

Structure and Properties of Water

3.1 STRUCTURE OF WATER

To understand the nature of water in soil and plants, we need a mental picture of the water molecule. The water molecule (Figure 3.1) is composed of two hydrogen atoms and one oxygen atom. The water molecule is positively charged on one side and negatively charged on the other and is, thus, a dipole. Two hydrogen atoms each share a pair of electrons with a single oxygen atom. The two hydrogen atoms of the water molecule are separated at an angle of 103° – 106° , measured with the oxygen atom as the apex of the angle and with the two hydrogen protons

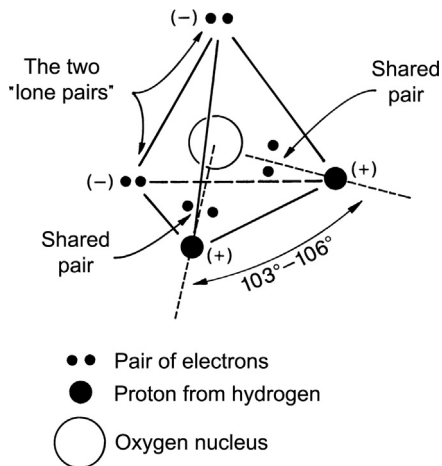


FIGURE 3.1 Tetrahedral charge structure of a water molecule. From *Kirkham and Powers (1972)*. This material is used by permission of John Wiley & Sons, Inc.

as points on the angle sides. The electron pairs shared between the oxygen nucleus and the two hydrogen protons only partially screen (neutralize) the positive charge of the protons. The result is that the proton side of the molecule becomes the positive side of the water molecule (Kirkham and Powers, 1972, p. 2).

There are two concentrations of negative electricity, one concentration above and one concentration below a plane defined by the two hydrogen protons and the oxygen atom. They are called the *lone-pair electrons*. One pair is above the plane and one pair is below. These two lone pairs of electrons do not take part directly in bond formation, as do the electrons shared between the hydrogen and oxygen atoms of the water molecule. The electric charge structure of the water molecule resembles a tetrahedron with the oxygen near the center, two of its corners positively charged due to the partially screened protons of the hydrogen, and the remaining two corners of the tetrahedron negatively charged due to the two pairs of lone-pair electrons. (The word *tetrahedron* comes from the late Greek *tetraedros*, which means four-sided, and is a solid figure with four triangular surfaces.) This arrangement makes the water molecule a dipole, that is, one end of the molecule tends to be positive and the other end tends to be negative (Kirkham and Powers, 1972, p. 3). *Dipole* is a term used in physics and physical chemistry and is anything having two equal but opposite electric charges or magnetic poles, as in a hydrogen atom with its positive nucleus and negative electron. The tetrahedral structure of water can be disrupted by changes in pressure and temperature, as well as high concentrations of salt (Leberman and Soper, 1995). New insights into the structure of water are being made with the development of modern experimental techniques and sophisticated models (Zubavicus and Grunze, 2004), which can require the use of supercomputers (Gerstein and Levitt, 1998).

3.2 FORCES THAT BIND WATER MOLECULES TOGETHER

3.2.1 Hydrogen Bonding

There are two attractive forces between water molecules: hydrogen bonding and the van der Waals–London force. Hydrogen bonding results from the electrical structure of water molecules that makes them group together in a special way. The negative lone-pair electrons of one water molecule are attracted to a positive partially screened proton of another water molecule (Kirkham and Powers, 1972, p. 3). Thus each corner of the four corners of the water tetrahedron can be attached, by electrostatic attraction, to four other water tetrahedron molecules in solution (Figure 3.2). This type of bonding is called hydrogen bonding.

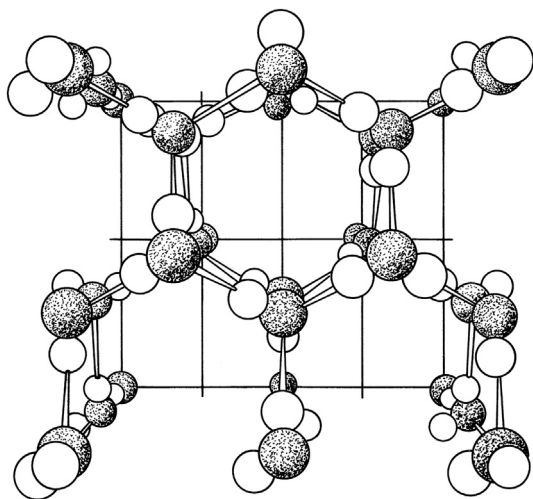


FIGURE 3.2 Diagram showing approximately how water molecules are bound together in a lattice structure in ice by hydrogen bonds. The dark spheres are oxygen atoms, and the light spheres are hydrogen atoms. From [Kramer \(1983\)](#). Reprinted by permission of Academic Press.

Hydrogen bonding is important in binding water molecules together. Hydrogen bonds play a crucial role in the behavior of water, and their spatial patterns and fluctuations characterize the structure and dynamics of the liquid ([Luzar and Chandler, 1996](#)). Hydrogen bonds have a binding force of about 1.3–4.5 kcal/mol in water ([Kramer, 1983](#), p. 11). [Nobel \(1974](#), p. 46) puts the value of hydrogen bonding at about 4.8 kcal/mol. The energy for hydrogen bonds in ice is 9.6 kcal/mol ([Pauling, 1964](#), p. 456.) (We shall return to this value in Chapter 20, when we calculate the tensile strength of water.) Although neighboring water molecules are predominantly held together in ice by electrostatic forces (hydrogen bonding), there is also a significant covalent component to the bond ([Isaacs et al., 1999](#)). Only part of the structure of water due to hydrogen bonding is destroyed by heating, and about 70% of the hydrogen bonds found in ice remain intact in liquid water at 100 °C ([Kramer, 1983](#), p. 12). [Postorino et al. \(1993\)](#) found that at 400 °C almost all hydrogen bonding is broken down.

3.2.2 van der Waals–London Force

A van der Waals–London force is one that exists between neutral nonpolar molecules, and, therefore, does not depend on a net electrical charge. The force was first described by van der Waals (1837–1923), a Dutch physicist. (See the Appendix, Section IV, for his biography.) [London \(1930\)](#) used quantum mechanics to obtain a quantitative expression for the van der Waals attractive force. This attractive force occurs because the electrons of one atom oscillate in such a way as to make it a rapidly fluctuating (about 10^{15} or 10^{16} Hz) dipolar atom, which in turn polarizes an

adjacent atom, making it, too, a rapidly fluctuating dipole atom such that the two atoms attract each other. The generated force varies inversely as the seventh power of the distance between the atoms (Kirkham and Powers, 1972, p. 4). An article in *Nature* puts the value as the sixth power (Maddox, 1985). Because this attractive force varies inversely as the sixth or seventh power, it is short-ranged. Quantum mechanics predicts that at distances greater than 100 Å one atom cannot polarize another. ($1 \text{ Å} = 10^{-10} \text{ m}$. The unit Ångstrom is named after Anders Jöns Ångström, 1814–1874, a Swedish physicist.) The exact proportion of attraction that we can attribute to the van der Waals–London force is not known. Kramer (1983, p. 11) puts the attractive force at about 1 kcal per mole. It is generally felt that this force contributes little to the attraction of water to itself.

3.3 PROPERTIES OF WATER

We now look at the unique physical properties of water. These properties permit life. If life exists on other planets, it probably is based on water rather than on any other molecule, like ammonia. In 1999, when scientists discovered a solar system 44 astronomical units (AUs) from earth, which was the first planetary system ever found around a normal star, aside from our solar system, it was postulated that some of those planets could be located at the right distance from their host star to have liquid water and, hence, life (Showstack, 1999). Life depends on water. The discovery of water on Mars (Haskin et al., 2005) stoked the talk of life on Mars (Kerr, 2004). Jupiter's small inner moon, Amalthea, seems to be mostly porous ice (Anderson et al., 2005). Sensors have found water on the moon (Kaku, 2009). Water molecules have been detected on a planet 370 trillion miles ($584.6 \times 10^{12} \text{ km}$) away (Hotz, 2007).

We will list 15 properties of water. The list is extracted from the book by Kramer (1983, pp. 8, 9, and 14), and the definitions of the properties come from the *Handbook of Chemistry and Physics* (Weast, 1964). Other authors have described the unique physical properties of water (Buchan, 1996; Perkowitz, 1999).

3.3.1 Specific Heat

Water has the highest specific heat of any known substance except liquid ammonia, which is about 13% higher. The handbook states (Weast, 1964, p. F-57) that if a quantity of heat H calories is necessary to raise the temperature of m grams of a substance from t_1 to t_2 °C, the specific heat, s , is

$$s = H/[m(t_2 - t_1)]$$

The units of specific heat are cal/g/°C. Table 3.1, adapted from van Wijk and de Vries (1966, p. 41), gives the specific heat of water at different temperatures.

From Table 3.1, one sees that the specific heat of water decreases with an increase of temperature up to 35 °C, and then the specific heat increases with further increase in temperature. Paul (1986) noted that the majority of isothermic animals maintain their body temperatures, during non-hibernation, within a few degrees of 36 °C (human temperature = 98.6 °F or 37 °C), because the specific heat of water is a minimum at 35 °C. He said:

As usual the key to much of life's mystery lies in the extraordinary behaviour of water.... [T]he relationship between the specific heat of water and temperature reveals that at 35 °C the specific heat of water is at its minimum value of $4.1779 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ An organism functioning at this temperature will find it necessary to generate or dissipate the minimum amount of heat energy in order to maintain its temperature constant. From the point of view of the organism's energy economy this temperature is clearly the most efficient at which to function. It seems likely that since the environmental temperatures on Earth are, with few exceptions, lower than 35 °C, organisms which have been able to set their working temperatures at a point just slightly above the temperature at which the specific heat of water is at its minimum value have thrived.

TABLE 3.1 Physical Properties of Liquid Water¹

Temperature (°C)	Density (g/cm ³)	Surface Tension (g/s ²)	Dynamic Viscosity (g/cm/s) × 10 ⁻²	Heat of Vaporization (cal/g)	Specific Heat (cal/g/°C)	Thermal Conductivity (cal/cm/s/°C) × 10 ⁻³
-10	0.99794	—	—	603.0	1.02	—
-5	0.99918	76.4	—	—	—	—
0	0.99987	75.6	1.7921	597.3	1.0074	1.34
4	1.00000	—	—	—	—	—
5	0.99999	74.8	1.5188	594.5	1.0037	1.37
10	0.99973	74.2	1.3077	591.7	1.0013	1.40
15	0.99913	73.4	1.1404	588.9	0.9998	1.42
20	0.99823	72.7	1.0050	586.0	0.9988	1.44
25	0.99708	71.9	0.8937	583.2	0.9983	1.46
30	0.99568	71.1	0.8007	580.4	0.9980	1.48
35	0.99406	70.3	0.7225	577.6	0.9979	1.50
40	0.99225	69.5	0.6560	574.7	0.9980	1.51
45	0.99024	68.7	0.5988	571.9	0.9982	1.53
50	0.98807	67.9	0.5494	569.0	0.9985	1.54

¹From van Wijk and de Vries (1966). Reprinted by permission of Prof. Daniel A. de Vries.

The idea supposes that the evolution of warm-blooded animals and the chemical properties of water are related (Kadler and Prockop, 1987). Paul's suggestion created a series of responses (Calder, 1986; Dunitz and Benner, 1986; Bird, 1987; Kadler and Prockop, 1987; McArthur and Clark, 1987; Stevenson, 1987).

The high specific heat of water stabilizes temperatures and results in the relatively uniform temperature of islands and land near large bodies of water (Kramer, 1983, p. 8). This is important for the growth of crops and natural vegetation.

3.3.2 Heat of Vaporization

The heat of vaporization of water is the highest known. The heat of vaporization is defined as the amount of heat needed to turn 1 g of a liquid into a vapor, without a rise in the temperature of the liquid. This term is not in the list of definitions given by Weast (1964), so the definition comes from Webster's New World Dictionary of the American Language (1959). The units are cal/gram and values for the heat of vaporization of water at different temperatures are given in Table 3.1. The heat of vaporization is a latent heat. *Latent* comes from the Latin *latere*, which means to lie hidden or concealed. Latent heat is the additional heat required to change the state of a substance from solid to liquid at its melting point, or from liquid to gas at its boiling point, after the temperature of the substance has reached either of these points. Note that a latent heat is associated with no change in temperature, but a change of state. Because of the high heat of vaporization, evaporation of water has a pronounced cooling effect and condensation has a warming effect (Kramer, 1983, p. 8). The cooling effect from evaporation is important in semiarid regions, such as Kansas (see Chapter 28).

3.3.3 Heat of Fusion

The heat of fusion of water is unusually high. The heat of fusion is the quantity of heat necessary to change 1 g of a solid to a liquid with no temperature change (Weast, 1964, p. F-44). It is also a latent heat and is sometimes called the latent heat of fusion. It has only one value for water, because water freezes at one value (0°C), and it is 79.71 cal/g or the rounded number 80 cal/g.

The high heat of fusion of water is used in frost control. Irrigation water drawn from the ground is often at a uniform temperature above freezing. In Nebraska, for example, groundwater is generally at about 12°C (Rosenberg, 1974, p. 276), and each gram can supply about 12 cal to the air with which it comes in contact. This thermal effect is small, however, when compared to the liberation of heat that occurs when

water freezes (80 cal/g). Irrigation water may contribute more than 90 cal/g (12 cal/g + 80 cal/g) in the process of cooling and freezing (Rosenberg, 1974). Fields may be flooded as a means of protecting crops from frost. Such a measure is extreme and is likely to be ineffective in an advective frost, because winds would remove the liberated heat from the flooded fields rapidly and freeze the unprotected vegetation. (In simple terms, advection means that wind is blowing and bringing hot or cold air into an area. We shall discuss advection when we talk about evapo-transpiration in Chapter 28).

Sprinkling is a more effective use of irrigation water in frost protection (Rosenberg, 1974, p. 276). Plants are sprinkled at the onset of freezing temperatures. As water freezes onto the plant parts, the heat of fusion is liberated. As long as the freezing continues, the temperature of the ice will remain at 0 °C. Sprinkling must be continued after the sun comes up the next day or until the temperatures have risen to melt the ice. If sprinkling is discontinued prematurely, heat will be drawn from the plant parts to melt the ice and frost damage may occur. Care must be taken when sprinkling tall plants. Ice loads of great weight will break them (Rosenberg, 1974, p. 276).

3.3.4 Heat Conduction

Water is a good conductor of heat compared with other liquids and nonmetallic solids, although it is poor compared to metals (Kramer, 1983, p. 8). Thermal or heat conductivity is not defined by Weast (1964), but it is defined in the 2013 edition of the *Handbook of Chemistry and Physics* (Haynes, 2013, p. 2–66) as the “[r]ate of heat flow divided by area and by temperature gradient.” Heat conductivity is defined in the 1959 edition of the *Handbook of Chemistry and Physics* (Hodgman, 1959, p. 2431) as “the quantity of heat in calories which is transmitted per second through a plate one centimeter thick across an area of one square centimeter when the temperature difference is one degree Centigrade.” The units, therefore, are cal/s/cm²/(°C/cm) or cal/cm/s/°C. Table 3.1 gives values of thermal conductivity of water at different temperatures. The table shows that at 20 °C, water has a thermal conductivity of 0.00144 cal/s/cm/°C. For comparison, copper, a metal, at 18 °C has a thermal conductivity of 0.918 cal/s/cm/°C (Hodgman, 1959, p. 2431), or about a thousand times greater than water. Table 3.1 shows that thermal conductivity of water increases as the temperature increases, and this fact is presented in many textbooks without explanation. Apparently a widely agreed upon explanation does not exist or it is too complicated to present succinctly (Gerard J. Kluitenberg, Department of Agronomy, Kansas State University, personal communication, October 27, 2010).

Survival of crops in the spring can depend on thermal conductivity. There are cases in which soil surface management can prevent a radiation freeze from occurring in row crops. In the spring of 1993, a number of Kansas farmers reported freeze damage in corn fields that had been cultivated. Uncultivated fields had no damage. In some cases the damaged and undamaged areas were adjacent, apparently in locations where the farmer had stopped cultivating for the day. Disturbing the soil by cultivation reduced the thermal conductivity and prevented stored heat from being released back toward the surface (Gerard J. Kluitenberg, personal communication, June 18, 1993). Both the solid soil and the water channels in the soil were disturbed by cultivation. If continuous water channels were broken, then the heat conducted by water upward from lower in the soil was reduced. Lower levels of the soil profile store heat, and, in the early cool spring months in Kansas, this heat can move upward to the cooler soil surface. Remember that in Nebraska groundwater is generally at about 12 °C. As we shall see later, when we discuss linear flow laws (Chapter 7), Fourier's heat flow law (Kirkham and Powers, 1972, p. 75) is a linear flow law and shows that heat is transported according to a temperature gradient. In Kansas, typically we do not start to worry too much about winter survival of winter wheat (*Triticum aestivum*) until temperatures at the crown level (usually 1–2 in or 2.5–5 cm deep) get below 10 to 12 °F (−12.2 to −11.1 °C). Where there is snow cover, soil temperatures will not get that cold. Where there is no snow cover, soil temperatures will depend on how much moisture is in the ground. Soil moisture holds a lot of heat, so even if we get temperatures of 0 °F (−17.8 °C) or below for a few days, the wet soil should not get that cold and winter wheat probably will not be damaged (James P. Shroyer, Kansas State University, personal communication, January 8, 2010).

3.3.5 Transparency to Visible Radiation

Water is transparent to visible radiation. This allows light to penetrate bodies of water and makes it possible for algae to photosynthesize at considerable depths (Kramer, 1983, p. 8).

3.3.6 Opaqueness to Infrared Radiation

Water is nearly opaque to longer wavelengths in the infrared range. Thus, water filters are good heat absorbers (Kramer, 1983, p. 8). A practical use of water to absorb heat was observed in Israel by Kirkham (1985), who said, "An unusual use of water is illustrated... at the Dead Sea, in Israel, where experiments are underway to get energy from the sun's heat. The salt water in these ponds is heated very hot by the sun, transferred by pipe to a nearby building; exposure to very cold water produces steam,

which becomes a potential source of energy.” The good absorption of heat by water helps to make this energy production in Israel possible.

We now define the visible and infrared regions of the spectrum. The visible region extends from 3900 to 7800 Å (390–780 nm or 390–780 mμ or 0.390–0.780 μ). The spectrum goes from violet (shortest wavelength), through blue, green, yellow, orange, and to red (longest wavelength). Chlorophyll absorbs in the blue and red regions and reflects in the green. That is why it looks green. The maximum (peak) absorptions in the blue and red regions for chlorophyll a and b are (Stewart, 1964, p. 51):

Chlorophyll a
 4300 Å (blue)
 6600 Å (red)
 Chlorophyll b
 4700 Å (blue)
 6500 Å (red)

The infrared region goes from 7800 to 4×10^6 Å (Giese, 1962, p. 164). The near infrared extends from 7800 to 2×10^4 Å, and the far infrared extends from 2×10^4 to 4×10^6 Å.

Figure 3.3 illustrates that water is transparent in visible wavelengths, but absorbs at wavelengths in the infrared region. Note that the abscissa in Figure 3.3 extends to 1400 nm (1 nm = 1 mμ), which is in the near infrared region. The near infrared extends to 2000 nm.

3.3.7 Surface Tension

Water has a much higher surface tension than most other liquids because of the high internal cohesive forces between molecules (Kramer,

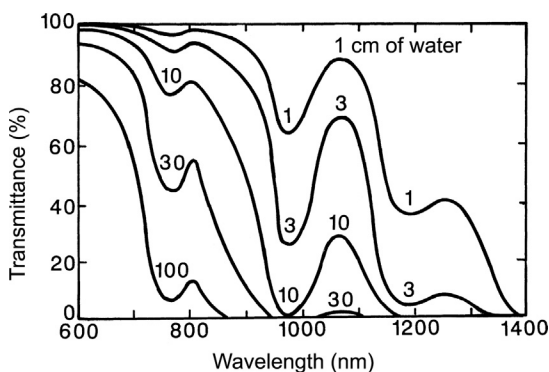


FIGURE 3.3 Transmission of radiation of various wavelengths through layers of water of different thicknesses. The numbers on the curves refer to the thickness of the layers in centimeters. Transmission is much greater at short than at long wavelengths. From Kramer (1983). Reprinted by permission of Academic Press.

1983, p. 8). In Chapter 6 we will discuss surface tension in detail, including Laplace's surface tension theory. The high surface tension of water provides the tensile strength required for the cohesion theory for the ascent of sap (water in the xylem). The cohesion theory is only a theory, but appears to be the best explanation for the rise of water in plants. We shall go into it in detail in Chapter 20 and calculate the tensile strength of water. Surface tension has units of force per unit length or dyne/cm. Table 3.1 gives values of surface tension at different temperatures. Note that the unit given for surface tension in the table is g/s^2 . This is equivalent to dyne/cm, because, as we saw in Chapter 2,

$$F = ma$$

$$1 \text{ dyne} = 1 \text{ g} \times 1 \text{ cm/s}^2$$

Rearranging, we get

$$\text{g/s}^2 = \text{dyne/cm}.$$

3.3.8 Density

Water has a high density and is remarkable in having its maximum density at 4°C instead of at the freezing point (Kramer, 1983; pp. 8, 9).

3.3.9 Expansion Upon Freezing

Water expands on freezing, so that ice has a volume about 9% greater than the liquid water from which it was formed (Figure 3.4). This explains

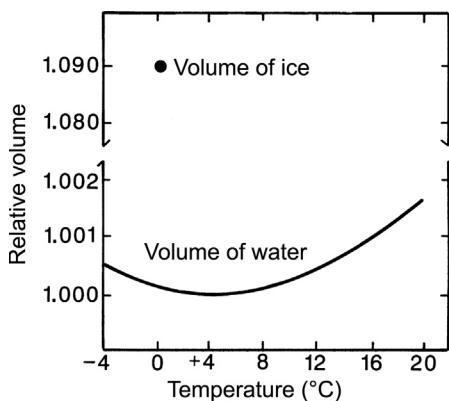


FIGURE 3.4 Change in volume of water with change in temperature. The minimum volume is at 4°C , and below that temperature there is a slight increase in volume as more molecules are incorporated into the lattice structure. The volume increases suddenly when water freezes, because all molecules are incorporated into a widely spaced lattice. Above 4°C , there is an increase in volume caused by increasing thermal agitation of the molecules. From Kramer (1983). Reprinted by permission of Academic Press.

why ice floats and pipes and radiators burst when the water in them freezes. If ice sank, bodies of water in the cooler parts of the world would be filled permanently with ice, and aquatic organisms could not survive (Kramer, 1983, p. 9).

3.3.10 Ionization

Water is very slightly ionized. Only one molecule in 55.5×10^7 is dissociated (Kramer, 1983, p. 9).

3.3.11 Dielectric Constant

Water has a high dielectric constant. We will not give the equation defining a dielectric, because it requires knowledge of capacitance, which is studied in physics courses. An interested reader can read a physics textbook such as Shortley and Williams (1971, pp. 517–520) to learn more about dielectrics. We will understand a dielectric by using the definition for dielectric in Webster's New World Dictionary of the American Language (1959): “(*dia* = through, across + *electric*: so called because it permits the passage of the lines of force of an electrostatic field, but does not conduct the current); a material, as rubber or glass, that does not conduct electricity; insulator”.

Water, therefore, is a good insulator. This might seem contradictory to the fact that we know we shall get electrocuted if we stand in water and put our finger in an electrical outlet. This is because we are standing in tap water, and tap water has salts in it. The electrical conductivity of tap water in Manhattan, Kansas, is 0.54 mmho/cm (=0.54 dS/m where dS is a deci-Siemen) (Kirkham, 1982). So when we say water is a good dielectric, we mean pure water. One should never touch any electrical appliance while taking a bath, including a radio, or work with electrical tools around water.

3.3.12 Solvent for Electrolytes

Water is a good solvent for electrolytes, because the attraction of ions to the partially positive and negative charge on water molecules results in each ion being surrounded by a shell of water molecules, which keeps ions of opposite charge separated (Figure 3.5).

3.3.13 Solvent for Nonelectrolytes

Water is a good solvent for many nonelectrolytes, because it can form hydrogen bonds with amino and carbonyl groups (Kramer, 1983, p. 9). An amino group has one hydrogen atom in the ammonia molecule replaced by an alkyl or other nonacid radical. A carbonyl is the bivalent radical CO.

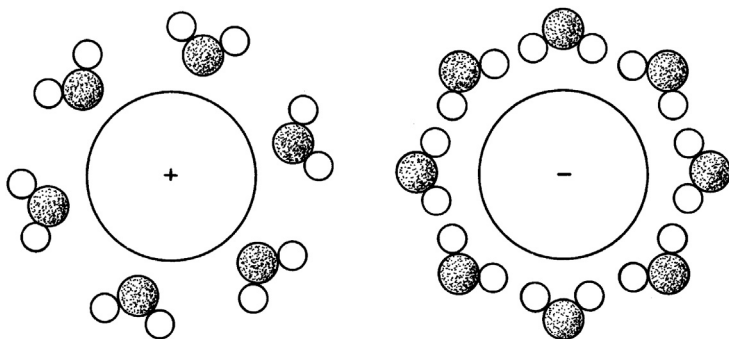


FIGURE 3.5 Diagram showing approximate arrangement of water molecules in shells oriented around ions. These shells tend to separate ions of opposite charge and enable them to exist in solution. They also disrupt the normal structure of water and slightly increase the volume. From [Kramer \(1983\)](#). Reprinted by permission of Academic Press.

3.3.14 Adsorption

Water tends to be adsorbed, or bound strongly, to the surfaces of clay micelles, cellulose, protein molecules, and many other substances. This characteristic is of great importance in soil and plant water relations ([Kramer, 1983](#), p. 9). We will see that it is important in the cohesion theory.

3.3.15 Viscosity

Water has a high viscosity. The *Handbook of Chemistry and Physics* defines viscosity as follows ([Weast, 1964](#), p. F-62): "All fluids possess a definite resistance to change of form and many solids show a gradual yielding to forces tending to change their form. This property, a sort of internal friction, is called viscosity; it is expressed in dyne seconds per cm^2 or poises." The poise is named after Poiseuille, and we will study Poiseuille's law for flow of liquids through capillary tubes in Chapter 15. [Table 3.1](#) gives values for the viscosity of water at different temperatures. The units in the table are $\text{g}/\text{cm}/\text{s}$. Again, using $F = ma$, we can see that these units are equivalent to dyne seconds per cm^2 , as follows. We substitute $(\text{g cm})/\text{s}^2$ for dyne, and we get

$$(\text{dyne s})/\text{cm}^2 = [(\text{g cm})/\text{s}^2] (\text{s}/\text{cm}^2) = \text{g}/\text{cm}/\text{s}.$$

3.4 APPENDIX: BIOGRAPHY OF JOHANNES VAN DER WAALS

Johannes Diderik van der Waals (1837–1923), a Dutch physicist, was born in Leyden, The Netherlands, November 23, 1837. He was a

self-taught man, who took advantage of the opportunities offered by the University of Leyden. He first attracted notice in 1873 with his treatise “On the Continuity of the Liquid and Gaseous State,” the basis for his doctoral degree. He taught physics at various schools, and, in 1877, he was appointed professor of physics at the University of Amsterdam, a post he kept until 1907 (Preece, 1971).

Van der Waals combined the determination of cohesion in the theory of capillarity by Laplace (1749–1827) with the kinetic theory of gases, and this led to the conception of the continuity of the liquid and gaseous states. He arrived at an equation that was the same for all substances by using the values of the volume, temperature, and pressure divided by their critical values (Preece, 1971). His work enabled the liquefaction of gases, which had important practical application during World War I (1914–1918). Although others had studied liquefaction of gases, it was van der Waals who was the first to treat the subject of the continuity of gases and liquids from the standpoint of the mathematical theory of gases (Cajori, 1929, pp. 210–211). Van der Waals was awarded the 1910 Nobel Prize in physics for his research on the equations of state for gases and fluids. He died in Amsterdam on March 9, 1923.

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