction, the molecules arrange themselves in a rigid array that optimizes the interactions. The rigid array is the solid state. Thermal energy in the solid is in the form of oscillations of the molecules about their fixed positions in the crystal. Warming a solid causes the molecules to oscillate faster and with a greater amplitude. When the temperature reaches the point where the intermolecular interactions are no longer sufficient to keep the particles in position, the crystal melts. The ***melting point*** is the temperature at which the solid and liquid are in ***dynamic equilibrium***, i.e., it is the temperature at which the rates of melting and freezing are the same. The dynamic equilibrium is expressed as follows.

Figure 7.19

A high melting point means that the thermal energy required to overcome the intermolecular interactions is high, so substances with high melting points have strong intermolecular interactions.

7.6-5. Graph of Solid-Liquid Equilibrium

The more dense phase can be determined from the slope of the P vs. T line for the solid-liquid equilibrium.

A plot of the pressure versus melting point is nearly a straight line with a steep slope. The slope is steep because large changes in pressure are required to produce small changes in melting point. The slope of the line depends upon whether the solid or liquid is the more dense state because the application of pressure to a solid-liquid equilibrium shifts the equilibrium to the more dense state. Consider the two possibilities shown in Figures 7.20a and 7.20b.

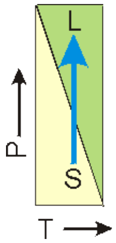


Figure 7.20a: Melting Point as a Function of Pressure The slope of the line is negative, so increasing the pressure (indicated by the arrow) on the solid-liquid equilibrium converts the solid into the liquid (melts the solid). In this case, the liquid is the more dense state, which is the situation for water.

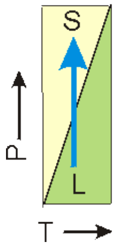


Figure 7.20b: Melting Point as a Function of Pressure The slope of the line is positive, so increasing the pressure on the solid-liquid equilibrium converts liquid into solid (freezes the liquid). In this case, the solid is more dense than the liquid. This is the more common situation.

Liquid-Vapor Equilibria

7.6-6. Liquid-Vapor Equilibria

Vapor pressure increases with temperature and decreases with the strength of the intermolecular force.

The same intermolecular forces that are responsible for the solid state are at play in the liquid state as well, but the kinetic energy of the particles is sufficient to keep the molecules from being locked into position. The molecules in the liquid can slip past one another. As a liquid is heated, its temperature rises as the molecules gain kinetic energy, but temperature is a measure of the *average* kinetic energy of the molecules. Thus, some molecules have much more kinetic energy than others. Indeed, some of the molecules have enough kinetic energy to break their intermolecular interactions completely and enter the gas or vapor state in a process known as ***evaporation***, or ***vaporization***. If the container is open, the liquid evaporates, but if it is closed, the concentration of molecules in the vapor reaches a point where some of the vapor undergoes ***condensation***. When the rate of vaporization equals the rate of condensation, the system reaches equilibrium. The pressure of vapor (gas) in equilibrium with the liquid at any temperature is known as the ***vapor pressure*** of the liquid at that temperature. Vapor pressures increase with temperature because the fraction of molecules with sufficient kinetic energy to break away increases as the temperature rises. Vapor pressures also depend upon intermolecular interactions—**strong intermolecular interactions result in low vapor pressures**. The liquid and vapor reach a dynamic equilibrium when molecules evaporate and condense at the same rate, so the process is written as shown in Figure 7.21.

$$\text{liquid} \underset{\text{condensation}}{\overset{\text{vaporization}}{\rightleftharpoons}} \text{vapor}$$

Figure 7.21

7.6-7. Vapor Pressure of Water, Dew Point, and Relative Humidity

Table 7.4 gives the vapor pressure of water at various temperatures. Note that the vapor pressure increases with temperature, as it must for all substances. Weather reports normally indicate the partial pressure of water in the atmosphere in terms of the relative humidity or dew point. The relative humidity is 100% times the ratio of the observed partial pressure of water in the atmosphere to the vapor pressure of water at that temperature. The dew point is the temperature at which the atmospheric water would begin to condense, i.e., the temperature at which the vapor pressure of H_2O equals its partial pressure in the atmosphere.

EXAMPLE:

For example, consider a day on which the temperature is 25 °C and the partial pressure of H_2O is 12.8 torr. We note from Table 7.4 that the vapor pressure of water is 12.8 torr at 15 °C, so 15 °C is the dew point. The vapor pressure of water at 25 °C is 23.8 torr, so:

$$\text{relative humidity} = \left(\frac{12.8}{23.8}\right)(100\%) = 53.8\%$$

T (°C)	**P (torr)**		**T (°C)**	**P (torr)**
0	4.6		50	92.5
5	6.5		55	118.0
10	9.2		60	149.4
15	12.8		65	187.5
20	17.5		70	233.7
25	23.8		75	289.1
30	31.8		80	355.1
35	41.2		85	433.6
40	55.3		90	525.8
45	71.9		95	633.9

Table 7.4: Vapor Pressure of Water at Various Temperatures

7.6-8. Graph of Liquid-Vapor Equilibrium

The vapor pressure of a compound at a given temperature depends upon the strengths of its intermolecular interactions. **Compounds with stronger intermolecular interactions have lower vapor pressures than those that interact only weakly** because stronger interactions favor the more condensed state. Figure 7.22 shows the vapor pressure of CCl_4 and H_2O as a function of temperature. From the graph, we can see that the vapor pressure of CCl_4 is 760 torr at 77 °C, while H_2O must be heated to 100 °C to obtain the same vapor pressure. We also note that the vapor pressure of H_2O is less than that of CCl_4 at every temperature, so the intermolecular interactions are stronger in H_2O. Although the dispersion forces are greater in CCl_4, water also has dipolar and hydrogen bonding forces, which results in its relatively low vapor pressure.

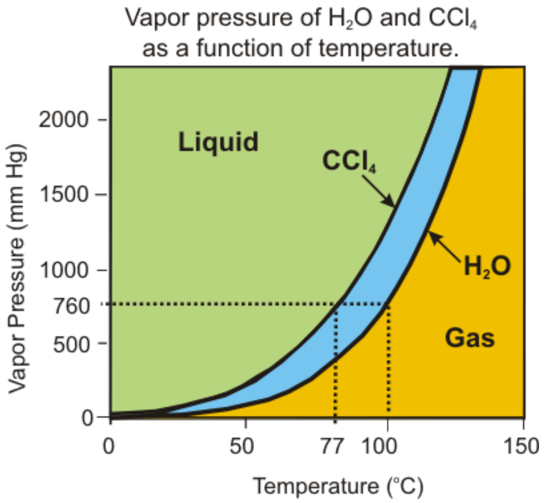


Figure 7.22: Vapor Pressure of CCl_4 and H_2O as a Function of Temperature Both substances are liquids at temperatures and pressures in the green region and both are gases at conditions in the orange region. CCl_4 is a gas while H_2O is a liquid in the blue region.

7.6-9. Boiling Points

Molecules with sufficient kinetic energy escape into the gas phase if they are on the surface of the liquid, but what about those that are not on the surface? The highly energetic molecules in the bulk of the liquid also attempt to escape into the gas by aggregating into bubbles, but the bubbles cannot withstand pressures greater than the vapor pressure of the gas at that temperature, so the bubbles cannot form if the external pressure exceeds the vapor pressure. However, the bubbles are sustained at the temperature where the vapor pressure of the liquid equals the external pressure, so we define the ***boiling point*** as that temperature at which the vapor pressure equals the external pressure. A liquid can be made to boil at other temperatures by reducing the external pressure to the vapor pressure of the liquid at that temperature, so Table 7.4 and Figure 7.22 can also be viewed as the boiling points as a function of pressure. Thus, the boiling point of water at 4.6 torr is 0 °C, and at 23.8 torr, it is 25 °C.

Typically, substances are boiled in a container open to the atmosphere, so the external pressure is 1 atm, and it is this boiling point that is assumed when a boiling point is given without reference to a pressure. We define the ***normal boiling point*** as the boiling point at 1 atm pressure. Whenever the boiling point of a substance is given without reference to an external pressure, it is assumed to be the normal boiling point. The normal boiling point of water is 100 °C.

7.6-10. Normal Boiling Points and Intermolecular Interactions

The higher the boiling point of a substance, the stronger are its intermolecular interactions.

Normal boiling points are good indicators of relative strengths of intermolecular forces because molecules with stronger intermolecular interactions have higher normal boiling points. For example, dispersion forces are the only intermolecular forces acting in the halogens and noble gases, and the fact that their normal boiling points increase with molar mass (Figure 7.23) is strong support for our conclusion that dispersion forces increase with molar mass. Fluorine is a gas at room temperature (boiling point = 85 K), while the much larger iodine molecule is a solid at room temperature (boiling point = 457 K). Helium has the weakest intermolecular interaction of any substance and the lowest boiling point (4 K).

It is more difficult to quantify dipolar interactions because they never occur in the absence of dispersion forces. However, the dispersion forces in CO and N_2 should be very similar because they are isoelectronic (they have the same number of valence electrons) and have the same molar mass, but CO is polar while N_2 is not. The normal boiling points are 77 K for N_2 and 81 K for CO, so the impact of the dipole is not very great in this case. The difference between F_2 and HCl, which have very similar molar masses, is more dramatic. The boiling point of polar HCl is over 100 K higher than that of nonpolar F_2 even though the molar mass of HCl is slightly less.

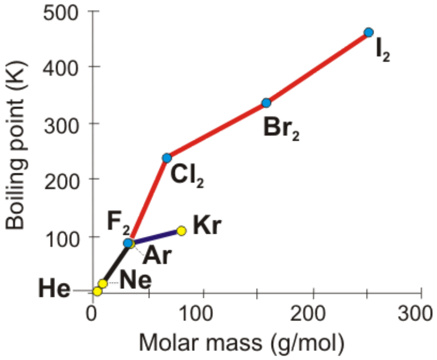


Figure 7.23: Boiling Points of the Halogens and the Noble Gases

Hydrogen bonding is a relatively strong interaction, and molecules that interact through hydrogen bonds have unusually high boiling points. The case of the boiling points of the hydrides of Groups 4, 5, 6, and 7 is considered in Figures 7.24a, 7.24b, 7.24c, and 7.24d.

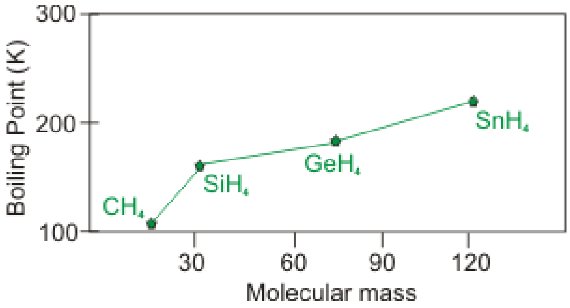


Figure 7.24a: Boiling Points of the Group 4 Hydrides as a Function of Molar Mass
Group 4A: None of the hydrides of Group 4A exhibit hydrogen bonding, so their boiling points decrease as their molar masses decrease.

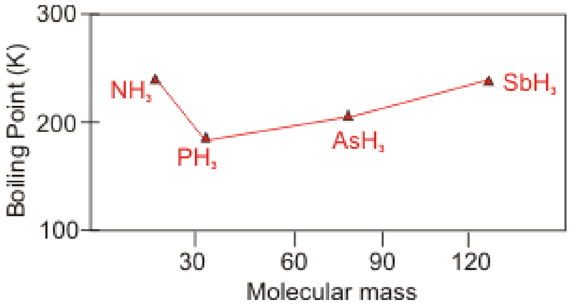


Figure 7.24b: Boiling Points of the Group 5 Hydrides as a Function of Molar Mass
Group 5A: Dispersion forces are the main differences between the intermolecular forces of SbH_3, AsH_3, and PH_3, so their boiling points decrease with decreasing molar mass. However, NH_3 exhibits hydrogen bonding, so its high boiling point is much higher than would be predicted based on the boiling points of the other members of the group.

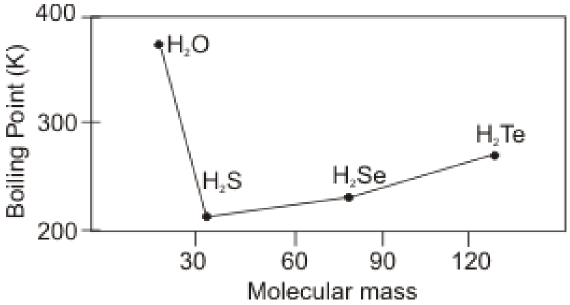


Figure 7.24c: Boiling Points of the Group 6 Hydrides as a Function of Molar Mass Group 6A: Water can hydrogen bond through two hydrogen atoms. Consequently, its boiling point is much higher than that of H_2S, which has stronger dispersion forces. Based solely on molar mass, water would be predicted to boil around 200 K rather than 373 K. Thus, water would be a gas rather than a liquid at normal conditions on Earth if it were not for the hydrogen bond.

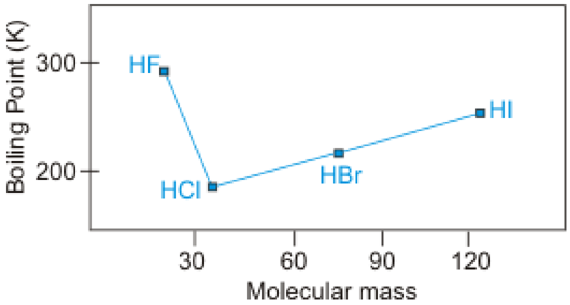


Figure 7.24d: Boiling Points of the Group 7 Hydrides as a Function of Molar Mass Group 7A: Note that HF exhibits hydrogen bonding, but, based on the above graph, HCl does not. Chlorine is electronegative enough, but it is too large.

7.6-11. Predicting Relative Boiling Points Exercise

EXERCISE 7.11:

Indicate the molecule with the higher boiling point in each pair.

N_2	CH_2Cl_2	CS_2
CO	CF_4	CO_2

7.6-12. Critical Point

Liquid-vapor equilibria, like the one shown for CCl_4 and H_2O in Figure 7.22, are established in closed containers (the liquid would evaporate before establishing equilibrium in an open container). However, as the liquid-vapor equilibrium is heated, the density of the liquid decreases, while the density of the gas increases. At a temperature known as the ***critical temperature***, T_c, the densities are the same, there is no longer a boundary between the two phases, and the liquid-vapor line ends. The pressure at this point is called the ***critical pressure***, P_c. The point established by the critical temperature and pressure is called the ***critical point***. Thus, the critical temperature is the highest temperature at which the liquid phase can exist, and the critical pressure is the pressure required to liquefy a gas at the critical temperature. The **critical temperature is also a function of intermolecular forces and increases in the same manner as the boiling point**. Above the critical point, the substance is neither a gas nor a liquid and has properties of both phases. Under these conditions, the substance is a ***supercritical fluid***.

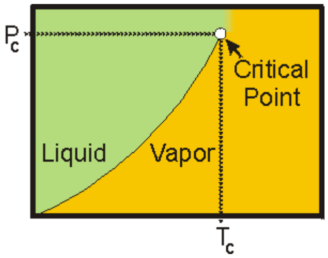


Figure 7.25

Solid-Vapor Equilibria

7.6-13. Solid-Vapor Equilibria

Under certain conditions, the vapor and solid states are in equilibrium. ***Sublimation*** is the process in which a solid is converted directly to a gas. The reverse process is called ***deposition***. Ice sublimes slowly, which is why snow can disappear without melting when the temperature does not rise above 0 °C. A dynamic equilibrium is established when the rate of sublimation equals the rate of deposition.

Figure 7.26

Dry ice, which is solid CO_2, does not exist as a liquid at pressures less than 5.1 atm, so it does not melt at 1 atm. Consequently, dry ice sublimes rapidly at room conditions. Figure 7.27 shows the temperatures and pressures at which the solid $\rightleftharpoons$ vapor equilibrium is established. Increasing the temperature increases the pressure of vapor above a solid, i.e., it causes the solid to sublime. Increasing the pressure of the gas at a point on the line causes more solid to deposit.

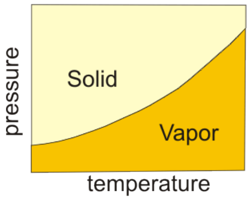


Figure 7.27: Sublimation Pressure as a Function of Temperature

Phase Diagrams

7.6-14. Phase Diagram of Water

A ***phase diagram*** shows the stable phases of a substance as a function of temperature and pressure. For example, consider the phase diagram of water shown in Figure 7.28. The lines separating the states represent the equilibria discussed in the previous sections.

- **Point A** is on the solid $\rightleftharpoons$ liquid line. The pressure is 1 atm, or 760 torr, so the temperature (0 °C) is called the normal melting point, or simply the melting point. Increasing the pressure at point A moves the system into the liquid region (melts the solid), so liquid water is more dense than ice (the reason ice floats).
- **Point B** is the ***triple point***, which is the temperature and pressure at which all three states of matter coexist. The triple point of water is 0.0098 °C and 4.58 torr (0.006 atm). Reducing the pressure at this point would cause the ice water to boil.
- **Point C** represents room conditions ($P = 760$ torr and $T = 298$ K (25 °C)). It is well within the liquid range for water, consistent with water being a liquid under these conditions. However, in a closed container there would also be 24 torr (0.031 atm) of vapor above the liquid. If the pressure over the liquid were reduced to 24 torr at this temperature, the water would boil.

- **Point D** is on the liquid $\rightleftharpoons$ vapor line. The pressure is 760 torr, so the temperature (100 °C) is the normal boiling point. Increasing the temperature or decreasing the pressure drives the system into the vapor region, while decreasing the temperature or increasing the pressure of vapor causes steam to condense.
- **Point E** is the critical point. The critical temperature is $T_c = 374$ °C, and the critical pressure is $P_c = 218$ atm. Water is a supercritical fluid above this point.

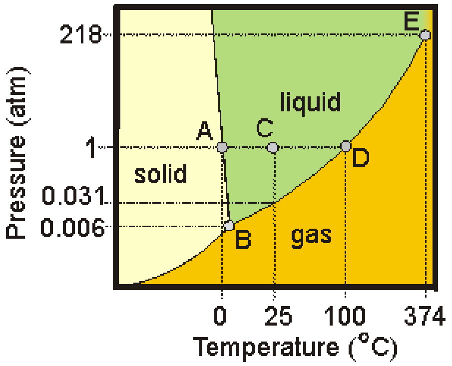


Figure 7.28: Phase Diagram of Water The above phase diagram shows how the state of matter of water varies with conditions of temperature and pressure. Water is a solid in the yellow region, a liquid in the green region, and a gas or vapor in the orange region. The temperatures and pressures are not to scale.

7.6-15. Phase Diagram of Carbon Dioxide

Consider the phase diagram of CO_2 shown in Figure 7.29.

- **Point A** is on the solid $\rightleftharpoons$ vapor line and is the point where the partial pressure of the vapor in equilibrium with the solid is 1 atm. Thus, CO_2 can be liquified at 1 atm by reducing its temperature to −78 °C.
- **Point B** is the triple point (5.1 atm and −56 °C).
- **Point C** represents room conditions. CO_2 is a gas under these conditions.
- **Point D** shows that CO_2 can be liquified at room temperature (25 °C) by increasing the pressure to 67 atm.
- **Point E** is the critical point. The critical temperature is $T_c = 31$ °C, and the critical pressure is $P_c = 73$ atm. Supercritical CO_2 is used as a dry cleaning solvent.

The slope of the solid $\rightleftharpoons$ liquid line indicates that the solid is more dense than the liquid. Finally, carbon dioxide does not have a normal boiling point because the liquid does not exist at pressures below 5.1 atm (the triple point pressure).

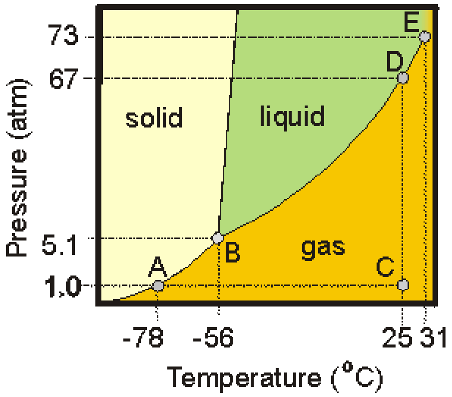
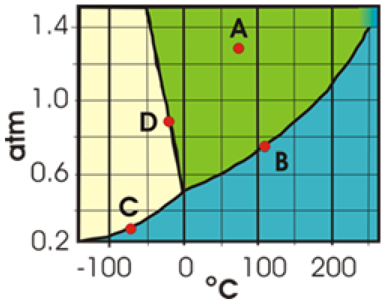


Figure 7.29: Phase Diagram of Carbon Dioxide

7.6-16. Phase Diagram Exercise

EXERCISE 7.12:

In the following exercises, give all temperatures to the nearest 25 °C and all pressures to the nearest 0.1 atm.



What is the normal boiling point of X in °C?

______________ °C

What is the melting point of X in °C?

______________ °C

What is the temperature in °C at the triple point?

______________ °C

What is the pressure in atm at the triple point?

______________ atm

What state of matter is X in at point A?
- solid
- liquid
- gas

What is the most dense state of X?
- solid
- liquid
- gas

What is the critical temperature of X in °C?

______________ °C

What is the critical pressure of X in atm?

______________ atm

Indicate the phase change that is caused by each of the following.

increasing T at point B
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

increasing T at point C
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

increasing P at point D
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

7.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.