The Whys and Wherefores of Permafrost

■ Water, Nature's Abundant Oddity

The most abundant single chemical substance near the surface of the earth is water,[1] and all living things are mostly water—somewhere between 60% and 90%. The average human being is 71%, and many of human society's measurements are in terms of water. Three very basic ones are:

1. The freezing and boiling points of water at sea level respectively define the 0° and 100° points on the centigrade (Celsius) temperature scale. (0°C is 273.15 K [the symbol K means degrees Kelvin].)
2. A liter is the volume of 1 kilogram of water. (Similarly, 1 gram is the mass or weight of 1 cubic centimeter of water.)
3. A *calorie* is the average amount of heat required to raise the temperature of 1 gram of water 1°C anywhere in the range 0°C to 100°C. To put it another way, the *specific heat* of water is 1 calorie.

The fact that water is plentiful does not by itself explain why life on this planet is based on water. It is of course convenient to have so much water around, but the reason why water is the crucial essence of life is the curiously odd nature of the water molecule. It has a strange shape and,

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1. Specific information on the abundance of water near the earth's surface is in Appendix A.

partly for that reason, water possesses an abnormal set of properties. Some of these properties are largely responsible for the nature of frozen ground and the interesting changes that occur when the ground freezes and thaws.[2]

Water Molecules and the Forces that Hold Them Together, to Each Other, and to Other Substances Such as Soil

The water molecule and all other molecules are composed of atoms bonded together, and atoms are constructed from three fundamental building blocks: **protons**, **neutrons**, and **electrons**. The inner core of each atom, the nucleus, is composed of protons and neutrons each having about equal mass, but the neutron has no electrical charge, and the proton carries an elemental unit of positive charge. The electron carries the same amount of charge as the proton, but it is negative charge, and the electron has very little mass, 1/1,846 that of the proton.[3]

As portrayed in **Figure 2.1**, one proton and one electron joined together create the hydrogen atom, the lightest of all atoms. Two protons, two neutrons and two electrons joined create the next lightest atom (element), helium. All the other elements are similarly constituted; always with equal numbers of electrons and protons in each atom (but the number of neutrons can be equal, less or greater). The oxygen atom, an important component of the water molecule, has eight electrons swarming around a nucleus composed of eight protons and eight neutrons.

Atomic nuclei are held together by somewhat mysterious forces not of concern here because, while very strong, they are effective only on the tiny scale of atomic nuclei. Of much greater interest are the forces that bind the electron clouds of atoms to the nuclei and those that bind atoms together to form molecules. These are electromagnetic forces that depend on the electrical character of matter but not its mass. By contrast, the force of gravity depends on the mass character of matter but not the electric character. Gravity binds the earth to the sun, the moon to the earth, and it makes us

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2. The overall discussion in this chapter relies heavily on three highly readable books: Davis and Day (1961); Knight (1967); Deming (1975). Another valuable source is the textbook by Pauling (1970), especially pp 420–46.
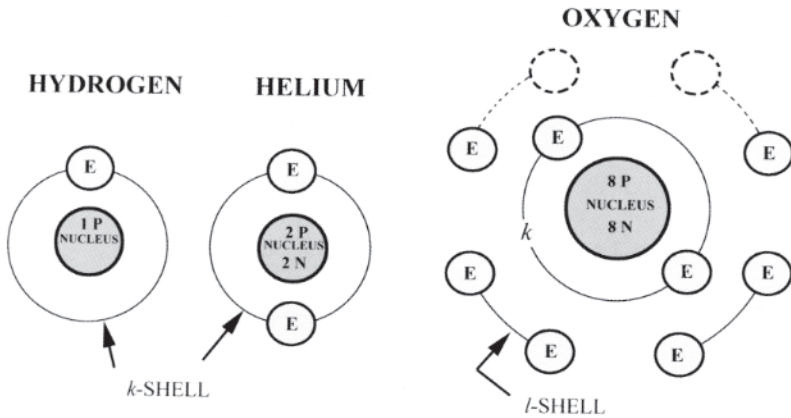3. See Appendix A for more information on these particles and their interactions.

Figure 2.1 Atoms. Although shown here as fixed circular objects, the electrons (E) are smeared out to envelop the nucleus of each atom. The helium nucleus contains two protons (P) and two neutrons (N), and the oxygen nucleus has eight of each. The closed *k* shell of the helium atom makes it very stable and not prone to join with other atoms, but the outer shell of the oxygen atom (the *l* shell) contains two paired electrons plus two unpaired ones that easily form pairs with unpaired electrons attached to other atoms.

fall down when our feet slide out too far from beneath our center of mass. It is an inverse square force because the strength of the gravity force between two objects depends on the square of the distance (*d* in **Figure 2.2A**) between them as well as upon their masses m_1 and m_2. Thus if the distance between the two objects is doubled, the gravity force between them falls to one-fourth its former value. The gravity force acts along the line joining the centers of mass of two objects, and it always causes them to pull towards each other. Gravity causes only the most minor attraction between atomic nuclei and their surrounding swarms of electrons, an attraction so weak that it is inconsequential compared to electromagnetic force.

It is useful to think of electromagnetic force as having two parts. One part (the electro part) depends on the *position* of electrical charge, and the other part (the magnetic part) depends on the *motion* of electrical charge.

The part of electromagnetic force depending only on the position of charge is called the **electrostatic force** or the **coulomb force**. As Figure 2.2A shows, the electrostatic force is like the force of gravity in that it acts only along the imaginary line drawn between the two objects involved and it grows weaker according to the square of their increasing separation. But since the electrostatic force depends on electrical charge instead of mass, and charge can be negative or positive, the force can be either attractive or
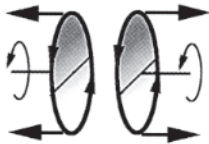
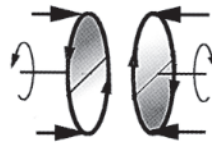$$\text{GRAVITY FORCE} = \text{CONSTANT} \times \frac{m_1 m_2}{d^2}$$
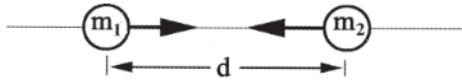
$$\text{ELECTROSTATIC FORCE} = \text{CONSTANT} \times \frac{q_1 q_2}{d^2}$$

UNLIKES ATTRACT

LIKE SIGNS REPEL
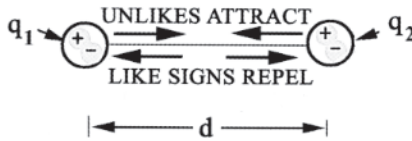
MAGNETIC FORCE BETWEEN SPINNING ELECTRONS

SAME SPINNING
ELECTRONS REPEL

OPPOSITELY SPINNING
ELECTRONS ATTRACT

Figure 2.2A The gravity force (top) causes attraction between objects having mass. The electrostatic force (center) causes attraction between charges of opposite sign and repulsion between those of like sign. The magnetic force (bottom) generated by moving charge creates repulsion between electrons spinning in the same direction, and attraction if they spin in opposite directions.

repulsive. The electrostatic force between unlike charges q_1 and q_2 pulls them together and the force between charges of the same sign pushes them apart. It is the primary force holding the electrons in an atom to the atomic nucleus, and also, as will be seen shortly, one of the two powerful forces that bind atoms together to form molecules.

The magnetic part of electromagnetic force is created by moving electrical charge, and it acts only on moving charge. The electrons in an atom are orbiting around the atomic nucleus and they also spin like tops on their own axes. Such motion causes them to generate what is called a magnetic force (or magnetic field). Each spinning electron generates a mag-

netic force field with exactly the same shape as the magnetic field of a bar magnet, so like bar magnets, two spinning electrons brought close together will experience an attracting or repelling magnetic force, depending on how they are oriented. Furthermore, if the two electrons are spinning in not exactly opposite directions their magnetic force fields will interact to bring the spins into exact opposition, maximizing the magnetic force tending to bring the electrons together. As the two electrons approach each other they also experience a repulsive electrostatic force, but if the electrons spin in opposite directions the magnetic force field will overcome that repulsion. Then the two electrons will move toward each other until the repulsive electrostatic force just balances the attractive magnetic force.

This tendency for two electrons to join in this fashion is called electron pairing, and it is responsible for a very strong bonding between atoms, ***covalent bonding***. The simplest example of covalent bonding is the joining of two hydrogen atoms to form the hydrogen molecule H_2. Each atom consists of one electron attached to a proton nucleus, and when hydrogen atoms come close enough together with proper orientation the electrons pair up. They become linked in tandem like a pair of oxen constrained by a yoke representing the balance between the electrons' electrostatic (coulomb) repulsion and their mutual magnetic attraction. Like the oxen, the linked electrons go where they must, but always side by side, forever turning in unison to face the same direction while dragging their heavy nuclei tails behind, thereby creating rigid molecular structures. The paired electrons now behave as a unit, appearing to be mutually shared between the two nuclei, and so covalent bonding is also referred to as electron sharing.[4]

Cooperating with covalent bonding is another strong kind of chemical bonding, called ***ionic bonding*** (also electrostatic and valence bonding). It depends on the electrostatic (coulomb) attraction that occurs between two atoms when each distorts the electron swarm of the other. The negatively charged swarm (typically consisting mainly of one or more electron pairs) shifts toward one of the atoms, making it slightly negatively charged, and away from the other, leaving it somewhat positively charged. The ionic bond is the consequence—a mutual attraction of the distorted atoms, each of which appears to the other to be carrying electrical charge of opposite sign.

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4. To get a direct feeling for how this works, experiment with two disk or ring magnets of the sort found in toy stores or often placed on refrigerator doors. Note how they orient themselves relative to each other when brought into proximity.

Ionic bonding is most important between atoms that differ greatly in how strongly their nuclei grasp their surrounding electron clouds, a characteristic known as ***electronegativity.***

Most atoms are prone to link together into molecules primarily through the influence of covalent bonding, while the bonding between others is mainly ionic bonding. In general, however, a mixture of ionic and covalent bonding acts to bind atoms together. The bond between two hydrogen atoms joined to make the hydrogen molecule H_2 is almost purely covalent; the one bonding sodium to chlorine to make ordinary salt $NaCl$ is nearly purely ionic, and the bonding of two hydrogen atoms to an oxygen atom to create the water molecule H_2O is about 60% covalent.[5]

These—the cooperating covalent and ionic bonding forces—are the two main glues that join most atoms together to form molecules, and in addition to them are two other much weaker but important bonding forces that involve both atoms and molecules. **Figure 2.2B** schematically illustrates the four bonding forces. One of them, called the **hydrogen bond**, owes its power to the special characteristics of the hydrogen atom— it is simply one proton tied to one electron. The electron swarms of all atoms larger than hydrogen (and all other atoms are larger) tend to form electrical shields around their nuclei that reduce their ability to project strong electrostatic forces outside the atoms. Unlike all these other nuclei, the positively charged hydrogen nucleus has virtually no shield, and so it is left hanging out almost naked when the hydrogen atom's electron covalently pairs up with an electron owned by another atom. The electro-static field of that nearly naked proton reaches out to pull toward itself any negative charge that might be in the vicinity. Because, like all electrostatic coulomb fields, the proton's field falls away with the square of the distance, it is too weak to form a chemical bond with most atoms. However, the field is strong enough that if the naked proton can approach an electron pair owned by another atom, the electrostatic attraction between the proton and those electrons is sufficient to form a weak bond. This, the hydrogen bond, is typically less than one-tenth as strong as the covalent bond, and it mainly forms only with small atoms like oxygen, nitrogen, and fluorine. Hydrogen bonds are of such a strength that their formation and rupturing play rich instrumental roles in the orchestra of life on this planet, and perhaps elsewhere.[6]

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5. Pauling (1960) 84–90.
6. Pauling (1960) 450–51.

COVALENT BOND
(VERY STRONG FORCE)

HYDROGEN BOND
(WEAK FORCE)

STRONG MAGNETIC FORCE BETWEEN
PAIRED OPPOSITELY SPINNING ELECTRONS

HYDROGEN NUCLEUS (PROTON) FORMS
ELECTROSTATIC ATTACHEMENT TO AN
ELECTRON PAIR OF ANOTHER ATOM

IONIC BOND
(STRONG FORCE)

VAN DER WAALS ATTRACTION
(VERY WEAK FORCE)

EFFECTIVE POSITIVE
CHARGE CENTER

EFFECTIVE NEGATIVE
CHARGE CENTER

DISTORTED ELECTRON CLOUD
UNBALANCES CHARGE DISTRIBUTION
CREATING ELECTROSTATIC ATTRACTION

REPULSIVE

ATTRACTIVE

THE SUM OF THE ATTRACTIVE FORCES
BETWEEN NUCLEI AND ELECTRON CLOUDS
SLIGHTLY EXCEEDS THE SUM OF ALL
REPULSIVE FORCES. THE LARGER THE
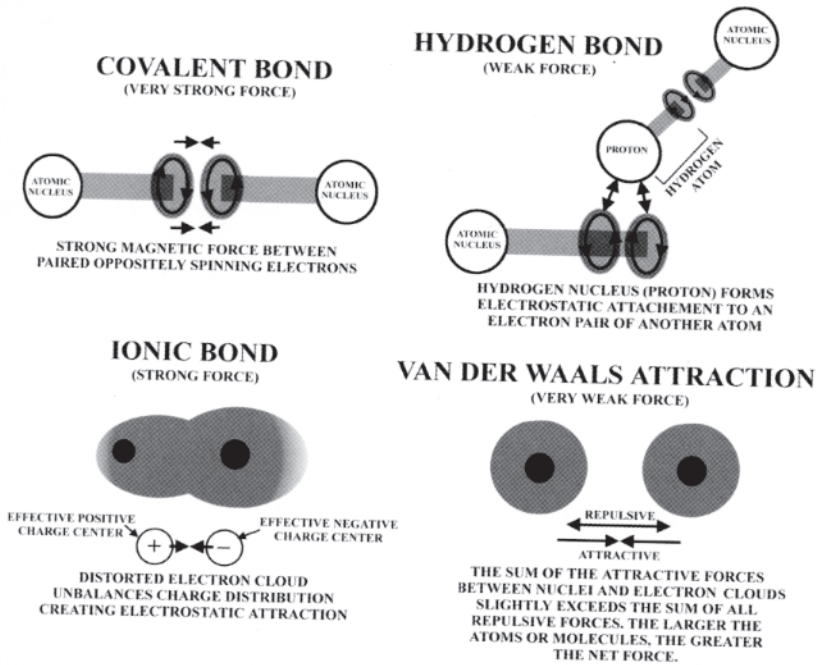ATOMS OR MOLECULES, THE GREATER
THE NET FORCE.

Figure 2.2B Schematic illustration of the four bonding forces important in binding atoms and molecules together.

The Four Kinds of Chemical Bonds Compared			
Covalent Bond (also called electron sharing)	**Ionic Bond** (electrostatic bond, also called valence bond)	**Hydrogen Bond** (occasionally called the *vital* bond)	**Van der Waals Attraction**
Very strong	Strong-very strong	Weak	Very weak
Magnetic in nature	Electrostatic (coulomb force) in nature		
Joins atoms together to form molecules.	Joins atoms together to form molecules.	Joins molecules together to from associated liquids or solids.	Makes atoms or molecules in liquid or solid state attract each other.
Special Feature: Widespread, so nearly universal it is sometimes called *the* chemical bond. It tightly joins atoms to form rigid molecules.	*Special Feature:* Joins individual atoms like sodium and chlorine into huge interlocking crystalline arrays: (Na - Cl - Na - Cl, etc.).	*Special Feature:* Joins comparatively small molecules (like H_2O) into arrays. Likes to hook to oxygen.	*Special Feature:* Important force holding liquids together: strength increases with size of molecules or atoms involved.

The fourth bonding force is even less strong. Called the **Van der Waals attraction**, it is a weak electrostatic attraction between atoms or molecules. Atoms or molecules in the liquid state come close enough together for the mutual attraction between each atomic or molecular nucleus for another's electron swarm to be slightly greater than the sum of the repulsive electrostatic forces between the positive nuclei and those between the negative electrons. The larger the atoms and molecules, the stronger the Van der Waals attraction, and that causes heavier atoms and molecules to have higher boiling points.[7] It is the Van der Waals attraction that must be overcome in the transition from the liquid to the gaseous state, though if the atoms or molecules participate in hydrogen bonding that too must be overcome.[8]

▪ Construction and Properties of the Water Molecule

When two hydrogen atoms join with an oxygen atom to create a water molecule (as depicted in **Figure 2.3**) the bonding is strongly covalent; that is, the bonding between each hydrogen atom and the oxygen atom is primarily due to the magnetic attraction between the hydrogen atom's single electron and one unpaired electron in the outer shell of the oxygen atom. The oxygen atom has two unpaired electrons in the outer shell, and hence the ability to join with two hydrogen atoms. It has six other electrons: two in the innermost shell (the *k*-shell) that do not interact chemically plus two sets of paired electrons. (The electrons in each pair have virtually identical orbits, but they spin in opposite directions and therefore hang together by their mutual magnetic attraction.)[9] When the covalent bonds develop, the new molecular entity consists of an oxygen nucleus core surrounded by a two-electron swarm in the inert inner *k*-shell and, outside of that (in the *l*-shell) four sets of paired electrons, two of which have attached hydrogen nuclei. The two-dimensional drawing in Figure 2.3 fails to do justice to the resulting three-dimensional structure of the water molecule, but **Figure 2.4** comes closer to portraying it. There it is shown that, because of the electro-

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7. The Van der Waals force also operates on solids; for example, it is the force acting across cleavage planes to hold sheets of mica together.
8. Additional discussion in Appendix A.
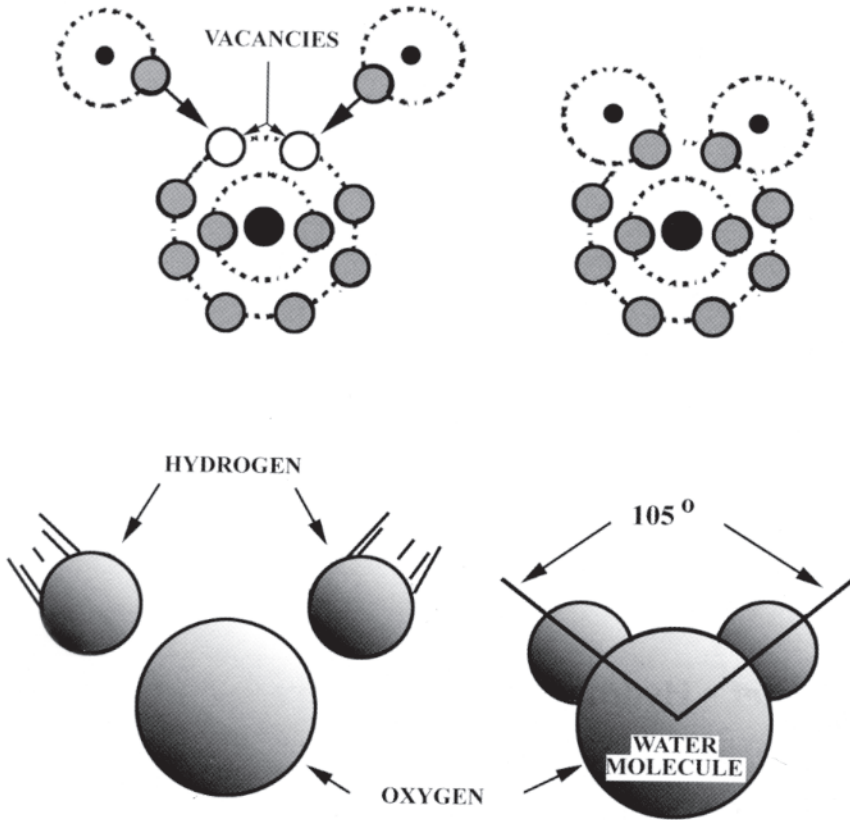9. And the same quantum numbers, except for the spin quantum number. See Appendix A.

Figure 2.3 The oxygen atom forms covalent bonds with the two hydrogen atoms, creating a very stable molecule not easily torn asunder.

static repulsive force between them, the four sets of electron pairs try to arrange themselves as far apart as possible within the outer shell, a configuration achieved if they are at the four corners of a regular tetrahedron with the oxygen atom at its center. (The regular tetrahedron is a four-sided figure with sides in the form of equilateral triangles. Its corners lie on the surface of a sphere, at points equidistant from each of the other three.) The angles between the lines joining any two sides of a tetrahedron are approximately 109°, but the presence of the two hydrogen nuclei in the structure of the water molecule weakens the repulsion between the bonding pairs of electrons enough to reduce the angle between the lines joining the oxygen and hydrogen nuclei to 105°, as indicated in Figure 2.3.
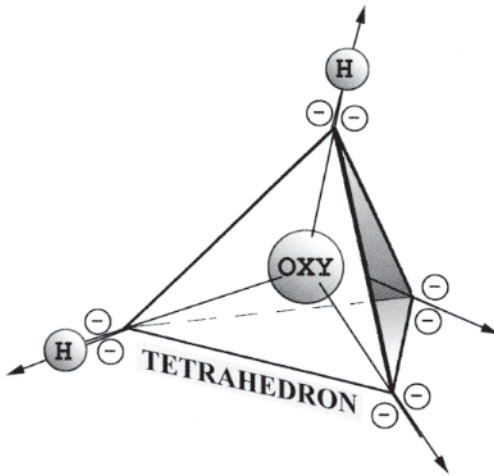
Figure 2.4 In the water molecule two sets of paired electrons and two sets of shared electrons (with their attached hydrogen nuclei) occupy the four corners of a regular tetrahedron with the oxygen atom at its center.

▪ Water's Hydrogen Bonds

The water molecule is one of the few naturally occurring molecules able to participate in hydrogen bonding. This ability results from the relative nakedness of the two hydrogen atoms in the molecule. Though each is tightly held to the central oxygen atom by a strong (magnetic) covalent bond, the two positively charged hydrogen nuclei stick out like little Velcro hooks ready to grasp electrostatically onto any negatively charged objects that come close enough. Favored candidates are electron pairs held in the outer shells of oxygen atoms because these atoms are physically small enough for the electrostatic Velcro hooks to make contact. Other water molecules are a great source of oxygen atoms, and each one has two sets of electron pairs available to be on the receiving end of a hydrogen bond. In Figure 2.4, these are the two pairs at the lower right-hand corners of the tetrahedron, the ones not involved in the covalent bonding that locks the water molecule together.

When water is in the gas state the individual water molecules are too far apart ever to form hydrogen bonds with each other. Thus H_2O truly is the proper formula for steam. But when water is cool enough to condense into the liquid state some of the molecules come close enough together to begin forming hydrogen bonds. Liquid water is not simply H_2O; rather it is $(H_2O)_n$, where $n = 1, 2,$ and 3 or more. Also, n has varying values in differ-

ent parts of the liquid, and it tends to get larger the more the water cools. As illustrated in **Figure 2.5**, water molecules come together through hydrogen bonding to form temporary and shifting associations, either in pairs, in strings or in rings composed of three to six (or perhaps even more) molecules.[10] Then when water cools enough to freeze into ice, the molecules lock together to form crystal arrays of water molecules held together by hydrogen bonds in a definite fixed pattern. As this happens the 105° angle between the covalent bonds of the water molecule open up to the 109° angle (the angle between the lines drawn from the center to any two corners of the regular tetrahedron) that gives ice a perfectly symmetrical crystal pattern, one called hexagonal and which is said to have cubic symmetry.[11] Diamond has this same pattern, but it is much harder than ice because the attachments between the carbon atoms in diamond are all tight covalent bonds that bring the atoms close together. Ice is much weaker because the bonds between water molecules are all hydrogen bonds, only 4% as strong as covalent bonds, and that gives the ice crystal a very open structure.
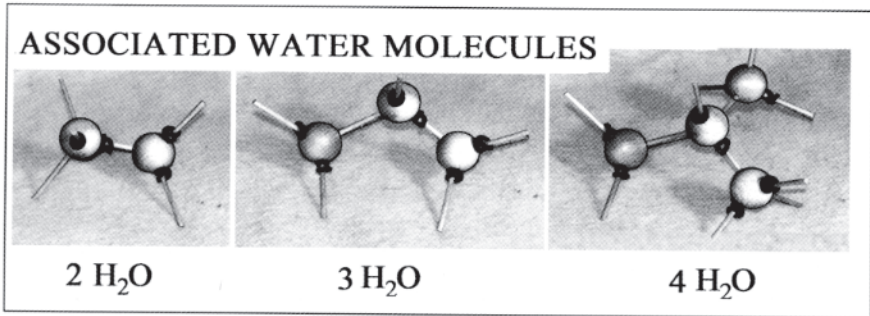

ASSOCIATED WATER MOLECULES

2 H_2O 3 H_2O 4 H_2O

Figure 2.5 Photographs of wooden models of water molecules joined together in temporary liaisons typical of liquid water. Other forms may also exist, such as strings or rings formed of four or five molecules. The wooden balls represent oxygen atoms, the wooden sticks portray the hydrogen bonds, and the black grommets wrapped around the sticks represent the hydrogen atoms in the water molecule.

10. Research on the nature of associated water clusters is ongoing. One recent paper [Gregory et al. (1997)] reports recent results on how the clustering affects the dipole moment of water molecules.
11. The cubic symmetry means that it is possible to draw cubes around portions of the crystal structure so that the structure in each cube is exactly like that in every adjoining one.

This tendency of water molecules to clump together (to associate, in technical parlance) through hydrogen bonding when in the liquid state is abnormal; most molecules cannot form hydrogen bonds so they keep the same formula when in the liquid state as they have when in the gaseous state. The strange situation with water is well described by an analogy following after one suggested by the famous British scientist Lord Kelvin. Water molecules can be likened to ships to illustrate their behavior in the solid, liquid and gaseous states. Molecules of water in the gaseous state are like ships on the high seas in that they are far apart and rarely in visual contact. Water molecules in the liquid state are like ships jammed together in a harbor—they are close by each other and some of them are temporarily linked by grappling hooks (the hydrogen bonds) as the ships transfer cargo or await berths. The molecules in the solid state are like ships in drydock, locked into total immobility by hydrogen bonds.

▪ Consequences of the Water Molecule's Shape and Ability To Form Hydrogen Bonds

Water, its strong electrical character

Even though it contains electrical charges, every atom appears to be electrically neutral when examined from a position well outside the atom. That is because the number of positive charges in the atom equals the number of negative charges, and these are symmetrically arranged so that the center position of the positive charges is identical to the center position of the negative charges (both are at the center of the atom). Each charge has its own electric field but in this situation the fields all cancel each other, so the atom looks to have no electrical character; that is, it appears to be electrically neutral. (Of course a person walking inside the atom with an electric field meter would recognize radical changes in electric field with position.)

A molecule might also appear to lack electrical character, but only if, like an atom, it is symmetric so that the centers of its positive and negative charge distributions are colocated. If the molecule is asymmetric so that the charge centers do not coincide, the molecule displays electrical character. Electrically, it looks like a little dumbbell having a positive charge in one end and an equal negative charge in the other. Called an electric dipole because of its two electrical poles (one positive, one negative), this configuration can be described quantitatively by saying that it has a *dipole moment* $m = ql$, where q is the amount of positive or negative charge and l is the separation between the two poles (the charge centers). **Figure 2.6**
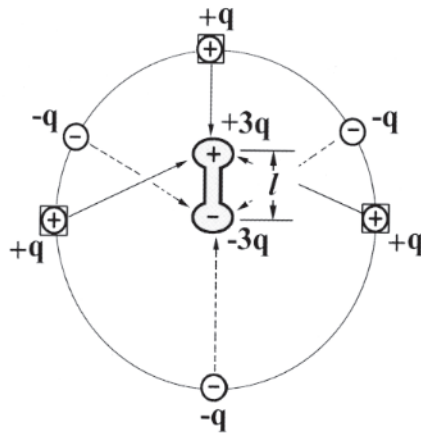
DIPOLE MOMENT = 3ql

Figure 2.6 The geometrical centers of the positive charges and the negative charges shown here do not coincide. Electrically, the distribution of charge is equal to that of a dipole having length l and charge 3q. Its dipole moment is 3ql. Notice that the centers of the positive and negative charge distributions are at the ends of the dipole.

schematically illustrates the relationship between a contrived unsymmetrical distribution of charges and an equivalent dipole.

The water molecule's distribution of charge is unsymmetrical in a fashion somewhat similar to that illustrated in Figure 2.6. As easily seen in Figure 2.4, the location of the center of the water molecule's negative charge distribution differs greatly from the location of the positive center. For that reason, the water molecule has an appreciable dipole moment, but that is only part of the story. If two of the little dumbbell dipoles can be locked together end to end the resulting dipole moment is twice that of the single dipole, and if three can be locked together the resulting dipole moment is tripled. Since liquid water has many hydrogen bonds linking molecules together, it contains molecular assemblies with abnormally high dipole moments.

The importance of water being so abnormally dipolar becomes evident when it is placed in an electric field. As shown in **Figure 2.7**, the molecular dipole arrays each try to swing around to orient themselves within the electric field in a direction that causes their electric fields to oppose the original field. Since electric fields are additive, the end result is a reduction in the overall electric field in the region. The greater the length of the dipoles
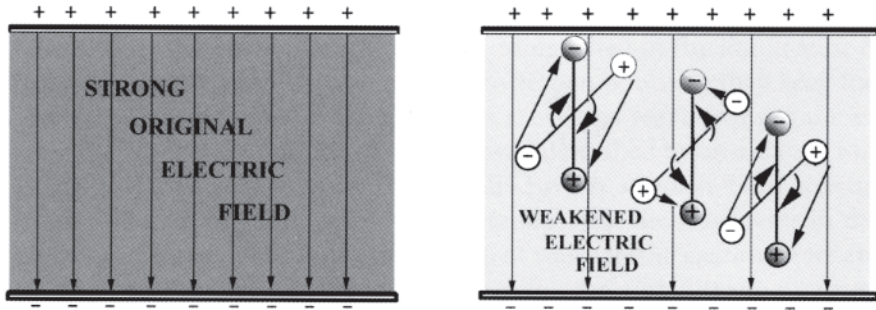
Figure 2.7 The electric field in a vacuum between the plates of a parallel-plate condenser is proportional to the number of (+) and (-) charges on the plates, as at left. When dipoles are introduced, as at right, the electric field pushes the positive end of each dipole toward the negative plate, and the negative end of each dipole toward the positive plate. The longer the dipole arms, the greater the shift in charge, and the more the electric fields of those shifted charges (shaded circles) oppose the original field, thereby reducing the electric field between the plates. The amount by which the field is reduced is defined as the dielectric constant of the introduced material. Water has dielectric constant 80.

introduced, the more profound the reduction to the original electric field, and so water—thanks to the odd shape of its molecule plus its hydrogen bonding—reduces the electric field to a remarkable 1/80 of its former value.

The amount by which a substance reduces an electric field is called its *dielectric constant* ε, and so water has dielectric constant $\varepsilon = 80$. The dielectric constant is much easier to deal with conceptually, and much easier to measure than dipole moments, so this is the term normally used in describing this electrical characteristic of a substance—its ability to reduce an electric field in which it is immersed. The dielectric constant of most liquids is in the range 1.5 to 10, so liquid water's dielectric constant of 80 truly departs from the norm. Hydrogen bonding is largely responsible because molecular linkages generally increase the effective dipole moment,[12] and the dielectric constant goes up proportionately.

Water, the universal solvent

Water's abnormally high dielectric constant is the cause of its capability to dissolve so many other substances, so many that it has been called the

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12. Not quite doubling because the molecular dipoles do not line up exactly end to end when the bonds form. See also Appendix A.

"universal solvent." Because of its high dielectric constant, water virtually destroys the electrostatic bonds, i.e. the electric fields, that hold so many substances together. Only those molecules held together by nearly pure covalent bonding (electromagnetic rather than electrostatic in character) are able to resist water's electrical onslaught. Water's ability to reduce the electrostatic (ionic) bond forces by a factor of 80 causes ionically bonded molecules like salt (NaCl) literally to collapse in water. As salt dissolves in water the molecules break up into positive sodium ions Na^+ and negative chlorine ions Cl^-. Moreover, these ions are attracted to water molecules by electrostatic forces: that between the negative oxygen end of a water molecule and the positive sodium ion, and that between the positive hydrogen end of the molecule and the negative chlorine ion. This additional attraction between water molecules and ions tends to keep the dissolved components of crystals from reforming as they might were the extra electrostatic forces absent. As far as each water molecule is concerned, the attraction is temporary and does not cause any lasting alteration. Thus water molecules remain unchanged and can participate again and again in dissolving other substances. That is important, as is the fact that water is so highly dipolar—otherwise water would not be such a powerful geologic force nor would it be able to carry enough dissolved mineral nutrients to permit vigorous plant growth.

Water, its elevated boiling and melting points and its high heat capacity

A general consequence of hydrogen bonding is the elevated temperature of water's melting point, and also its boiling point, compared to that of similar triatomic molecules such as H_2S and H_2Se (S for sulfur and Se for selenium) that do not normally enter into hydrogen bonding. Without hydrogen bonding, the expected melting point of ice would be −95°C and the boiling point −80°C. If that were to be the case, then the earth's surface now probably would have no water since any around would have been in vapor form and would have escaped into space long ago.

The **heat capacity**[13] of a substance is, by definition, the amount of energy per unit mass required to raise the temperature by 1°C. Water's heat capacity is very high, 1 calorie per gram per degree centigrade. Most elemental and molecular substances have much lower heat capacities, typically

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13. A related term is *specific heat*, the ratio of a substance's heat capacity to the heat capacity of water. Water has specific heat = 1.

one-half to less than one-tenth that of water. Recall that the temperature of a collection of atoms or molecules is merely a measure of their degree of agitation or motion. For water molecules to take up the increasing motion represented by a given increase in temperature, some of their hydrogen bonds must be broken, and that takes additional energy beyond that required just to increase the motion. This requirement for extra energy is the cause of liquid water's high heat capacity, about twice that of water in solid form (ice) and in vapor form (steam) because raising the temperature of those molecules does not require breaking hydrogen bonds. See **Table 2.1**.

Closely related to liquid water's high heat capacity is the large amount of energy required to break the rigid hydrogen bonds in ice when melting it and the even higher amount of energy required to break all the Van der Waals and hydrogen bonds when converting liquid water to steam. The energy stored in these bonds is called latent heat. The ***latent heat of fusion***, 80 calories per gram, is the amount of energy required to break the hydrogen bonds in ice when converting it to water, and the ***latent heat of vaporization***, 540 calories per gram, is the amount needed to break all the bonds when converting water to steam.[14] And of course just the opposite happens when steam is cooled down enough to convert it back to liquid water: as the Van der Waals and hydrogen bonds corral the rapidly wandering steam molecules, their energy of motion must be cast off. The liquid molecules still mill around in their confined situation but their motion is now comparatively slow, and it becomes slower yet as cooling continues. Water molecules then suddenly cast off the last of their energy of motion and essentially stop in their tracks as freezing occurs. The amount of energy involved when water changes state is large since, compared to other common substances like acetone, alcohol, sulfuric acid, turpentine and benzene that lack hydrogen bonding, water's latent heats of fusion and vaporization are abnormally high, by factors ranging from 2 to 30. When the ground freezes, water's high latent heat of fusion causes the release of much heat, and if the freezing is to continue that heat must somehow be carried away.

The combination of water's high heat capacity and latent heats together with its plentiful nature makes it the great moderator of climate. Each year, sunlight evaporates about 95,000 cubic miles of water from the earth's surface, and all those molecules racing around in gaseous form

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14. If ice sublimates directly to vapor, then the heat of sublimation is the sum of the heats of fusion and vaporization.

Table 2.1 Densities, heat capacities and thermal conductivities of various substances, listed within each column in order of decreasing magnitude. (Compiled primarily from data given by Williams and Smith (1989), pages 90 and 109.)

Density (kg/m°)	Thermal Conductivity (Watts/m °K)	Heat Capacity (Joules/kg °K)
Quartz: 2,660	Quartz: 8.8	Water: 4,180
	Clay Minerals: 2.92	Unfrozen Peat with 80% H_2O: 3,600
Clay Minerals: 2,650		
	Ice: 2.24	
		Unfrozen Peat with 40% H_2O: 3,300
Sandy or Clay Soil: 1,500 to 2,000	Frozen Soil: 2–3	
		Ice: 2,100
	Unfrozen Sandy Soil with 40% H_2O: 2.20	
Organic Matter: 1,300		Dry Peat & Dry Organic Matter:1,920
	Frozen Peat: ~2	
		Unfrozen Clay Soil with 40% H_2O: 1,480
Water: 1,000	Unfrozen Sandy Soil with 20% H_2O: 1.80	
		Unfrozen Clay Soil with 40% H_2O: 1,150
Ice: 917	Unfrozen Clay Soil with 20% H_2O: 1.58	
		Unfrozen Sandy Soil with 20% H_2O: 1,180
Peat: 300 to 1,100	Water: 0.56	
	Unfrozen Peat with 80% H_2O: 0.50	
Air: 1.2		Air: 1,010
	Unfrozen Dry Sandy Soil: 0.30	Clay Minerals: 900
		Unfrozen Dry Clay Soil: 890
	Unfrozen Peat with 40% H_2O: 0.29	
		Dry Sandy Soil: 800
	Unfrozen Dry Clay Soil: 0.25	
		Quartz: 800
	Dry Organic Matter: 0.25	
	Snow (220 kg/m^2): 0.11	
	Dry Peat: 0.06	
	Air: 0.025	

transport huge amounts of energy from low to high latitudes, making life possible everywhere—again, thanks to the hydrogen bond.

On a smaller scale we see illustrations of water's high heat capacity and latent heats in everyday life:

- The long-lasting warmth of a hot water bottle placed between the sheets, illustrating water's high heat capacity.
- The coolness of a wet shirt on the skin as the evaporating water molecules suck up energy because of water's high heat of vaporization.
- On cold nights the use by citrus fruit growers of water sprayed over their orchards to release energy that will slow the drop in temperature and possibly protect the fruit from freezing. Similarly illustrating the high heat of fusion is the way that the temperature often falls to freezing on a cold night, then pauses there until most of the moisture has frozen out of the air.

Water, its high viscosity, surface tension, and wetting ability

All liquids tend to resist changes to their form. This resistive property, called *viscosity*, is an internal friction or stickiness that increases with the degree to which the molecules of a liquid cling to each other. That is right down water's alley because its hydrogen bonding causes so many of its molecules to stick together that water has higher viscosity than almost any other liquid. Water's viscosity is high near the boiling point, but it increases as water cools because that allows greater numbers of hydrogen bonds to form between the molecules. The viscosity at 0°C is more than six times the viscosity at 100°C.

Related to water's high viscosity is its high surface tension, the tendency of the surface of a liquid to contract. Like viscosity, *surface tension* depends on the attractive forces between the molecules in the liquid. Water has the highest surface tension of all commonly occurring molecular liquids. Mercury, not a molecular substance, has even higher surface tension. In dynes/cm, a unit often used to express surface tension, mercury's surface tension is 470, water's is 73, while most liquids have surface tensions in the range 10 to 40. Some people find it good sport to place bits of mercury on a glass plate since, because of its high surface tension, the mercury beads up and rolls around over the glass in little balls. By comparison, playful people find that water is no fun at all because it tends to spread out over the glass. It is not just a matter of the difference in surface tension; the different behaviors are due to the fact that mercury molecules have no affinity for glass molecules,

but water molecules have a strong affinity. Why? Again, the graspy little hydrogen bond is the culprit. It causes water molecules to reach out for oxygen atoms, and glass contains many since its formula is SiO_2. Water also wets other materials that contain oxygen, such as cotton fiber, rock, clay, and both organic and inorganic soil particles.

This tendency for water to adsorb, that is, to stick to the surface of soil particles and plant materials, is of extreme importance to plant growth—and also to what happens to water when the ground freezes. Water's propensity to stick to itself and to the surface of other materials is the crucial element in its ability to rise up through the soil from below, to climb up to the tops of the tallest trees and to crawl right through frozen ground and even layers of ice. But before going into these matters we need to examine one other important consequence of the hydrogen bond, the strange fact that ice floats on water.

Water, why it floats ice

That ice is less dense than water and therefore floats on it is extremely peculiar because virtually every other substance gets more dense when it changes from the liquid to the solid state. Most every liquid steadily contracts as it cools and when it reaches its freezing point suddenly contracts by about another 10%, so the solidifying portion sinks to the bottom.[15]

The reason why liquids contract as they cool is that the Van der Waals forces pull the molecules increasingly close together. As with other liquids, in water the Van der Waals forces pull cooling molecules closer together, but only until the cooling proceeds down to 4°C. At that temperature the influence of water's hydrogen bonds overpowers the influence of the Van der Waals attraction. Any two water molecules held together by a hydrogen bond stand a definite distance apart—no farther and no closer than the spacing at which an exact balancing occurs among all the forces involved. These are mainly the attraction between the hydrogen nucleus and the oxygen's electron pairs, and the repulsion between the hydrogen nucleus and the oxygen nucleus. This spacing, 2.76×10^{-8} cm between each two oxygen atoms, is more than twice the spacing normally attained between other nonmetallic atoms when chemically bonded or crystallized. The carbon-carbon spacing in diamond is only 1.54×10^{-8} cm, the oxygen-oxygen separation in

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15. Among the few substances that do not contract upon freezing are antimony and bismuth alloys, which makes them useful as casting metals because a slight expansion on freezing creates crisp outlines, as on type face. Pure bismuth expands 3.3% upon solidification.

molecular oxygen is but 1.2×10^{-8} cm, and that between carbon and hydrogen in paraffin is 1.1×10^{-8} cm. (However, the spacing between crystallized metallic atoms may also be large, ranging to more than 5×10^{-8} cm.)

The transition at 4°C is smooth: it is just that at this temperature the standoffishness of the hydrogen bond reverses the contraction of water upon further cooling. Some of the molecules continue to move closer together as the temperature falls, but more and more of them are pushing farther apart as they form new hydrogen bonds. As the cooling progresses, the water molecules continue to mill around like a crowd of soldiers relaxing just prior to a battalion review. Some stand alone while others clump together, but below 4°C they are almost imperceptibly moving apart slightly and gradually becoming more orderly because of the pressure from increasing numbers of hydrogen bonds. Then, after the temperature has fallen a few more degrees, it is as if a command barks out and the molecular soldiers stiffen their hydrogen-bond arms and push apart, freezing into regular ranks. Each then stands the hydrogen bond-length 2.76×10^{-8} cm from four others to create a perfectly symmetrical pattern. A key element of the pattern is the open hexagonal ring-like structure illustrated schematically in **Figure 2.8** and with photographs of a wooden model in **Figure 2.9**. The six oxygen atoms (with their attached hydrogen atoms) in each hexagon do not all lie in the same plane, rather they lie in a corrugated sheet—one having regular ups and downs as indicated in Figure 2.8. Stacked one above the next, these corrugated ring arrays form ice crystals with much open space between the molecules, most easily seen in Figure 2.9. In the upper left part of Figure 2.9 the oxygen atoms marked with an "X" all lie at one level in a corrugated sheet, and those marked "O" lie in the other level.

The view along the direction identified as the c-axis of the crystal (see sketch at lower right in Figure 2.9) shows the most openness, and a view along any of the three a-axes shows almost as much, since these views also are looking through a series of hexagonal rings shaped slightly different from those seen looking down the c-axis. The view taken midway between two a-axes illustrates mainly the tiered nature of the crystal, i.e., the stacking of one corrugated sheet above another. Notice that the views along the three a-axes in the basal plane[16] are identical, and that these are 120° apart. Thus, an ice crystal rotated 120° around its c-axis merely moves every oxygen atom into the position formerly occupied by another.

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16. The basal plane is perpendicular to the c-axis. Ice crystals tend to grow fastest in the basal plane [Knight (1967)].
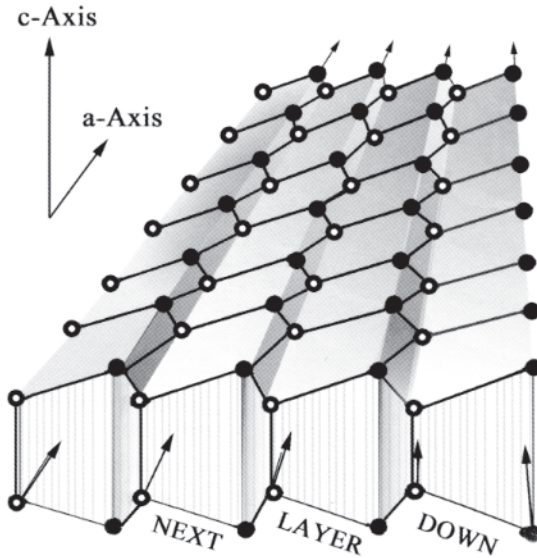
Figure 2.8 The main features of the structure in an ice crystal are hexagonal rings of water molecules lying in corrugated sheets. These lie perpendicular to the *c*-axis of the crystal, and the ring structure also is seen in a view looking along an *a*-axis. Compare with Figure 2.9.

Ice crystals melt and grow preferentially in the *a*- or *c*-axis directions according to the circumstances, so the identification of the axes is more than a matter of just wanting to give names to things. However, for the purpose here the primary significance of the structuring depicted in Figures 2.8 and 2.9 is the open nature of the ice crystal, and that openness is what makes ice 11% lighter than water (its density is 0.917 that of water). Hydrogen bonding is the basis for the openness because it causes each oxygen atom in an ice crystal to have only four nearby neighbors, and these cannot get very close because the hydrogen bonds grasp them and hold them at bay with stiff, outstretched arms. Curiously enough, the amount of energy given off as ice melts indicates that the melting involves the breaking of only about 15% of the hydrogen bonds holding an ice crystal together.[17] This means that water near the melting point is a highly **associated liquid**; that is, a high majority of the water molecules are joined together into hydrogen-bonded multiple arrays.
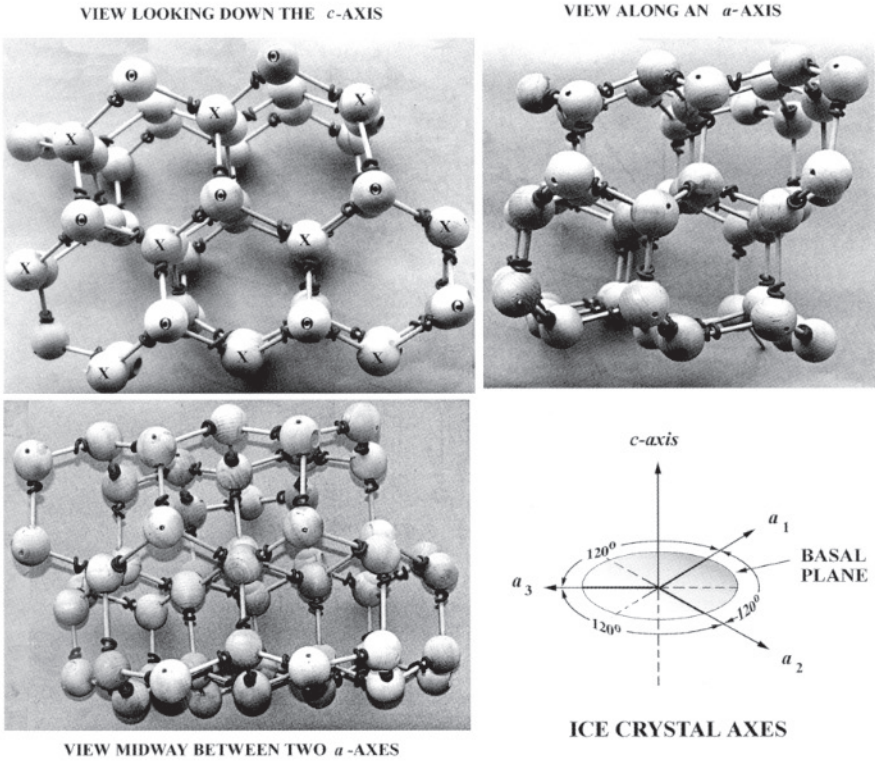
17. Pauling (1960) p 468.

VIEW LOOKING DOWN THE *c*-AXIS   **VIEW ALONG AN** *a*-AXIS

VIEW MIDWAY BETWEEN TWO *a*-AXES

ICE CRYSTAL AXES

Figure 2.9 Photographs of a wooden model depicting the structure of ordinary ice. Large balls represent oxygen atoms, and adjacent rubber grommets the hydrogen atoms.

■ Supercooling, the Consequence of the Universal System Happiness Rule

Although ice always melts at 0°C, water does not necessarily freeze at that temperature. Perfectly pure and still water can remain liquid when cooled to approximately −40°C. The barking command that initiates the freezing can be a stirring, a shaking, or the introducing of a tiny crystal that acts as a nucleating agent. If no command is given by the time the temperature reaches −40°C, the molecular troops jump to dress-parade positions by their own volition.

Any substance that remains liquid when cooled below its melting point is said to be supercooled. **Supercooling** is a common phenomenon in nature, and in fact it is not amiss to say that every liquid always under-

goes some supercooling prior to freezing. A person occasionally hears about supercooling but almost never about what really causes it. Supercooling is too important in the field of permafrost to let go unexplained, and to help with that I introduce what I call here the Universal System Happiness Rule:

▪ **Universal System Happiness Rule** ▪
Every System Is Happiest When It Contains The Least Possible Amount Of Free Energy

My name and phraseology for this rule is merely a mnemonic gimmick intended to anchor in the reader's mind this crucial idea that governs all things: the formation and behavior of atoms and molecules, why permafrost is as it is, why an ice cream cone melts before you can get it all in your mouth, and whatever else that you can think of. This rule appears repeatedly in this book, and even if left unstated the rule is still there governing what happens—or fails to happen, such as water not always turning into ice as the temperature falls through the melting point, 0°C.

The Universal System Happiness Rule really is an expression of the Second Law of Thermodynamics, about which one author[18] of a college-level physics text said, "Unfortunately all formal statements of this law are given in technical terms that require lots of explanation...." Though perhaps requiring lengthy explanation, some of the Second Law's familiar consequences are that water runs downhill, heat moves from hot places to cold places, and perpetual motion machines never really work.

The name "Universal System Happiness Rule" conveys the general idea but a more suitable and rigorous statement of the principle is: *The stable, equilibrium state of a system is the state of minimum free energy.* Two terms in this statement require explanation.

System.   The term "system" here is in the sense of Webster's first meaning of the word: "a regularly interacting or independent group of items forming a unified whole," and more specifically "an assemblage of substances that is in or tends to equilibrium." In essence, a system is some portion of matter that stands alone, essentially free of outside influence. Our solar system is an example, as would be an atom floating around all by itself far

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18. Weniger (1940).

from others. A system can also be some portion of matter in between these two extremes that is sufficiently isolated that we can consider it as an entity unto itself. Examples are the hot cocoa contained in a thermos bottle, a spinning top, or perhaps a pair of ring-shaped magnets constrained to encircle a vertical wooden stick. Another example more directly related to the topic of this book is a bucket containing partially frozen moist soil.

Free energy.   Free energy is available energy; that is, the energy that a system possesses that is available to do work. The amount of free energy in a system depends on the mass of the system, its temperature, and perhaps the location of the matter of which the system is composed. The free energy also depends on the system's heat capacity—that is, the ability of the system to carry heat energy. (Recall that water has very high heat capacity compared to most other substances: a kilogram of water will carry far more heat than a kilogram of soil or rock.)

A system only possesses free energy when it is capable of doing work, and it is only capable of doing work if it will change spontaneously into a configuration of greater stability. A system that is stable—and therefore in possession of minimum free energy and also unable to do work—can be changed into an unstable system if work is performed on it or it receives a transfer of free energy from another system.

Back in 1886 the famous Austrian scientist Ludwig Boltzmann made note that the struggle for life in all its forms is a battle for free energy. The main source of free energy here on earth is sunlight. Some of that energy is used by plants to build up unstable organic compounds that are the source of free energy in food, and some sunlight converts to mechanical energy that powers the motions of the atmosphere and the oceans. Were it not for all that free energy arriving from the sun, the earth would be a miserable place to live. The solar energy is free not in the sense that we do not have to pay for it, but rather free in the sense of not being locked up, and therefore available to do work.

Just why every system adjusts itself (by whatever means is available) to a condition of minimum free energy seems, at first glance, rather mysterious. What magic allows the system to know when it has achieved a state of minimum free energy? Actually, like a magician's trickery, the magic is merely illusory and always has a common-sense explanation. For example, imagine a system consisting of a marble that happens to be placed on an absolutely level table which, at one place, has a bowl set into the table so that its lip is exactly at the level of the tabletop. While the marble is resting on the tabletop it is stable and unable to do any work—it has mini-

mum free energy. Now imagine that the marble is placed on the lip of the bowl in the table. It is still at the same level as before, but now it can do work by rolling down the side of the bowl. Relative to the bottom of the bowl, the marble has free energy in the form of potential energy, the energy of position. Where does the marble finally come to a stop? The answer of course is the bottom of the bowl, the place where it has achieved a minimum of free energy, the place where it is stable, and the place where it no longer can do any work. (You might well ask what work was involved in the marble's rolling down the bowl. It did not actually do any useful work other than to stir up the air in the bowl and perhaps heat it slightly, but had a fly been in its path, the marble could have performed enough work to flatten the fly. The point is that having free energy provides the capability to perform work, whether or not the work actually gets performed.) And of course it is easy to see how the marble apparently knew it had reached a state of minimum free energy when it got to the bottom of the bowl. Obviously it had lost what free energy it had, the potential energy directly proportional to the height of the bowl, and so the marble could do nothing except rest happily in the bottom of the bowl forever.

Another simple example is a system consisting of a weight suspended from a spring. The system achieves a minimum of free energy when the downward force of gravity pulling on the weight just balances the upward force created by the stretching of the spring. This system is stable and it is not capable of doing any work. But now suppose that an external agent (like a person's hand) pulls the weight down some distance. The pulling involved doing work on the system, an amount equal to the force required times the distance the weight is moved. The system now is not happy: it is unstable and it has free energy in the form of potential energy, the energy of position. That free (potential) energy is equal to the work done on the system, and it is available to do the same amount of work. When the weight is released, the system will get rid of its free energy and oscillate back to its former stable, equilibrium state, the state of minimum free energy.

The Universal System Happiness Rule, *The stable, equilibrium state of a system is the state of minimum free energy,* applies to whatever system is at hand. That system might even be a horribly complicated one that involves matter in solid, liquid and gaseous forms and that is influenced by all conceivable kinds of interactions, chemical, mechanical, and electromagnetic.

When liquid water freezes it is merely minimizing its free energy, in keeping with the Universal System Happiness Rule. As water cools, its decreasing thermal motion permits a growing number of its molecules to

clump together through hydrogen bonding (to associate), and those associated molecules possess less free energy than do the remaining unattached molecules. At temperatures above the freezing point, the free energy carried by unattached molecules and the lesser free energy of the associated ones add up to a free energy less than that of ice, hence the water remains liquid. However, when a given mass of water becomes supercooled, that is, remains unfrozen even though the temperature is below 0°C, its free energy is actually *greater than* the free energy of an equal mass of ice. According to the Universal System Happiness Rule, this is an unstable situation, and it would seem that the water should have sought stability (happiness) by becoming frozen. Nevertheless, the system is stable, but just barely, because a certain tiny amount of work must be done if the water molecules are going to solidify into ice. Going back to the analogy of the milling soldiers, we might think of the work necessary to the forming of ranks as akin to the exertion involved in the soldiers' stiffly extending their arms. This extra work relates to the fact that as soon as water begins to convert to ice the overall system changes from being one of only liquid water to one consisting partly of water, partly of ice and partly of the interface between the two. Physically, the interface consists of the ice's outermost layer of water molecules, which recent studies are indicating is sort of half-molten and half-solid, with the vibrational motions of the molecules three to four times greater than those of molecules deeper in the ice crystal,[19] and free energies correspondingly higher as well. This interface has relatively high free energy associated with it in an amount that depends on the area and shape of the interface. If the interface is very small and has high curvature (as would be true if the ice were in the shape of a tiny sphere) any growth of the interface causes the overall system free energy to increase, so conversion of water to ice does not occur. Yet if the temperature drops low enough, or if a foreign object with radius bigger than what is called the **critical radius** is introduced into the liquid, freezing can occur without increasing the system's overall free energy. Then, in fact, freezing does decrease the system's overall free energy. The mathematics of the situation is given in Appendix A.

Herein lies the explanation of why a tiny foreign particle introduced into a supercoooled liquid may cause sudden freezing. The foreign particle substitutes for ice in forming a nucleus for further growth and so **nucleation** is the term applied to this process. The foreign particle must

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19. Seife (1996).

have a radius at least as large as the critical radius (typically about 10^{-7} cm) so that the energy associated with building the ice-water interface around it no longer is a barrier to further freezing.[20] Stirring the liquid may also work because agitation can increase the free energy of the water locally. At that local spot the water then may have enough extra energy to supply that needed to make the ice-water interface grow until it reaches the critical radius. In essence, free energy is borrowed by one part of the liquid from other parts, and even though an increase in free energy occurs in the borrowing part, the overall free energy decreases. Once the critical radius is reached, the whole mass of liquid water may quickly freeze.

When water does freeze, an amount of energy equal to water's latent heat of fusion must be cast off. The latent heat is the difference between the free energy carried by the mixed collection of solo and clumped molecules and that of molecules locked into the ice crystal lattice.

One consequence of that slight expansion of water as it cools below 4°C is that the temperature in the lower reaches of a deep lake can never fall below 4°C. The heaviest water, that at 4°C, sinks to the bottom of the lake, and so the freezing of a lake is from the top down.[21] Even lakes located in permafrost areas do not freeze completely if they are deep enough. The lack of freezing is crucial to the survival of some aquatic plants and animals, and it can have profound influence on the topography of lake shores in permafrost areas.

Another consequence of water's expanding at temperatures below 4°C is that increasing pressure causes water's melting point to decrease rather than to increase, as with most substances. For this reason it has long been suggested that the pressure created by an ice skater's blades provides a layer of water on which to glide along. (However, the so-called premelting phenomenon to be discussed in Chapter 3 contributes to forming a water layer and, except near 0°C, that contribution is more important in aiding the progress of the skater.) Similarly, the pressure from the weight of a glacier on the ice at its bottom is suggested to create a fluid layer there for the glacier to slide upon, and also make the lower part of the glacier plastic so that

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20. Nucleation—sometimes called seeding—works best if the introduced particle has a crystal structure similar to that of the solid to be formed. Because of similar crystal spacing and shape, silver iodide crystals are effective for seeding clouds to form ice which then can melt as it falls, and perhaps collect more water to form raindrops big enough to reach the ground before evaporating.

21. However, in a fast running river the mixing of cold and warm water may allow ice to form on the riverbed or within the stream.

it can deform internally. The mechanism is thought to be a collapsing of some of the hydrogen bonds in ice so that some molecules return to the liquid state, even if the temperature is below 0°C. These molecules then are supercooled and subject to refreezing once the pressure is relieved, a process sometimes referred to as pressure-induced ***regelation***. An often-cited example of the process is the slow movement downward of a weighted wire through a block of ice—the wire cuts through leaving no obvious sign of its passage. Related also to the rupturing of hydrogen bonds in ice's open crystal lattice is a process called ***translation*** wherein only a partial melting occurs, but it is enough to allow ice crystals to slide (translate) past one another, and thus for the ice to undergo plastic flow. Pressure alone probably does not explain all observed regelation and translation processes since some appear to be driven by temperature gradients.

The Universal System Happiness Rule governs these and all other things. Examples, some from matters previously discussed, include:

- An electron and a proton will come together to form a hydrogen atom because by doing so they will have less free energy than they had standing alone. Similarly, two hydrogen atoms will join to form the stable hydrogen molecule H_2 because that molecule has less free energy than two hydrogen atoms standing alone. The water molecule forms because it has less free energy than one oxygen atom and two hydrogen atoms standing alone. Similarly, the oxygen atom's outer shell has two sets of paired electrons and two unpaired ones because that arrangement gives the atom lower free energy than it would have if all those six electrons were paired.
- The 105° separation between the water molecule's projecting hydrogen atoms occurs because that configuration has less free energy than any other involving one oxygen atom and two hydrogen atoms. Likewise, the spacing between the oxygen and hydrogen atoms gives the molecule less free energy than any other spacing.
- Water molecules clump together by hydrogen bonding (they associate) because by doing so they have less free energy than when standing alone.
- And, somewhat in reiteration: Water turns to steam because, above the boiling temperature, water molecules in the gaseous state have less free energy than they would have if still liquid. Similarly, water freezes into ice whenever the total free energy of the ice-water system (including the energy associated with the interface) is lowered

by the freezing. If the freezing requires an increase in overall system energy the water will supercool even though the free energy of ice is less than the free energy of water at the temperature of the system. When the interface between ice and water has high curvature (small radius) the free energy associated with the interface is very high, so it takes a lot of energy to make the interface grow. Once the interface reaches the critical radius its further growth always reduces the overall free energy of the ice-water system.

- Dogs lie down to sleep because they have less free energy in that position than when standing up. That's why sleeping dogs are happy dogs, and it's best to let them lie.

Chapter Summary

When atoms join together to form molecules, two main bonding forces hold them together. One, called covalent bonding, depends on the powerful magnetic force that acts between two nearby but oppositely spinning electrons, each belonging to separate atoms. Another strong bonding force that causes atoms to join to form molecules is electrostatic in nature: the negative charges of one atom attract the positive charges of the other to bind the atoms together. Most molecules actually are held together by a combination of these two strong bonding forces, but when the hydrogen atom is involved yet another force can operate. Called the hydrogen bond, this relatively weak electrostatic attachment binds the hydrogen component of a molecule like water to certain other molecules or atoms that are small enough to allow the hydrogen nucleus to approach and electrostatically attach to one of their electron pairs. Oxygen is such an atom, so it is a likely partner in hydrogen bonding, and this fact has important consequences.

In part because of its ability to form hydrogen bonds, water has abnormally strong electrical character that makes it the universal solvent. Water's hydrogen bonding not only enhances its electrical nature, it causes water to have abnormally high viscosity, abnormally high surface tension, and proclivity to cling strongly to itself and to many other substances, especially those containing oxygen in their makeup: glass, dirt, and organic matter. These characteristics are crucial to the explanation of what happens when soil freezes.

Unlike almost all other substances—thanks to hydrogen bonding— water expands as it freezes. It also typically undergoes supercooling, the

phenomenon of remaining liquid below the melting temperature, 0°C. The explanation of how that comes about involves the important concept of free energy and the fact that systems are most stable when containing minimum free energy. Called here the Universal System Happiness Rule, this principle comes up again repeatedly in this book as we now move ahead to delve into the behavior of the ground when it freezes and thaws.