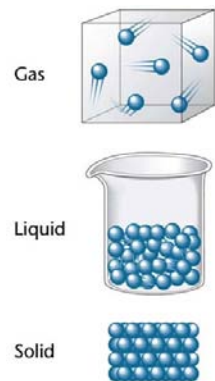


10.2.3 LIQUIDS AND SOLIDS

In general, the liquid and solid states show many similarities and are strikingly different from the gaseous state. The best way to picture the solid state is in terms of closely packed, highly ordered particles, in contrast to the widely spaced, randomly arranged particles of a gas (see Figure 10.2.3.1). The liquid state lies in between, but its properties indicate that it much more closely resembles the solid than the gaseous state. It can be useful to picture a liquid in terms of particles that are generally quite close together, but with a more disordered arrangement than for the solid state, and with some empty spaces.



10.2.3.1 Water and its Phase Changes

Pure water is a colourless, tasteless substance that at 1 atm pressure freezes to form a solid at 0 °C and vaporises completely to form a gas at 100 °C. Thus, at 1 atm pressure, the liquid range of water occurs between the temperatures 0 °C and 100 °C.

At 1 atm pressure, liquid water always changes to gaseous water at 100 °C, the **normal boiling point** for water. At 1 atm pressure, water freezes (or, in the opposite process, ice melts) at 0 °C, the **normal freezing point** of water (or, in the opposite process, the **normal melting point** of ice).

The conditions under which any particular substance exists as a solid, liquid and gas can be illustrated in a phase diagram, as illustrated in Figure 10.2.3.2.

Note that, under special conditions, all three phases of a substance can exist at once. This is known as the **triple point** for the substance. The triple point for water occurs at 0.06 atm pressure and 0.01 °C.

Interestingly, water is rather unique in that while most liquids contract when they freeze, water expands when it freezes. This has important practical implications. Water in a confined space can break its container when it freezes and expands. This is a fundamental aspect of weathering in rocks, and also why pipes burst when they freeze in cold weather.

The expansion of water when it freezes also explains why ice cubes float. If a mass of liquid water freezes, its volume increases. Since density is defined as mass/volume, its density will decrease and we know that a substance of lower density will float in one of higher density.

Figure 10.2.3.1
States of Matter

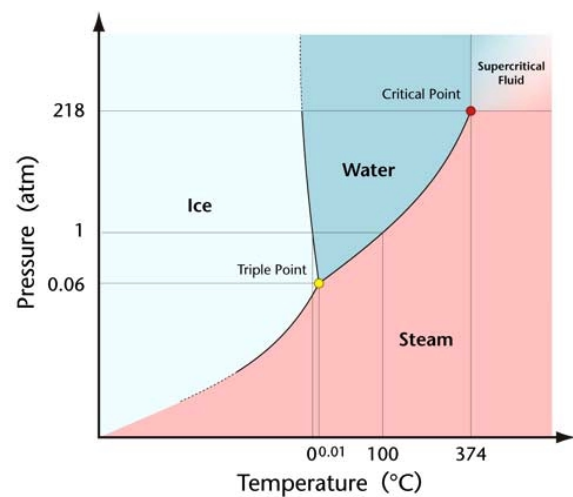


Figure 10.2.3.2 H₂O Phase Diagram

10.2.3.1.1 Energy Requirements for the Changes of State

It is important to recognise that changes of state from solid to liquid and from liquid to gas are *physical* changes. No *chemical* bonds are broken in these processes. Ice, water and steam all contain H_2O molecules. When water is boiled to form steam, water molecules are separated from each other, but the individual molecules remain intact.

The bonding forces that hold the atoms of a molecule together are called **intramolecular** (within the molecule) **forces**. The forces that occur among molecules that cause them to aggregate to form a solid or a liquid are called **intermolecular** (between the molecules) **forces**.

It takes energy to melt ice—just to change from ice at $0\text{ }^\circ\text{C}$ to water at $0\text{ }^\circ\text{C}$ —and to vaporise water—just to change from water at $100\text{ }^\circ\text{C}$ to steam at $100\text{ }^\circ\text{C}$ —because intermolecular forces between water molecules must be overcome (see Figure 10.2.3.3). The energy required to melt 1 mol of a substance called the **molar heat of fusion**. Similarly, the energy required to change 1 mol of liquid to its vapour is called the **molar heat of vaporisation**.

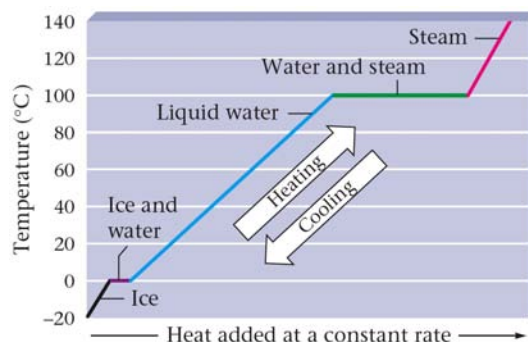


Figure 10.2.3.3
Heat and Phase Changes in Water

10.2.3.2 Intermolecular Forces

We noted briefly in Section 9.1.2 that water is a polar molecule—it has a dipole moment. Molecules with dipole moments can attract each other by lining up so that the positive and negative ends are close to each other. This is called a **dipole-dipole attraction**. Dipole-dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they become weaker as the distance between the dipoles increases so that in the gas phase these interactions are relatively unimportant.

Particularly strong dipole-dipole forces occur between molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen or fluorine. Because dipole-dipole interactions of this type are so unusually strong, they are given a special name—**hydrogen bonding**. Water is typical of molecules that display hydrogen bonding (Figure 10.2.3.4).

Even molecules without dipole moments exert forces on each other. We know this because all substances, even the noble gases, exist in liquid and solid states at very low temperatures. The forces that exist between noble gas atoms and non-polar molecules are called **London dispersion forces**. London forces become more

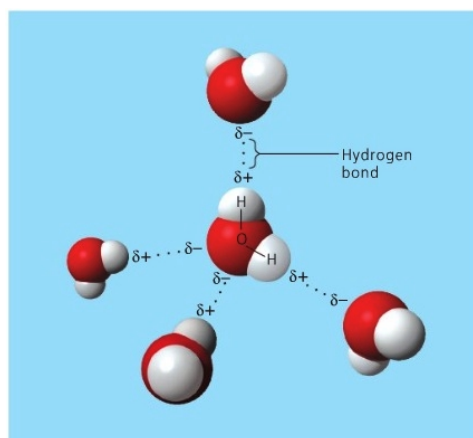


Figure 10.2.3.4
Hydrogen bonding between water molecules

significant as the sizes of atoms or molecules increase. Larger size means there are more electrons available to form the dipoles.

10.2.3.3 Evaporation and Vapour Pressure

When we place a given amount of liquid in a container and then close it we observe that the amount of liquid at first decreases slightly but eventually becomes constant. The decrease occurs because there is a transfer of molecules from the liquid to the vapour phase, a process known as **evaporation**. At the same time, however, molecules transfer back from the vapour phase to the liquid phase, via a process known as **condensation**. Initially, not very many molecules undergo this reverse process (because there are not many molecules in the vapour phase to begin with), but ultimately numbers of molecules transfer from vapour to liquid phase as do from liquid to vapour phase. At this point, no further change occurs in the amounts of liquid or vapour, because the two opposite processes balance each other—the system is in equilibrium.

The pressure of the vapour present at equilibrium with its liquid is called the equilibrium vapour pressure or simply the **vapour pressure** of the liquid. The vapour pressures of liquids vary widely, and liquids with high vapour pressures are said to be **volatile**—they evaporate readily.

The vapour pressure of a liquid, at a given temperature, is determined by the intermolecular forces that act between the molecules of the liquid. Liquids in which the intermolecular forces are large have relatively low vapour pressures, because more energy is required to overcome these forces and release molecules into the vapour phase.

10.2.3.4 The Solid State: Types of Solid

Many substances form **crystalline solids**—those with a regular arrangement of their components. There are, however, many difference types of crystalline solid. For example, while both salt (sodium chloride) and sugar (sucrose) form regular, colourless crystals, and dissolve readily in water, the properties of the resulting solutions are quite different.

These examples illustrate two important types of crystalline solids: **ionic solids**, represented by sodium chloride; and **molecular solids**, represented by sucrose or ice (Figure 10.2.3.5).

A third type of crystalline solid is represented by elements such as graphite and diamond (both pure carbon), boron, silicon and all metals. These substances, which contain atoms of only one element covalently bonded to each other, are called **atomic solids** (*e.g.* the various forms of carbon).

The properties of a solid are determined primarily by the nature of the forces that hold the solid together.

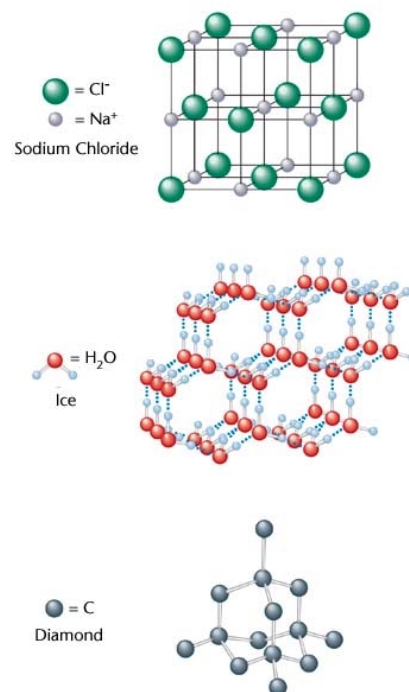


Figure 10.2.3.5
Examples of Crystalline Solids

10.2.3.4.1 Bonding in Solids

Ionic Solids

Ionic solids are stable substances, with high melting points, that are held together by the strong forces that exist between oppositely charged ions.

Molecular Solids

In a molecular solid, the fundamental particle is a molecule. Molecular solids tend to melt at relatively low temperatures because the intermolecular forces that exist among the molecules are relatively weak.

Atomic Solids

The properties of atomic solids vary greatly because of the different ways in which the fundamental particles, the atoms, can interact with each other.

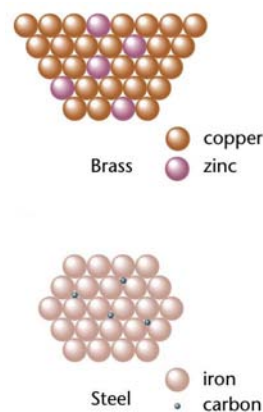
Bonding in Metals

Metals are a particular type of atomic solid. Although metals are malleable, they are also durable and have high melting points. These observations indicate that the bonding in metals is *strong* but *nondirectional*.

Because of the nature of the metallic crystal, other elements can be introduced relatively easily to produce substances called alloys. An **alloy** is *a substance that contains a mixture of elements and has metallic properties*. There are two common types of alloys.

In a **substitutional alloy**, some of the host metal atoms are replaced by other metal atoms of similar sizes. For example, in brass approximately one third of the atoms in the host copper metal lattice have been replaced by zinc atoms.

An **interstitial alloy** is formed when some of the interstices (holes) in a metal crystal lattice are occupied by atoms much smaller than the host atoms. Steel, the best-known interstitial alloy, contains carbon atoms in the holes of an iron crystal lattice.

**References**

Introductory Chemistry—A Foundation (6th Ed), Zumdahl, S.S. and DeCoste, D.J. (Houghton Mifflin, 2009) [ISBN 13: 978-0-618-80327-9]

Work directly from text, with exercises:

Chapter 14 Liquids and Solids