CHAPTER 13: PROPERTIES OF LIQUIDS AND WATER

Enhanced Introductory College Chemistry

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Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry (https://ecampusontario.pressbooks.pub/enhancedchemistry/) to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The types of intermolecular forces possible between atoms/molecules and within atoms/

molecules, based on their structure and makeup
- The difference between adhesive and cohesive forces, and how these forces affect viscosity, surface tension, and capillary rise
- Phase transitions and phase transition temperatures, and how intermolecular forces and kinetic energy affect these phenomena
- The processes represented by heating and cooling curves, and the enthalpy changes accompanying these processes
- The special characteristics of water, and how its structure gives it these unique properties

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The difference between a physical and a chemical property of matter
- Enthalpy, and its classification as a state function
- Atomic properties and periodic table trends
- Molecular structure, as determined by VSEPR theory, and polarity of molecular bonds

Figure 13a: Solid carbon dioxide ("dry ice", left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a fog of condensed water vapour above the cylinder. (credit: modification of work by Paul Flowers in *Chemistry (OpenStax)*, CC BY 4.0).

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid state, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of the liquid phase will be examined.

Attribution & References

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13.1 INTERMOLECULAR FORCES

Learning Objectives

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behaviour of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 13.1a illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

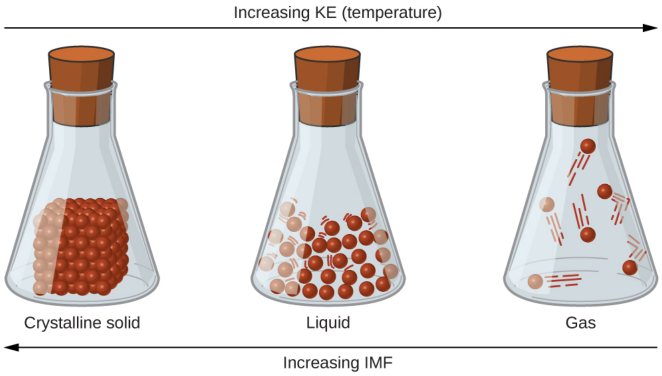

Figure 13.1a: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favour the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold window as the water vapour in the air is cooled by the cold glass, as seen in Figure 13.1b.

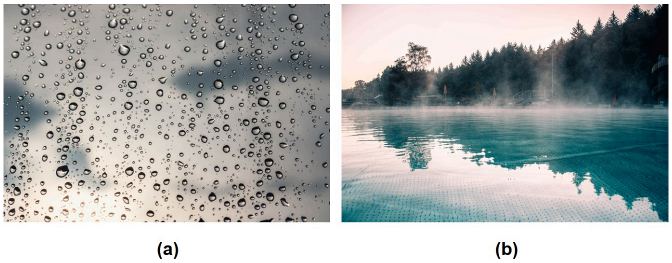

Figure 13.1b: Condensation forms when water vapour in the air is cooled enough to form liquid water, such as (a) on the outside of a window or (b) in the form of fog. (credit a: work by Christian Wiediger, Unsplash license; credit b: work by Mary Noe, Unsplash license)

We can also liquefy many gases by compressing them if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 13.1c.

Figure 13.1c: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by Sam-Cat, CC BY 2.0)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Exercise 13.1a

Practice using the following PhET simulation: States of Matter (https://phet.colorado.edu/sims/html/states-of-matter/latest/states-of-matter_en.html)

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 13.1d illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

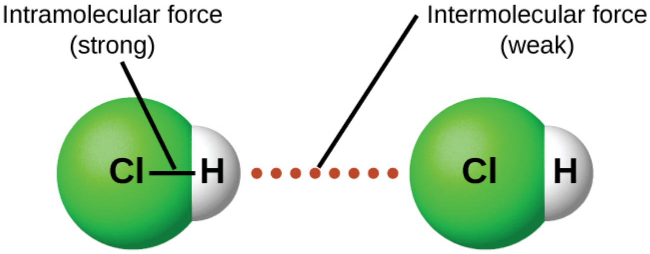

Figure 13.1d: *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the **London dispersion force** in honour of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighbouring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 13.1e.

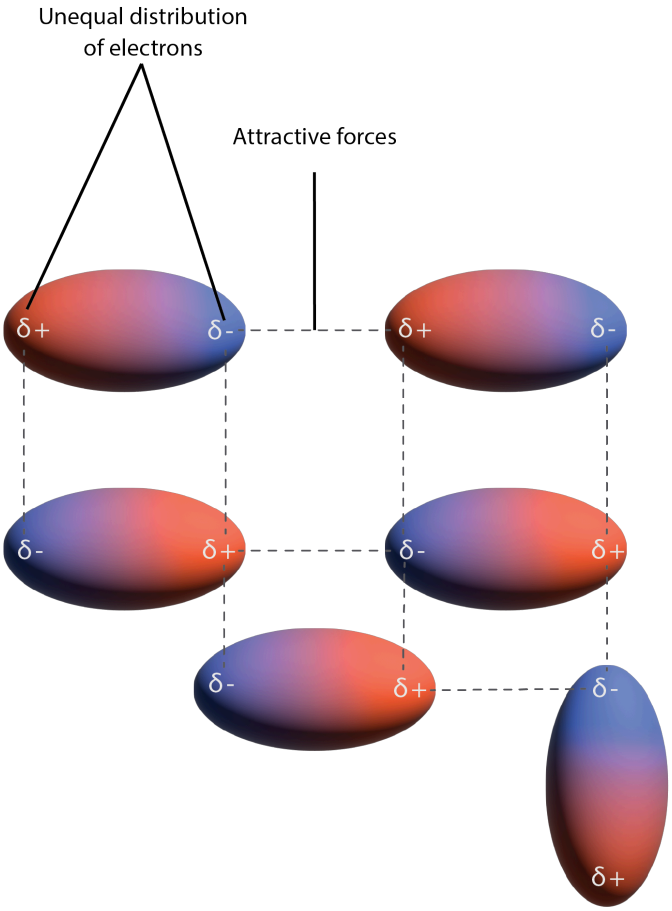

Figure 13.1e: Dispersion forces result from the formation of temporary dipoles, as illustrated here for several nonpolar diatomic molecules (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 13.1a.

Table 13.1a: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 13.1a

London Forces and Their Effects

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$ (Figure 13.1f).

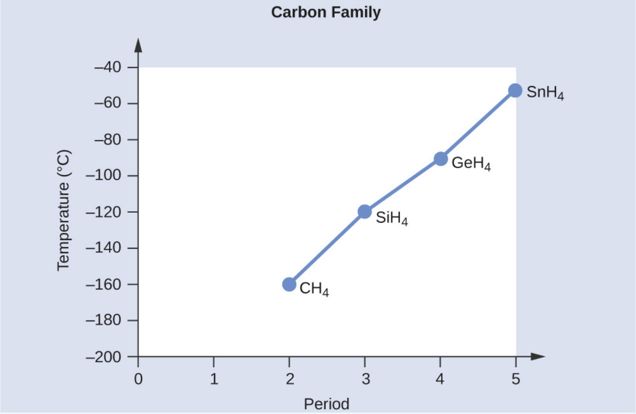

Figure 13.1f: Boiling points of hydrogen compounds containing Group 14 elements (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct.

Exercise 13.1b

Check Your Learning Exercise (Text Version)
Order the following hydrocarbons from lowest to highest boiling point: C_3H_6, C_3C_8 and C_4C_{10}.

a. $C_3H_6 < C_3C_8 < C_4C_{10}$
b. $C_3C_8 < C_3H_6 < C_4C_{10}$
c. $C_4C_{10} < C_3H_6 < C_3C_8$
d. $C_3C_8 < C_3H_6 < C_4C_{10}$

Check Your Answer[1]

Source: "Exercise 13.1b" is adapted from "Example 10.1-1" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 13.1g) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behaviour is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

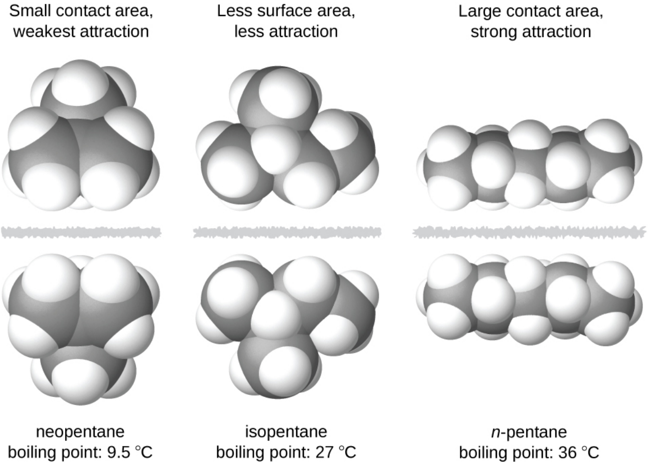

Figure 13.1g: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 13.1h, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally non-sticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

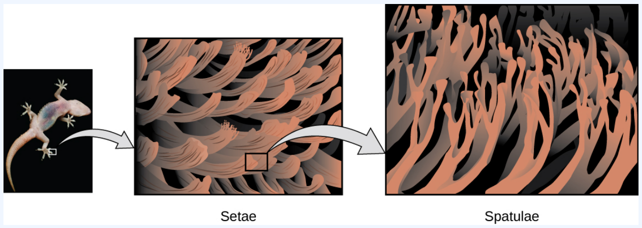

Figure 13.1h: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off" (credit photo: modification of work by JC+A, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Watch Smart materials (1 of 5): Gecko Adhesive fit for Spiderman (9 mins) (https://www.youtube.com/watch?v=gzm7yD-JuyM)

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 13.1i.

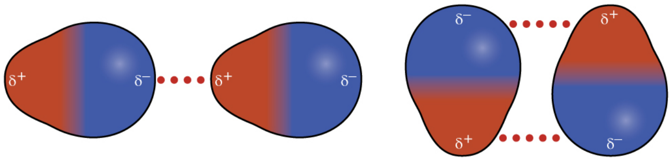

Figure 13.1i: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 13.1b

Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 13.1c

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Check Your Answer[2]

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure 13.1i illustrates hydrogen bonding between water molecules.

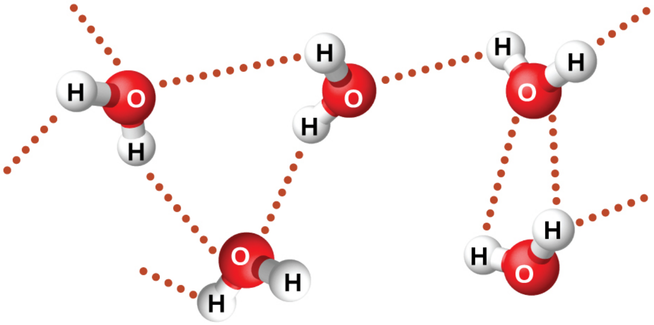

Figure 13.1j: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 13.1j. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

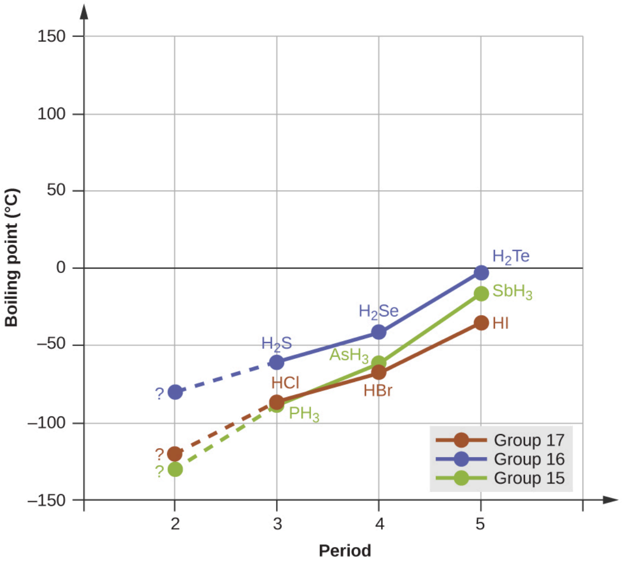

Figure 13.1k: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 13.1k. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

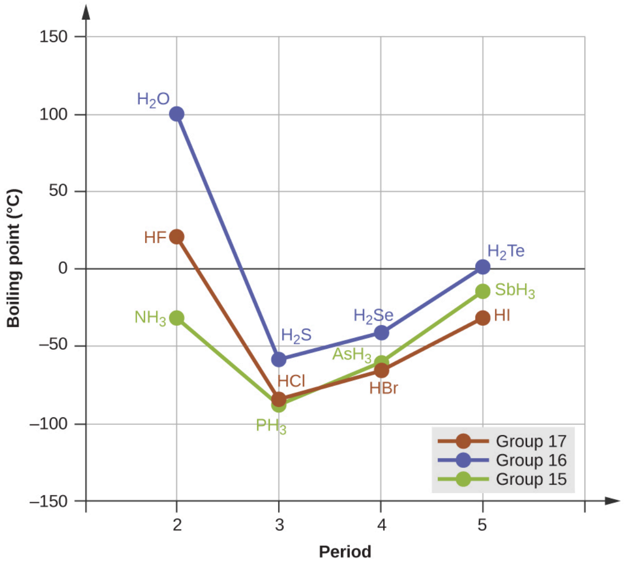

Figure 13.1l: In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.1c

Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 13.1d

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Check Your Answer[3]

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 13.1m.

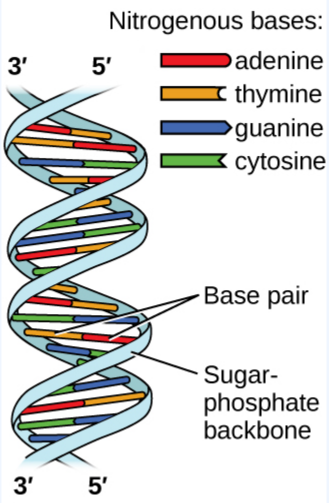

Figure 13.1m: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts, CC BY 4.0)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 13.1n.

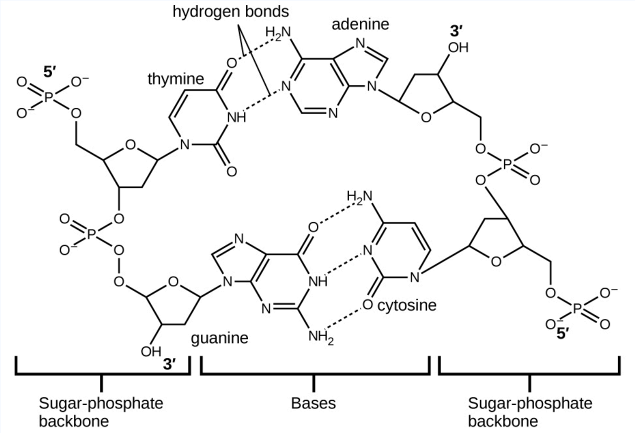

Figure 13.1n: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs." (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Attribution & References

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Notes

1. $C_3H_6 < C_3C_8 < C_4C_{10}$

2. ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.
3. The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

13.2 PROPERTIES OF LIQUIDS

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure 13.2a, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).

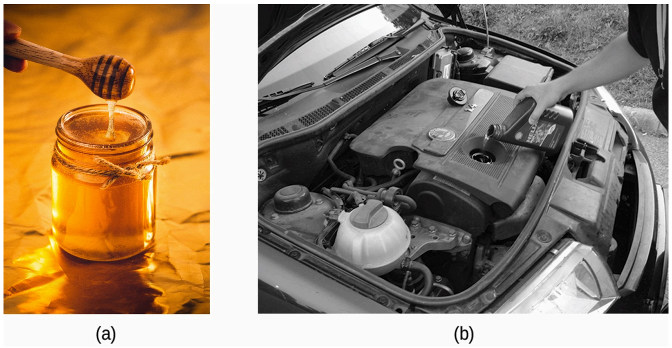

Figure 13.2a: (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: work by Art Rachen, Unsplash license; credit b: modification of work by David Nagy, CC BY 2.0)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table 13.2a shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table 13.2a: Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of **cohesive forces**. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure 13.2b, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

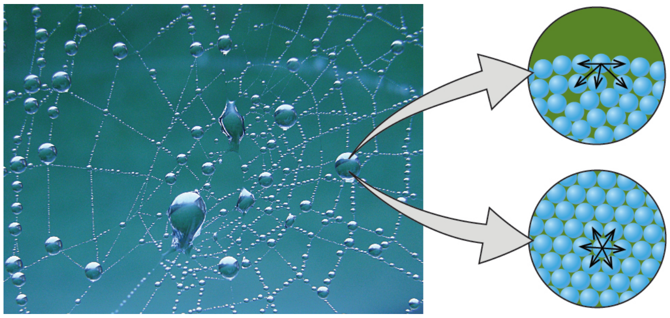

Figure 13.2b: Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by OliBac, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table 13.2b. Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure 13.2c, even though they are denser than water, move on its surface because they are supported by the surface tension.

Table 13.2b: Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

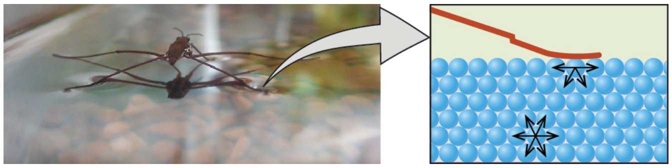

Figure 13.2c: Surface tension (right) prevents this insect (left), a "water strider," from sinking into the water. (credit: modification of work by TimVickers, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure 13.2d).

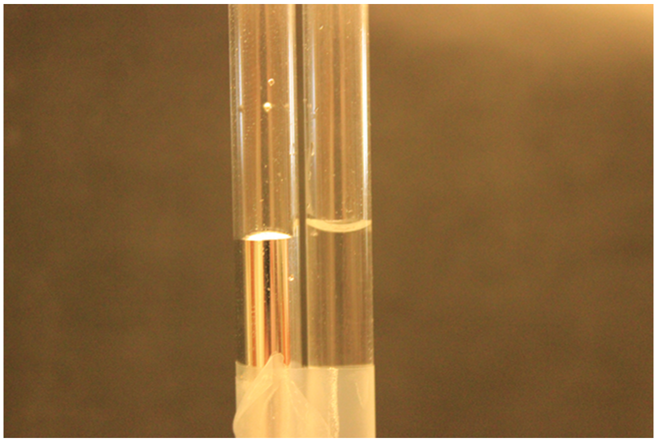

Figure 13.2d: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

If you place one end of a paper towel in spilled wine, as shown in Figure 13.2e, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

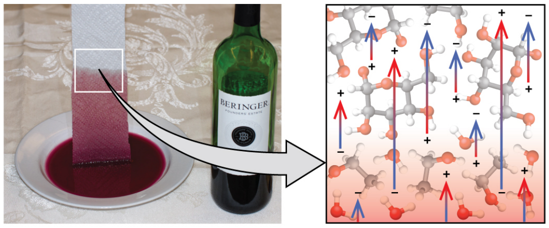

Figure 13.2e: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the –OH groups on the towel's cellulose fibres and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser in *Chemistry (OpenStax)*, CC BY 4.0).

Towels soak up liquids like water because the fibres of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many –OH groups. Water molecules are attracted to these –OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibres.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure 13.2f. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

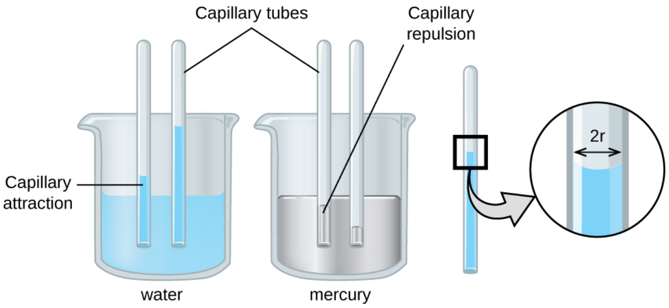

Figure 13.2f: Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\ \cos\theta}{r\rho g}$$

In this equation, h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube, T is the surface tension of the liquid, θ is the contact angle between the liquid and the tube, r is the radius of the tube, ρ is the density of the liquid, and g is the acceleration due to gravity, 9.8 m/s^2. When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

Example 13.2a

Capillary Rise

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?

For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.

Solution

The liquid will rise to a height h given by: $h = \frac{2T\,\cos\theta}{r\rho g}$

The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:

$$h = \frac{2(0.07199\ \mathrm{kg/s^2})}{(0.000125\ \mathrm{m})(1000\ \mathrm{kg/m^3})(9.8\ \mathrm{m/s^2})} = 0.12\ \mathrm{m} = 12\ \mathrm{cm}$$

Exercise 13.2a

Check Your Learning Exercise (Text Version)
Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

a. 0.36 mm
b. 0.35 mm
c. 0.37 mm
d. 0.34 mm

Check Your Answer[1]

Source: “Exercise 13.2a” is adapted from “Example 10.2-1” in General Chemistry 1 & 2, a derivative of

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Biomedical Applications of Capillary Action

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in the video below. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.

Watch Capillary Action Demonstration (35 s) (https://youtu.be/mtB8rfI2-qU)

Key Equations

- $h = \dfrac{2T\ \cos\theta}{r\rho g}$

Attribution & References

Except where otherwise noted, this page is adapted by Gregory A. Anderson from "10.2 Properties of Liquids (https://boisestate.pressbooks.pub/chemistry/chapter/10-2-properties-of-liquids/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* .

Notes

1. 0.36 mm

13.3 PHASE TRANSITIONS

Learning Objectives

By the end of this section, you will be able to:

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures, intermolecular attractive forces, and kinetic energy
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

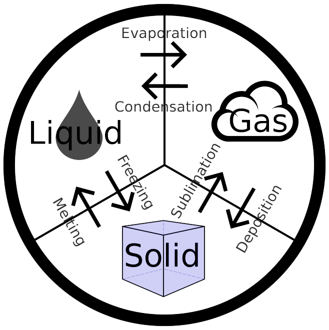


Figure 13.3a: Phase Change Diagram: Condensation changes a gas to a liquid. Evaporation changes a liquid to a gas. Freezing changes a liquid to a solid. Melting changes a solid to a liquid. Sublimation changes a solid to a gas; whereas, deposition changes a gas to a solid. (credit: work by SiliconProphet, CC BY-SA 4.0).

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. Figure 13.3a shows a simple phase change diagram. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapour in the container changes. The vapour in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapour in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapour pressure** (or equilibrium vapour pressure). The area of the surface of the liquid in contact with a vapour and the size of the vessel have no effect on the vapour pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapour pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure 13.3b, and using a manometer to measure the increase in pressure that is due to the vapour in equilibrium with the condensed phase.

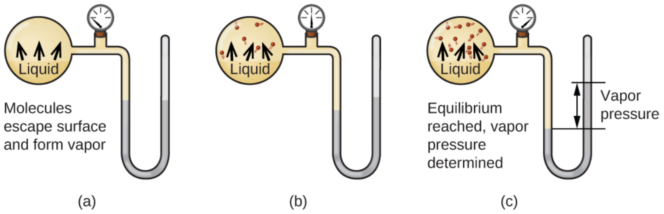


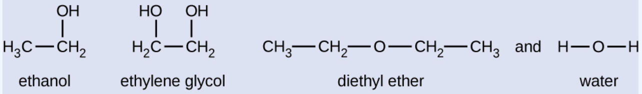
Figure 13.3b: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapour pressure of the gas is constant, although the vaporization and condensation processes continue (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapour pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favouring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapour pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapour pressures. The following example illustrates this dependence of vapour pressure on intermolecular attractive forces.

Example 13.3a

Explaining Vapour Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapour pressures in terms of types and extents of IMFs:



Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapour pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapour pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapour pressure than for either diethyl ether or ethanol. Ethylene glycol has two –OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapour pressure the lowest.

Exercise 13.3a

At 20 °C, the vapour pressures of several alcohols are given in this table. Explain these vapour pressures in terms of types and extents of IMFs for these alcohols:

Data Table for Exercise 13.3a

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapour Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Check Your Answer[1]

As temperature increases, the vapour pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 13.3c. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapour pressure.

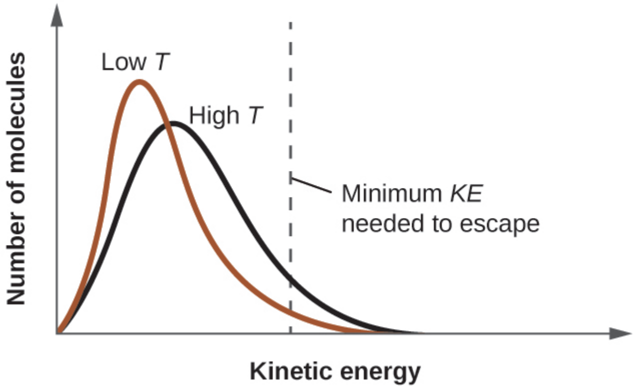


Figure 13.3c: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Boiling Points

When the vapour pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The **boiling point** of a liquid is the temperature at which its equilibrium vapour pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 13.3d shows the variation in vapour pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.

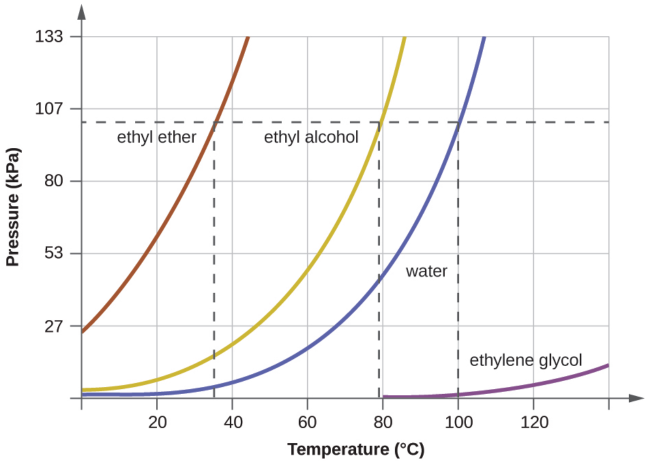


Figure 13.3d: The boiling points of liquids are the temperatures at which their equilibrium vapour pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.3b

A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure 13.3d to determine the boiling point of water at this elevation.

Solution

The graph of the vapour pressure of water versus temperature in Figure 13.3d indicates that the vapour pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapour pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Exercise 13.3b

Check Your Learning Exercise (Text Version)
The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure 13.3d to determine the approximate atmospheric pressure at the camp.

a. 40 kPa
b. 41 kPa
c. 39 kPa
d. 51kPa

Check Your Answer[2]

Source: "Exercise 13.3b" is adapted from "Example 10.3-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The quantitative relation between a substance's vapour pressure and its temperature is described by the **Clausius-Clapeyron equation**:

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and ln A is a constant whose value depends on the chemical identity of the substance. This equation is often rearranged into logarithmic form to yield the linear equation:

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

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature T_1, the vapour pressure is P_1, and at temperature T_2, the vapour pressure is T_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + \ln A \quad \text{and} \quad \ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + \ln A$$

Since the constant, ln A, is the same, these two equations may be rearranged to isolate ln A and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$

which can be combined into:

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

Example 13.3c

Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapour pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapour pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation:

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

Since we have two vapour pressure-temperature values (T_1 = 34.0 °C = 307.2 K, P_1 = 10.0 kPa and T_2 = 98.8 °C = 372.0 K, P_2 = 100 kPa), we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

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

$$= \frac{(8.3145\ \text{J/mol·K}) \times \ln\left(\frac{100\ \text{kPa}}{10.0\ \text{kPa}}\right)}{\left(\frac{1}{307.2\ \text{K}} - \frac{1}{372.0\ \text{K}}\right)}$$

$$= 33,800\ \text{J/mol}$$

$$= 33.8\ \text{kJ/mol}$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

Exercise 13.3c

At 20.0 °C, the vapour pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapour pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Check Your Answer[3]

Example 13.3d

Estimating Temperature (or Vapour Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapour pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap}, then the temperature that corresponds to a different vapour pressure (or the vapour pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation:

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

Since the normal boiling point is the temperature at which the vapour pressure equals atmospheric pressure at sea level, we know one vapour pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapour pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$\begin{aligned} T_2 &= \left(\frac{-R \times \ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{\text{vap}}} + \frac{1}{T_1}\right)^{-1} \\ &= \left(\frac{-(8.3145\ \text{J/mol·K}) \times \ln\left(\frac{83.4\ \text{kPa}}{101.3\ \text{kPa}}\right)}{30{,}800\ \text{J/mol}} + \frac{1}{353.3\ \text{K}}\right)^{-1} \\ &= 346.9\ \text{K or } 73.8\ ^\circ\text{C} \end{aligned}$$

Exercise 13.3d

For acetone $(CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapour pressure of acetone at 25.0 °C?

Check Your Answer[4]

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g) \qquad \Delta H_{\text{vap}} = 44.01\ \text{kJ/mol}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l) \qquad \Delta H_{\text{con}} = -\Delta H_{\text{vap}} = -44.01\ \text{kJ/mol}$$

Example 13.3e

Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 13.3e). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at *T* = 37 °C (normal body temperature); ΔH_{vap} = 43.46 kJ/mol at 37 °C.

Figure 13.3e: Evaporation of sweat helps cool the body. (credit: work by Kullez, CC BY 2.0)

Solution

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5\ \cancel{\text{L}} \times \frac{1000\ \cancel{\text{g}}}{1\ \cancel{\text{L}}} \times \frac{1\ \cancel{\text{mol}}}{18\ \cancel{\text{g}}} \times \frac{43.46\ \text{kJ}}{1\ \cancel{\text{mol}}} = 3.6 \times 10^3\ \text{kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Exercise 13.3e

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Check Your Answer[5]

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state or **melting**. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 13.3f).

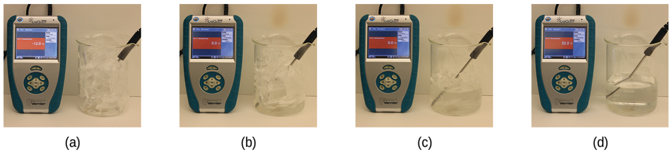


Figure 13.3f: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott in *Chemistry (OpenStax),* CC BY 4.0).

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the **freezing point** of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H_{\mathrm{fus}} = 6.01\ \mathrm{kJ/mol}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(s) \qquad \Delta H_{\mathrm{frz}} = -\Delta H_{\mathrm{fus}} = -6.01\ \mathrm{kJ/mol}$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapour forms (Figure 13.3g). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

Figure 13.3g: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_{\mathrm{sub}} = 26.1\ \mathrm{kJ/mol}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \qquad \Delta H_{\mathrm{dep}} = -\Delta H_{\mathrm{sub}} = -26.1\ \mathrm{kJ/mol}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modelled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 13.3h. For example:

$$\begin{array}{rll} \text{solid} & \longrightarrow \text{liquid} & \Delta H_{\mathrm{fus}} \\ \text{liquid} & \longrightarrow \text{gas} & \Delta H_{\mathrm{vap}} \\ \hline \text{solid} & \longrightarrow \text{gas} & \Delta H_{\mathrm{sub}} = \Delta H_{\mathrm{fus}} + \Delta H_{\mathrm{vap}} \end{array}$$

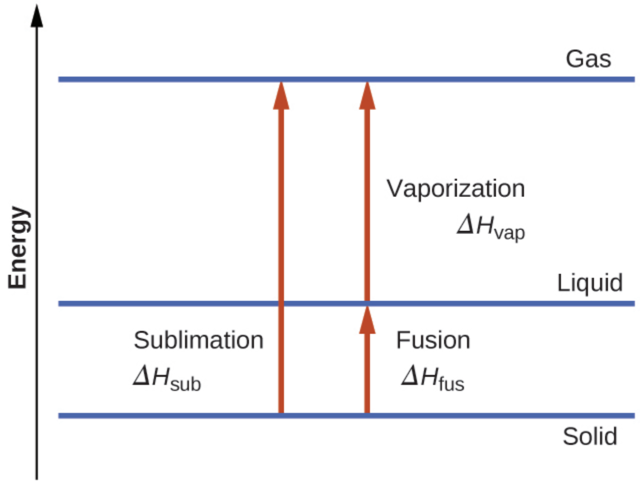


Figure 13.3h: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance is heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 13.3i shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behaviour is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.

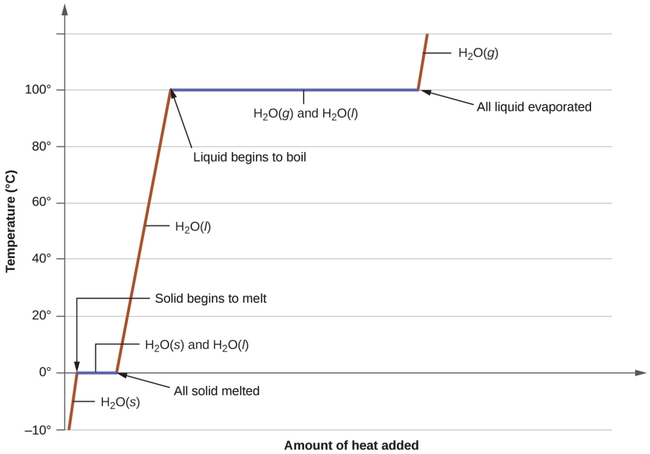


Figure 13.3i: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.3f

Total Heat Needed to Change Temperature and Phase for a Substance

How much heat is required to convert 135 g of ice at −15 °C into water vapour at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$\begin{aligned} q_{\text{total}} = \;& (m{\cdot}c{\cdot}\Delta T)_{\text{ice}} \;+\; n{\cdot}\Delta H_{\text{fus}} \;+\; (m{\cdot}c{\cdot}\Delta T)_{\text{water}} \;+\; n{\cdot}\Delta H_{\text{vap}} \;+\; (m{\cdot}c{\cdot}\Delta T)_{\text{steam}} \\ = \;& (135\text{ g} \;\times\; 2.09\text{ J/g}{\cdot}\,^\circ\text{C} \;\times\; 15\,^\circ\text{C}) \\ & + (135\text{ g} \;\times\; \tfrac{1\text{ mol}}{18.02\text{ g}} \;\times\; 6.01\text{ kJ/mol}) \\ & + (135\text{ g} \;\times\; 4.18\text{ J/g}{\cdot}\,^\circ\text{C} \;\times\; 100\,^\circ\text{C}) \\ & + (135\text{ g} \;\times\; \tfrac{1\text{ mol}}{18.02\text{ g}} \;\times\; 40.67\text{ kJ/mol}) \\ & + (135\text{ g} \;\times\; 1.84\text{ J/g}{\cdot}\,^\circ\text{C} \;\times\; 20\,^\circ\text{C}) \\ = \;& 4230\text{ J} \;+\; 45.0\text{ kJ} \;+\; 56,500\text{ J} \;+\; 305\text{ kJ} \;+\; 4970\text{ J} \end{aligned}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

$$= 4.23\text{ kJ} \;+\; 45.0\text{ kJ} \;+\; 56.5\text{ kJ} \;+\; 305\text{ kJ} \;+\; 4.97\text{ kJ} = 416\text{ kJ}$$

Exercise 13.3f

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Check Your Answer[6]

Exercise 13.3g

Practice using the following PhET simulation: Energy Forms and Changes (https://phet.colorado.edu/sims/html/energy-forms-and-changes/latest/energy-forms-and-changes_en.html)

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$
- $\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- $q = mc\Delta T$

Attribution & References

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Notes

1. All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapour pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapour pressures decrease as observed:
   $P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}$.
2. 40 kPa
3. 47,782 J/mol = 47.8 kJ/mol
4. 30.1 kPa
5. 28 kJ
6. 40.5 kJ

13.4 PHASE DIAGRAMS

Learning Objectives

By the end of this section, you will be able to:

- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapour pressure with temperature was described. Considering the definition of boiling point, plots of vapour pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in Figure 13.4a.

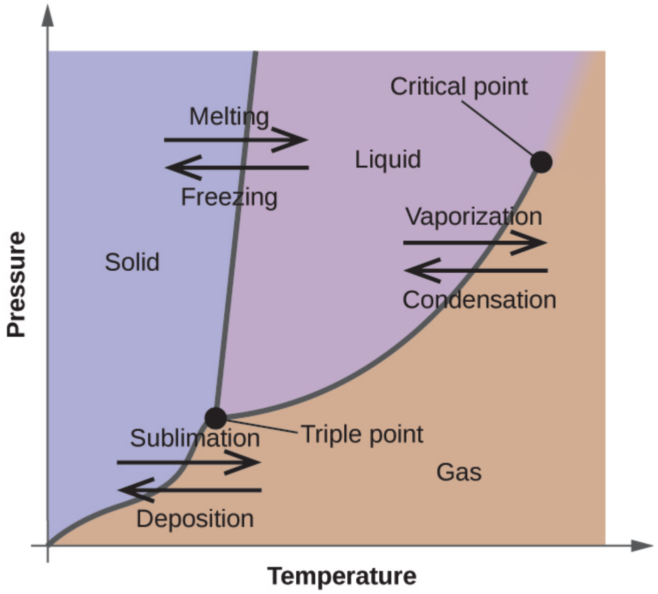

Figure 13.4a: The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram (credit: *Chemistry (OpenStax)*, CC BY 4.0).

To illustrate the utility of these plots, consider the phase diagram for water shown in Figure 13.4b.

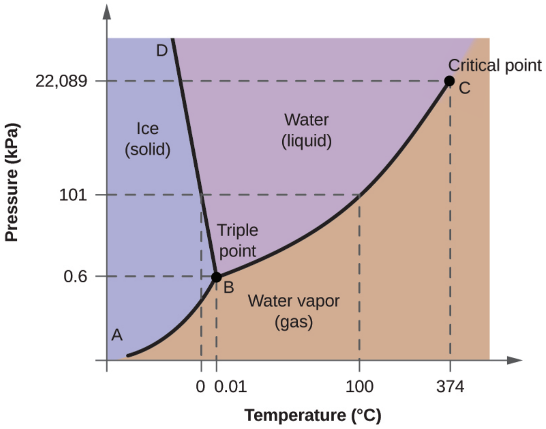

Figure 13.4b: The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of −10 °C correspond to the region of the diagram labeled "ice." Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the "water" region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in Figure 13.4b is the plot of vapour pressure versus temperature as described in the previous module of this chapter. This "liquid-vapour" curve separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapour curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapour curve, labeled AB in Figure 13.4b, indicates the temperatures and pressures at which ice and water vapour are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in Figure 13.4b, we would see that ice has a vapour pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the "freeze-drying" process often used to preserve foods, such as the ice cream shown in Figure 13.4c.

Figure 13.4c: Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: work by Iwao, CC BY 2.0)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behaviour is partly responsible for the movement of glaciers, like the one shown in Figure 13.4d. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.

Figure 13.4d: The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: work by NASA, Image use policy)

The point of intersection of all three curves is labeled B in Figure 13.4b. At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the **triple point**. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example 13.4a

Determining the State of Water

Using the phase diagram for water given in Figure 13.4b, determine the state of water at the following temperatures and pressures:

a. −10 °C and 50 kPa
b. 25 °C and 90 kPa
c. 50 °C and 40 kPa
d. 80 °C and 5 kPa
e. −10 °C and 0.3 kPa
f. 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure gave are as follows:

a. solid;
b. liquid;
c. liquid;
d. gas;
e. solid;
f. gas.

Exercise 13.4a

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? Is the pressure held at 50 kPa?

Check Your Answer[1]

Consider the phase diagram for carbon dioxide shown in Figure 13.4e as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.

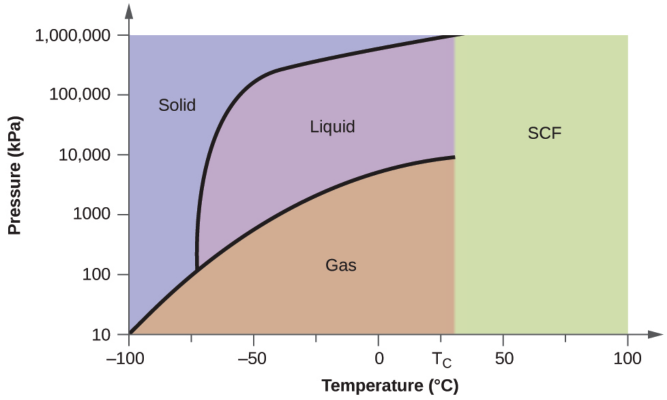

Figure 13.4e: The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.4b

Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in Figure 13.4e, determine the state of CO_2 at the following temperatures and pressures:

a. −30 °C and 2000 kPa
b. −60 °C and 1000 kPa
c. −60 °C and 100 kPa
d. 20 °C and 1500 kPa
e. 0 °C and 100 kPa
f. 20 °C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows:

a. liquid;
b. solid;
c. gas;
d. liquid;
e. gas;
f. gas.

Exercise 13.4b

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Check Your Answer[2]

Supercritical Fluids

If we place a sample of water in a sealed container at 25 °C, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapour at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapour increases, as described by the liquid-gas curve in the phase diagram for water (Figure 13.4b), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of 374 °C, the vapour pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapour phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** (see video below). Above its critical temperature, a gas cannot be liquefied no matter how much pressure is applied. The pressure required to liquefy a gas at its critical temperature is called critical pressure. The critical temperatures and critical pressures of some common substances are given in Table 13.4a.

Table 13.4a: Critical temperatures and pressures of common substances.

Substance	Critical Temperature (K)	Critical Pressure (atm)
hydrogen	33.2	12.8
nitrogen	126.0	33.5
oxygen	154.3	49.7
carbon dioxide	304.2	73.0
ammonia	405.5	111.5
sulfur dioxide	430.3	77.7
water	647.1	217.7

Watch Supercritical CO2 (5 mins) (https://www.youtube.com/watch?v=P9EftqFYaHg)

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavour and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

Example 13.4c

The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day (18 °C), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day (35 °C). Explain these observations.

Solution

On a cool day, the temperature of the CO_2 is below the critical temperature of CO_2, 304 K or 31 °C (Table 13.4a), so liquid CO_2 is present in the cylinder. On a hot day, the temperature of the CO_2 is greater than its critical temperature of 31 °C. Above this temperature, no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

Exercise 13.4c

Check Your Learning Exercise (Text Version)
Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behaviour?

a. The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.
b. The critical temperature of ammonia is 405.5 K, which is lower than room temperature. The critical temperature of oxygen is above room temperature; thus oxygen cannot be liquefied at room temperature.
c. Ammonia is at the lower level in the periodic table compared to Oxygen; thus oxygen cannot be liquefied at room temperature.
d. Oxygen is present in abundant compared to oxygen; thus oxygen cannot be liquefied at room temperature.

Check Your Answer[3]

Source: “Exercise 13.4c” is adapted from “Example 10.4-3” in General Chemistry 1 & 2, a derivative

Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O, hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($CH_3CO_2C_2H_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavour and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method (Figure 13.4f). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97−99% of the caffeine, leaving coffee's flavour and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.

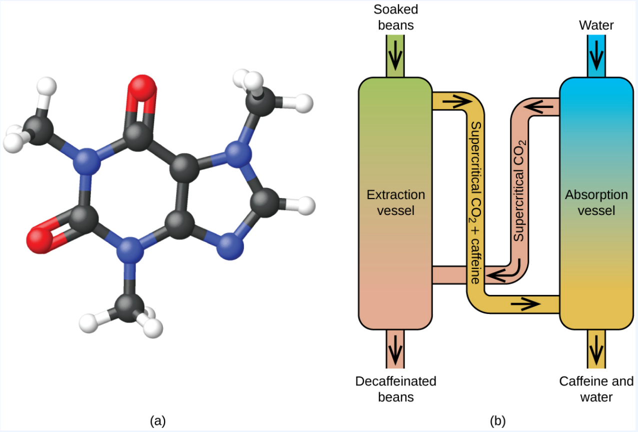

Figure 13.4f: Decaffeination of coffee beans using supercritical CO_2. (a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical car (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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Notes

1. At 0.3 kPa: $\text{s} \longrightarrow \text{g}$ at −58 °C. At 50 kPa: $\text{s} \longrightarrow \text{l}$ at 0 °C, $\text{l} \longrightarrow \text{g}$ at 78 °C
2. at 1500 kPa: $\text{s} \longrightarrow \text{l}$ at −45 °C, $\text{l} \longrightarrow \text{g}$ at −10 °C;
   at 500 kPa: $\text{s} \longrightarrow \text{g}$ at −58 °C
3. The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

13.5 WATER: A SPECIAL LIQUID

Learning Objective

By the end of this section, you will be able to:

- To describe the unique characteristics of water in terms of its structure

Indigenous Perspective: Sea Ice and Snow

Figure 13.5a: Sea ice in the Arctic (credit: work by Matti&Keti, CC BY-SA 4.0)

Inuit survival has always depended upon the important and stable coverage of the Arctic Ocean in ice. Sea ice (Figure 13.5a) is an essential gateway to freedom for the Inuit, and it makes life possible due to its many unique chemical properties. On the other hand, the chemistry of snow is equally important, especially given the fact that it covers the Arctic for most of the year. The chemical properties of snow make it an important insulator, building material, and an important cultural symbol for the Inuit.

To learn more about the chemistry of both sea ice and snow, read the following articles:

- Sea Ice: Essential for northern survival [New Tab] (https://uwaterloo.ca/chem13-news-magazine/fall-2022-special-edition/feature/sea-ice)
- Snow: Making life possible in the Arctic [New Tab] (https://uwaterloo.ca/chem13-news-magazine/fall-2022-special-edition/feature/snow)

Water: A Special Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in **solution**. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small **molecule**. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favourable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighbouring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of arrangement in the ice crystal. This arrangement requires that the molecules are somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water (Figure 13.5b).

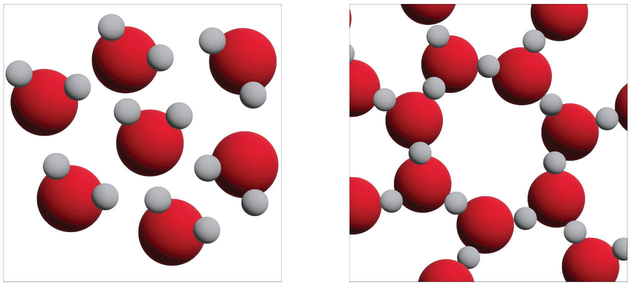

Figure 13.5b: Three-dimensional views of a typical local structure of liquid water (left) and ice (right). (credit: graphics by Revathi Mahadevan, CC BY 4.0)

In Figure 13.5b we can see three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of **hydrogen bonding** in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Watch Why does ice float in water? (3:55 min) (https://www.youtube.com/watch?v=UukRgqzk-KE)

Watch The Properties of Water (4:58 min) (https://www.youtube.com/watch?v=0eNSnj4ZfZ8)

Structure of the Water Molecule

Because oxygen is such an electronegative element, the two covalent OH bonds in water are polar and are formed by the overlap of the 1*s* orbital of hydrogen with an unpaired 2*p* orbital of oxygen.**Valence shell electron-pair repulsion theory (VSEPR theory)** (see chapter 11.7) tells us that the water molecule has a bent shape with bond angles of approximately 105^0, making water a very **polar molecule**. These bond angles and bent shape result in a partial negative charge on the oxygen atom and a partial positive charge on each hydrogen atom (Figure 13.5c) (**Source: Hein et al., 2013, p. 298)**.

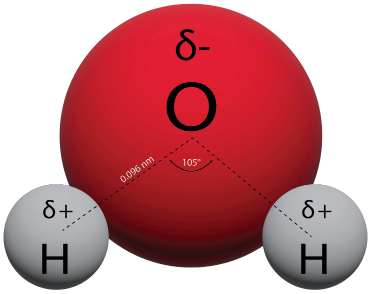

Figure 13.5c: The figure illustrates the water molecular structure, O-H bond length, and bond angle. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Scientists in Action: Dr. Katsuko Saruhashi

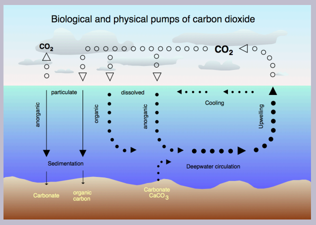

Figure 13.5d: Working of the biological and physical pumps of carbon dioxide. (credit: work by Hannes Grobe, CC BY-SA 2.5)

Japanese geochemist Katsuko Saruhashi (March 1920 – September 2007) was the first woman to earn a doctorate degree in chemistry from the prestigious University of Tokyo. Interested in environmental toxicology from an early age, Katsuko conducted research and created tools that let her take the first measurements of carbon dioxide (CO_2) levels in seawater (Figure 13.5c). This groundbreaking research allowed her and her team to demonstrate that previous hypotheses based on the idea that elevated CO_2 levels found in seawater could not be blamed on the dissolution of calcium carbonate, and instead were related to global warming caused by human activity. Among her many honours, she was the first woman elected to the Science Council of Japan and the first woman to be awarded the Miyake prize for geochemistry.

Read more about Katsuko Saruhashi in the article “Meet Katsuko Saruhashi, a resilient geochemist who detected nuclear fallout in the Pacific” [New Tab] (https://massivesci.com/articles/katsuko-saruhashi-geochemistry-seawater-japan/)

Watch The science of snowflakes (4:29 min) (https://www.youtube.com/watch?v=FwGH4gulLX4)

Attribution & References

Except where otherwise noted, this section is adapted by Gregory A. Anderson from “8.2: Solids and Liquids (https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/08%3A_Solids_Liquids_and_Gases/8.02%3A_Solids_and_Liquids)” In *Basics of General, Organic and Biological Chemistry (LibreTexts)* by David W. Ball, John W. Hill, and Rhonda J. Scott, licensed under CC BY-NC-SA 3.0

Reference

Hein, M., Pattison, S., Arena, S., & Best, L. (2013). Introduction to general, organic, and biochemistry(11th ed.). John Wiley & Sons, Inc.

CHAPTER 13 - SUMMARY

13.1 – Intermolecular Forces

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behaviour of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

13.2 – Properties of Liquids

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

13.3 – Phase Transitions

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

13.4 – Phase Diagrams

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

13.5 – Water: A Special Liquid

Water has many unique properties that not only allow life on Earth to flourish, but make it the most common solvent used in chemistry labs. The polar nature of the water (H_2O) molecule, as determined by VSEPR theory, impart these properties to water; for instance, solid H_2O (ice) is less dense than liquid H_2O, a rare property for a liquid to possess. As well, although it is a small molecule, water requires a relatively large amount of energy in order to change physical states.

Attribution & References

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- "10.1 Intermolecular Forces", "10.2 Properties of Liquids", "10.3 Phase Transitions", "10.4 Phase Diagrams", In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* . / Extracted and reused the key-takeaways/summary from each section used.
- "8.2: Solids and Liquids (https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/08%3A_Solids_Liquids_and_Gases/8.02%3A_Solids_and_Liquids)" In *Basics of General, Organic and Biological Chemistry (LibreTexts)* by David W. Ball, John W. Hill, and Rhonda J. Scott, licensed under CC BY-NC-SA 3.0

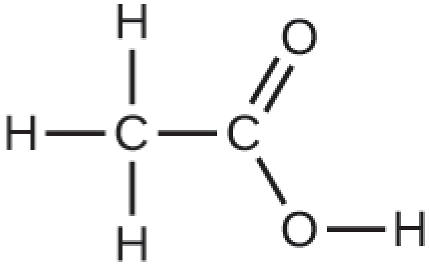
CHAPTER 13 - REVIEW

13.1 – Intermolecular Forces

1. In terms of their bulk properties, how do liquids and solids differ? How are they similar? **Check Answer:** [1]
2. In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?
3. In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases? **Check Answer:** [2]
4. Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.
5. What is the evidence that all neutral atoms and molecules exert attractive forces on each other? **Check Answer:** [3]
6. Open the PhET States of Matter Simulation (https://phet.colorado.edu/sims/html/states-of-matter/latest/states-of-matter_en.html) to answer the following questions:
    a. Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
    b. For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
    c. Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.
7. Define the following and give an example of each: **Check Answer:** [4]
    a. dispersion force
    b. dipole-dipole attraction
    c. hydrogen bond
8. The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?
9. Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe? **Check**

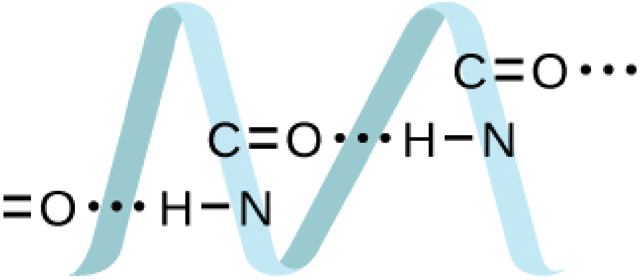
Answer: [5]

10. Neon and HF have approximately the same molecular masses.
    a. Explain why the boiling points of Neon and HF differ.
    b. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.
11. Arrange each of the following sets of compounds in order of increasing boiling point temperature: **Check Answer:** [6]
    a. HCl, H_2O, SiH_4
    b. F_2, Cl_2, Br_2
    c. CH_4, C_2H_6, C_3H_8
    d. O_2, NO, N_2
12. The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.
13. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses. **Check Answer:** [7]
14. On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.
15. The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer. **Check Answer:** [8]
16. Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?
17. Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules. **Check Answer:** [9]
18. Under certain conditions, molecules of acetic acid, CH_3COOH (shown below), form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

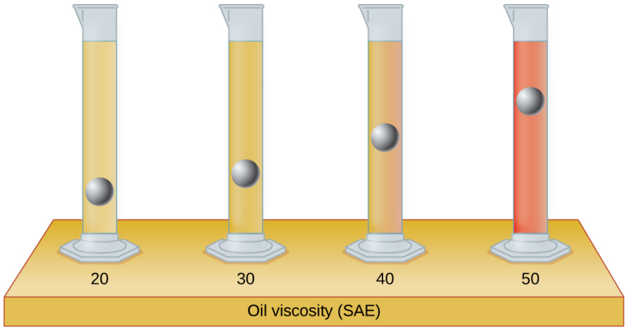
19. Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image below, show the locations of the IMFs that hold the protein together: **Check Answer:** [10]



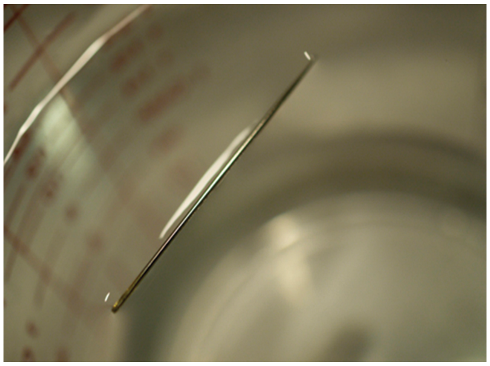
20. The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.
21. Identify the intermolecular forces present in the following solids: **Check Answer:** [11]
    a. CH_3CH_2OH
    b. $CH_3CH_2CH_3$
    c. CH_3CH_2Cl

13.2 – Properties of Liquids

1. The test tubes shown below contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration. Rank the motor oils in order of increasing viscosity, and explain your reasoning:

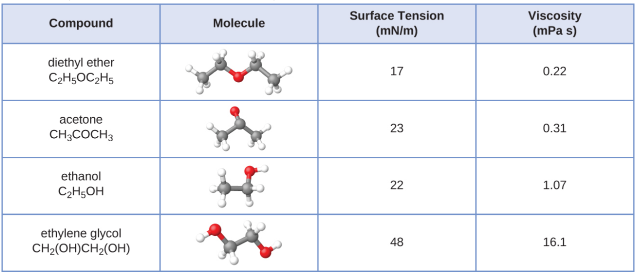


2. Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. See figure below. Explain at a molecular level how this is possible: **Check Answer:** [12]



(credit: Cory Zanker)

3. The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown in the figure below.



Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

   a. Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.
   b. Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:
4. You may have heard someone use the figure of speech "slower than molasses in winter" to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature. **Check Answer:** [13]
5. It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.
6. The surface tension and viscosity of water at several different temperatures are given in the data table below. **Check Answer:** [14]

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

    a. As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
    b. As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
7. At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 13.2a for the required information.
8. Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube? **Check Answer:** [15]

13.3 – Phase Transitions

1. Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?
2. Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change? **Check Answer:** [16]
3. What feature characterizes the dynamic equilibrium between a liquid and its vapour in a closed container?
4. Identify two common observations indicating some liquids have sufficient vapour pressures to noticeably evaporate? **Check Answer:** [17]
5. Identify two common observations indicating some solids, such as dry ice and mothballs, have vapour pressures sufficient to sublime?
6. What is the relationship between the intermolecular forces in a liquid and its vapour pressure? **Check Answer:** [18]
7. What is the relationship between the intermolecular forces in a solid and its melting temperature?
8. Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day? **Check Answer:** [19]
9. Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapour pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.
10. When is the boiling point of a liquid equal to its normal boiling point? **Check Answer:** [20]
11. How does the boiling of a liquid differ from its evaporation?
12. Use the information in Figure 13.3d to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa. **Check Answer:** [21]
13. A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapour. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapour, what would be the approximate pressure of the vapour produced?
14. Explain the following observations:
    a. It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in

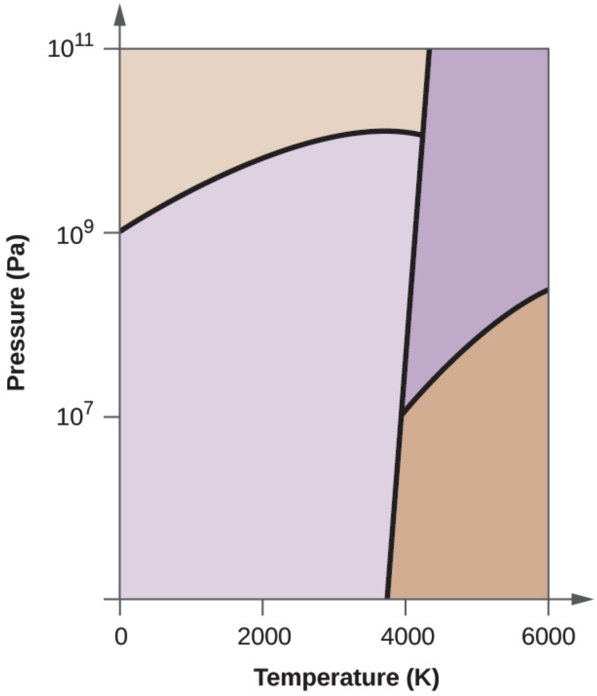
Boston (at sea level).
   b. Perspiring is a mechanism for cooling the body. **Check Answer:** [22]

15. The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.
16. Explain why the molar enthalpies of vaporization of the following substances increase in the order CH_4 < C_2H_6 < C_3H_8, even though the type of IMF (dispersion) is the same. **Check Answer:** [23]
17. Explain why the enthalpies of vaporization of the following substances increase in the order CH_4 < NH_3 < H_2O, even though all three substances have approximately the same molar mass.
18. The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers. **Check Answer:** [24]
19. The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.
20. Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride. **Check Answer:** [25]
21. Which contains the compounds listed correctly in order of increasing boiling points?
    a. $N_2 < CS_2 < H_2O < KCl$
    b. $H_2O < N_2 < CS_2 < KCl$
    c. $N_2 < KCl < CS_2 < H_2O$
    d. $CS_2 < N_2 < KCl < H_2O$
    e. $KCl < H_2O < CS_2 < N_2$
22. How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C? **Check Answer:** [26]
23. Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapour? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)
24. Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a ΔH_{fusion} = 9.37 kJ/mol.
    a. How much energy is required to melt 263.1 g $TiCl_4$?
    b. For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning. **Check Answer:** [27]

13.4 – Phase Diagrams

1. From the phase diagram for water (Figure 13.4b), determine the state of water at:

   a. 35 °C and 85 kPa
   b. −15 °C and 40 kPa
   c. −15 °C and 0.1 kPa
   d. 75 °C and 3 kPa
   e. 40 °C and 0.1 kPa
   f. 60 °C and 50 kPa
2. What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C? **Check Answer:** [28]
3. Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.
4. From the phase diagram for carbon dioxide in Figure 13.4e, determine the state of CO_2 at:
   a. 20 °C and 1000 kPa
   b. 10 °C and 2000 kPa
   c. 10 °C and 100 kPa
   d. −40 °C and 500 kPa
   e. −80 °C and 1500 kPa
   f. −80 °C and 10 kPa **Check Answer:** [29]
5. Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at −50 °C? If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in Figure 13.4e.)
6. Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature. **Check Answer:** [30]
7. Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 13.4e for the phase diagram.)
8. If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer. **Check Answer:** [31]
9. Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.
10. Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the



phase diagram below:

a. On the phase diagram, label the gas and liquid regions.
b. Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
c. If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
d. Circle each triple point on the phase diagram.
e. In what phase does carbon exist at 5000 K and 10^{8} Pa?
f. If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^{6} Pa, which phase transition occurs, if any? **Check Answer:** [32]

Attribution & References

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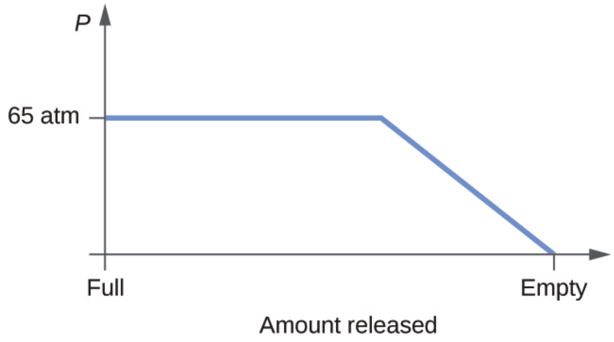
- “10.1 Intermolecular Forces“, “10.2 Properties of Liquids“, “10.3 Phase Transitions“, “10.4 Phase Diagrams“, In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* . / Extracted and reused the key-takeaways/summary from each section used.

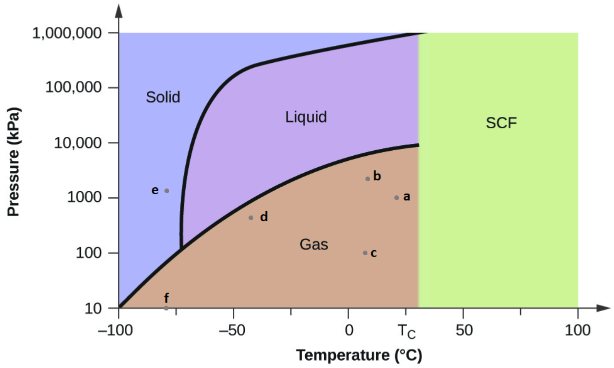
Notes

1. Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.
2. They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.
3. All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.
4. (a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $\mathbf{HF\cdots HF}$).
5. The London forces typically increase as the number of electrons increase.
6. (a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$
7. Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.
8. −85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.
9. The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.
10. H-bonding is the principle IMF holding the DNA strands together. The H-bonding is between the $\mathbf{N-H}$ and $\mathbf{C=O}$.
11. (a) hydrogen bonding and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces
12. The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of "skin" at its surface. This skin can support a bug or paper clip if gently placed on the water.
13. Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the temperature, the lesser the intermolecular forces are overcome, and so the less viscous the liquid.
14. (a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

15. 9.5×10^{-5} m
16. The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.
17. We can see the amount of liquid in an open container decrease and we can smell the vapour of some liquids.
18. The vapour pressure of a liquid decreases as the strength of its intermolecular forces increases.
19. As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.
20. When the pressure of gas above the liquid is exactly 1 atm
21. approximately 95 °C
22. (a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapour than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.
23. Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.
24. The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.
25. The thermal energy (heat) needed to evaporate the liquid is removed from the skin.
26. 1130 kJ
27. (a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.
28. At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapour; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.
29. (a) liquid; (b) solid; (c) gas; (d) gas; (e) gas; (f) gas
30. 

31. Yes, ice will sublime, although it may take it several days. Ice has a small vapour pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

32.


1,000,000
100,000
10,000
1000
100
10
Pressure (kPa)
Solid
Liquid
SCF
Gas
a
b
c
d
e
f
–100
–50
0
T$_C$
50
100
Temperature (°C)