

Introduction

Water is abundant in all living things and, consequently, is in almost all foods, unless steps have been taken to remove it. It is essential for life, even though it contributes no calories to the diet. Water also greatly affects the texture of foods, as can be seen when comparing grapes and raisins (dried grapes), or fresh and wilted lettuce. It gives crisp texture or turgor to fruits and vegetables, and it also affects perception of the tenderness of meat. For some food products, such as potato chips, salt, or sugar, lack of water is an important aspect of their quality, and keeping water *out* of such foods is important to maintain quality.

Almost all food processing techniques involve the use of water or modification of water in some form: freezing, drying, emulsification (trapping water in droplets or trapping oil in a water phase to give salad dressings their characteristic mouth-feel), breadmaking, thickening of starch, and making pectin gels are a few examples. Further, because bacteria cannot grow without water, the water content has a significant effect on maintaining quality of the food. This explains why freezing, dehydration, or concentration of foods increases shelf life and inhibits bacterial growth.

Water is important as a solvent or dispersing medium, dissolving small molecules to form true solutions, and dispersing larger molecules to

form colloidal solutions. Acids and bases ionize in water; water is also necessary for many enzyme catalyzed and chemical reactions to occur, including hydrolysis of compounds such as sugars. It is also important as a heating and cooling medium and as a cleansing agent.

Since water has so many functions that are important to a food scientist, it is important to be familiar with some of its unique properties. When modifying the water content of a food, it is necessary to understand these functions in order to predict the changes that are likely to occur during processing of such foods.

Drinking water is available to the consumer in convenient bottled and aseptic containers in addition to the tap.

Chemistry of Water

The chemical formula for water is H_2O . Water contains strong **covalent bonds** that hold the two hydrogen atoms and one oxygen atom together. The oxygen can be regarded to be at the center of a tetrahedron, with a bond angle of 105° between the two hydrogen atoms in *liquid water* and a larger angle of $109^\circ 6'$ between the hydrogens in *ice* (Fig. 2.1).

The bonds between oxygen and each hydrogen atom are polar bonds, having a 40 % partial ionic character. This means that the outer-shell electrons are unequally shared between the

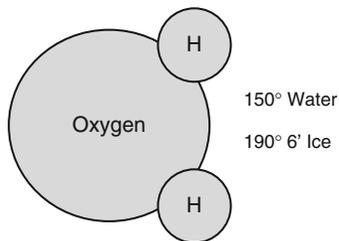


Fig. 2.1 Bond angle of water and ice

oxygen and hydrogen atoms, the oxygen atom attracting them more strongly than each hydrogen atom. As a result, each hydrogen atom is slightly positively charged and each oxygen atom is slightly negatively charged. Therefore they are able to form **hydrogen bonds**.

A hydrogen bond is a *weak* bond between polar compounds where a hydrogen atom of one molecule is attracted to an electronegative atom of another molecule (Fig. 2.2). It is a weak bond relative to other types of chemical bonds such as covalent or ionic bonds, but it is very important because it usually occurs in large numbers and, therefore, has a significant cumulative effect on the properties of the substance in which it is found. Water can form up to four hydrogen bonds (oxygen can hydrogen bond with two hydrogen atoms).

Water would be expected to be gas at room temperature if compared with similar compounds in terms of their positions in the periodic table, yet due to the many hydrogen bonds it contains, it is liquid. Hydrogen bonds between hydrogen and oxygen are common, not just between water molecules, although between many other types of molecules that are important in foods, such as sugars, starches, pectins, and proteins.

Due to its V-shape, each molecule of water can form up to four hydrogen bonds with its nearest neighbors. Each hydrogen atom can form one hydrogen bond, and the oxygen atom can form two, which results in a three-dimensional lattice in ice. The structure of ice—frozen water, is dynamic, and hydrogen bonds are continually breaking and reforming between different water molecules. Liquid water also contains hydrogen bonds and, therefore, has a variety of ordered structures that are continually changing as hydrogen bonds break

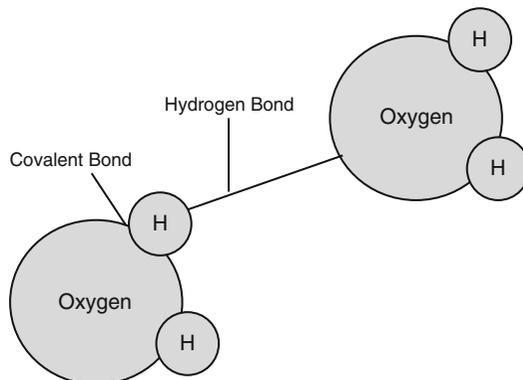


Fig. 2.2 Hydrogen and covalent bonds in water molecules

and re-form. In liquid water, it is estimated that about 80 % of water molecules are involved in hydrogen bonding at any one time at 212 °F (100 °C), whereas 90 % are involved in liquid water at 32 °F (0 °C).

For the reason that *liquid* water has a smaller bond angle than ice, the molecules can be packed together more tightly, and so the *coordination number* or, in other words, the average number of nearest neighbors is higher for water than for ice. The average distance between water molecules is also affected by temperature and increases with temperature as the molecules have more kinetic energy and can move around faster and further at higher temperatures. Both of these affect the density of water, although the coordination number has a much more dramatic effect. Ice is less dense than water because the molecules have a smaller coordination number and cannot be packed together as tightly as water. Therefore, ice floats.

As water *freezes*, its density decreases and its *volume increases* by about 9 %. This is very significant when freezing foods with high water content. Containers and equipment must be designed to accommodate the volume increase when the product freezes, for example, molds for popsicles must allow room for expansion. This volume increase also contributes to the damage to the structure of soft fruits on freezing. This is discussed in Chap. 7. As water is heated above 39 °F (4 °C), the increase in the average distance

between molecules causes a slight decrease in density.

Specific Heat and Latent Heat of Water

When ice is heated, the temperature increases in proportion to the amount of heat applied. The *specific heat* of water is the energy (in calories or in joules) required to raise the temperature of 1 g of water by 1 °C, and is the same whether heating water or ice. It is relatively high compared to other substances due to the hydrogen bonds. The specific heat of water is 1 cal/g/°C. This means that it takes 100 cal to raise the temperature of 1 g of water from 0 to 100 °C.

Once ice has reached 0 °C, energy needs to be put in to break the hydrogen bonds and enable ice to change to the liquid form. Until the ice has been converted to liquid, there is no further change in temperature until liquid water created.

The *latent heat of fusion* is the energy required to convert 1 g of *ice to water* at 0 °C and is 80 cal; that is, 1 g of ice at the freezing point absorbs approximately 80 cal as it changes to the liquid state.

The *latent heat of vaporization* is the energy required to convert 1 g of *water into vapor* at 100 °C and is 540 cal; that is, 1 g of water at the boiling point absorbs approximately 540 cal as it becomes steam.

Both the *specific heat* and *latent heat* for water are fairly high compared with most substances, and this is an important consideration when water is used as a medium of heat transfer. It takes considerable energy to heat water, and that energy is then available to be transferred to the food. Foods *heated* in water are slow to heat. Water also must take up considerable heat to evaporate. It takes heat from its surroundings, thus, it is a good *cooling agent*.

When ice is subjected to vacuum and then heated, it is converted into vapor *without* going

through the liquid phase. This phenomenon is known as *sublimation*, and is the basis for the food processing method known as *freeze drying*. Coffee is an example of a food product that is freeze-dried. The process is expensive and is only used for foods that can be sold at a high price, such as coffee. The coffee beans are frozen and then subjected to a high vacuum, after which radiant heat is applied until almost all of water is removed by sublimation. Freezer burn is also the result of sublimation.

Vapor Pressure and Boiling Point

Vapor Pressure

If a puddle of water is left on the ground for a day or two, it will dry up because the liquid evaporates. The water does not boil, yet individual water molecules gain enough energy to escape from the liquid as vapor. Over a period, an *open*, small pool of water will dry up in this way. If the liquid is in a *closed* container, at equilibrium, some molecules are always evaporating and vapor molecules are condensing, so there is no overall change in the system. The *vapor* (gaseous) molecules that have escaped from the *liquid* state exert a pressure on the surface of the liquid known as the *vapor pressure*.

When the vapor pressure is *high*, the liquid evaporates (is vaporized) easily and *many* molecules exist in the vapor state; the boiling point is low. Conversely, a *low* vapor pressure indicates that the liquid does not vaporize easily and that there are few molecules existing in the vapor state. The boiling point for these liquids is higher. The liquid boils when the vapor pressure reaches the external pressure.

The vapor pressure *increases* with increasing temperature. At higher temperatures, the molecules have more energy and it is easier for them to overcome the forces holding them within the liquid and to vaporize, and so there are more molecules in the vapor state.

The vapor pressure *decreases* with addition of solutes, such as salt or sugars. In effect, the

solutes dilute the water; therefore, there are less water molecules (in the same volume) available for vaporization and, thus, there will be fewer molecules in the vapor state, and the vapor pressure will be lower. Attraction to the solute also limits evaporation.

Boiling Point

Anything that lowers the vapor pressure (pressure by gas above the liquid) increases the boiling point. This is due to the fact that as the vapor pressure is lowered at a particular temperature, more energy must be put in; in other words, the temperature must be raised to increase the vapor pressure again. The external pressure does not change if salts or sugars are added, although it becomes harder for the molecules to vaporize and so the temperature at which the vapor pressure is the same as the external pressure (boiling point) will be higher. One mole of sucrose elevates the boiling point by 0.52 °C, and 1 mol of salt elevates the boiling point by 1.04 °C. Salt has double the effect of sucrose because it is ionized, and for every mole of salt, there is 1 mol of sodium ions and 1 mol of chloride ions. Salts and sugars depress the freezing point of water in a similar fashion.

If the external pressure is increased by heating in a pressure cooker or retort (commercial pressure cooker), the boiling point increases and a shorter time than normal is required to cook a particular food (the basis of preserving foods by canning). For example, food may be heated in cans in retorts, and the steam pressure is increased to give a boiling point in the range 239–250 °F (115–121 °C). Conversely, if the external pressure is decreased, for example, at high altitude, water boils at a lower temperature and so food may require a longer time to cook.

CULINARY ALERT! Even when water comes to a rapid boil in high altitude locations, its temperature is not as high as rapidly boiling water at sea level!

Water as a Dispersing Medium

Substances are either *dissolved*, *dispersed*, or *suspended* in water depending on their particle size and solubility. Each is described below. Water is the usual dispersion medium.

Solution

Water *dissolves* small molecules such as salts, sugars, or water-soluble vitamins to form a true **solution**, which may be either **ionic** or **molecular**. (A discussion of unsaturated, saturated, and supersaturated solutions appears in Chap. 14.)

An ionic solution is formed by dissolving substances that ionize in water, such as salts, acids, or bases. Taking sodium chloride as an example, the solid contains sodium (Na^+) and chloride (Cl^-) ions held together by ionic bonds. When placed in water, the water molecules reduce the attractive forces between the oppositely charged ions, the ionic bonds are broken, and the individual ions become surrounded by water molecules, or **hydrated**. Each ion is usually surrounded by six water molecules; the ions move independently of each other.

Polar molecules, such as sugars, which are associated by hydrogen bonding, dissolve to form **molecular solutions**. When a sugar crystal is dissolved, hydrogen-bond interchange takes place and the hydrogen bonds between the polar hydroxyl groups on the sugar molecules are broken and replaced by hydrogen bonds between water and the sugar molecules. Thus, the sugar crystal is gradually hydrated; each sugar molecule being surrounded by water molecules.

Water molecules bind to polar groups on the sugar molecules by hydrogen bonds. The sugar molecules are removed from the sugar crystal and hydrated as water molecules surround them and bind to them by hydrogen bonds.

When a hydrogen-bond interchange is involved, solubility increases with increasing temperature. Heating disrupts hydrogen bonds and reduces

water–water and sucrose–sucrose attraction, thus facilitating formation of hydrogen bonds between water and sucrose, and hydration of sucrose molecules. Therefore, sucrose is much more soluble in hot water than in cold water. Solutes increase the boiling point of water, and the dramatic increase in sucrose solubility with temperature, particularly at temperatures above 100 °C (the boiling point of pure water), makes it possible to determine the sucrose concentration by measuring the boiling point of sucrose solution (Chap. 13). This is important when making candies or pectin jellies.

Colloidal Dispersion

Molecules that are *too big* to form true solutions may be dispersed in water. Those with a particle size range 1–100 nm are dispersed to form a **colloidal dispersion** or *sol*. Examples of such molecules include cellulose, *cooked* starch, pectic substances, gums, and some food proteins. Colloidal dispersions are often unstable; thus, food scientists must take care to stabilize them where necessary if they occur in food products. They are particularly unstable to factors such as heating, freezing, or pH change. Changing the conditions in a stable dispersion can cause precipitation or gelation; this is desirable in some cases, for example, when making pectin jellies.

(The reader is referred to Chap. 4 for a discussion of sols and gels; *sol* is a colloid that pours—a two-phase system with a solid dispersed phase in a liquid continuous phase, for example, a hot sauce. A *gel* is also a two-phase system, containing an elastic solid with a liquid dispersed phase in a solid continuous phase.)

Colloid science is important to food scientists as many convenient or packaged foods have colloidal dimensions, and their stability and sensitivity to certain types of reactions can only be understood with knowledge of colloid science.

Suspension

Particles that are *larger than 100 nm* are too large to form a colloidal dispersion. These form a **suspension** when mixed with water. The particles in

a suspension separate out over a period, whereas no such separation is observed with colloidal dispersions. An example of a suspension would be *uncooked* starch grains in water. It may be temporarily suspended and then easily settle out, no longer “suspended,” but rather, falling to the bottom of the container/pan.

CULINARY ALERT! Starches remain suspended throughout the liquid by stirring. If left undisturbed, they settle downward, and a sediment is observed at the bottom of the container. Starches do not “dissolve.”

Free, Bound, and Entrapped Water

Water is abundant in all living things and, consequently, in almost all foods, unless steps have been taken to remove it. Most natural foods contain water up to 70 % of their weight or greater unless they are dehydrated, and fruits and vegetables contain water up to 95 % or greater. Water that can be extracted easily from foods by squeezing or cutting or pressing is known as **free water**, whereas water that cannot be extracted easily is termed as **bound water**.

Bound water is usually defined in terms of the ways it is measured; different methods of measurement give different values for bound water in a particular food. Many food constituents can bind or hold onto water molecules, such that they cannot be easily removed and they do not behave like liquid water. Several characteristics of bound water include the following:

- It is not free to act as a solvent for salts and sugars.
- It can be frozen only at very low temperatures (below freezing point of water).
- It exhibits essentially no vapor pressure.
- Its density is greater than that of free water.

Bound water has more structural bonding than liquid or free water, thus it is unable to act as a

solvent. As the vapor pressure is negligible, the molecules cannot escape as vapor; and the molecules in bound water are more closely packed than in the liquid state, so the density is greater. An example of bound water is the water present in cacti or pine tree needles—the water cannot be squeezed or pressed out; extreme desert heat or a winter freeze does not negatively affect bound water and the vegetation remains alive. Even upon dehydration, food contains bound water.

Water molecules bind to polar groups or ionic sites on molecules such as starches, pectins, and proteins. Water closest to these molecules is held most firmly, and the subsequent water layers are held less firmly and are less ordered, until finally the structure of free water prevails. A more detailed discussion of bound water is given in books such as Fennema's *Food Chemistry* (Reid and Fennema 2007).

Water may also be **entrapped** in foods such as pectin gels, fruits, and vegetables. Entrapped water is immobilized in capillaries or cells, yet if released during cutting or damage, it flows freely. Entrapped water has properties of free water and no properties of bound water.

CULINARY ALERT! Freshness of any produce is evaluated in part by the presence of water. Food items appear wilted when free water is increasingly lost through dehydration.

Water Activity (A_w)

Water activity, or A_w , is a ratio of the vapor pressure of water in a solution (P_s) to the vapor pressure of pure water at a given temperature (P_w):

$$A_w = P_s/P_w$$

A_w must be high as living tissues require sufficient level of water to maintain turgor. However, microorganisms such as bacteria, mold, and yeast multiply at a high A_w . Because their growth must be controlled, preservation techniques against spoilage due to these microorganisms take into account the water

activity of the food. Less bacterial growth occurs if the water level is lowered to less than 0.85 (FDA Model Food Code). Microbial growth (especially molds) can still occur at $A_w < 0.8$. Of course, there are other factors in addition to the water that must be present for bacterial growth to occur (food, optimum pH, etc.).

Jams, jellies, and preserves are prepared using high concentrations of sugar and brines, which contain high concentrations of salt that are used to preserve hams. Sugar and salt are both effective preservatives, as they decrease A_w . Salt decreases A_w even more effectively than sugar due to its chemical structure that ionizes and attracts water.

Role of Water in Food Preservation and Shelf Life of Food

Drying and *freezing* are common food preservation techniques. Foods are dehydrated or frozen to reduce the available water and extend shelf life.

The control of water level in foods is an important aspect of food quality as water content affects the shelf life and bacterial quality of food. For example, foods may be more desirable either crispy or dry. Freezing and drying are common food preservation processes that are used to extend the shelf life of foods because they render water unavailable for pathogenic or spoilage bacteria. If the water in foods is frozen quickly, there is less damage to the food at the cellular level. Preservatives may be added to a formulation to prevent mold or yeast growth. Humectants, which have an affinity for water, are added to retain moisture in foods.

Water content influences a food's structure, appearance taste and even susceptibility to degradation. Depending upon the foodstuff, water may function as a free-flowing liquid or be a component of a larger matrix, visibly (pudding) or invisibly (granola bar).

Gums and starches can act together providing a moisture-management system, and can "help prevent staling, which results from the retrogradation of starch in baked goods. Retrogradation releases moisture over time, leading to staling. . . Because gums do not undergo the retrogradation process,

they can slow the staling process by holding onto moisture.” (Berry 2012)

with some nutritional benefits (fruit and vegetable juices, whole milk, alcohol, and sports drinks), and calorically sweetened, nutrient-poor beverages. (Popkin et al. 2006)

Water Hardness and Treatments

The hardness of water is measured in parts per million or in “grains,” with one grain equivalent to 0.064 g of calcium carbonate. *Soft water* contains 1–4 grains per gallon some organic matter, and has no mineral salts. *Hard water* contains 11–20 grains per gallon. Water may exhibit *temporary* hardness due to iron or calcium and magnesium bicarbonate ions $[(\text{Ca}(\text{HCO}_3)_2 \text{ and } \text{Mg}(\text{HCO}_3)_2]$. The water may be softened by boiling (soluble bicarbonates precipitate when boiled and leave deposits or scales) and insoluble carbonates may be removed from the water.

Permanently hard water *cannot* be softened by boiling as it contains either calcium or magnesium sulfates (CaSO_4 or MgSO_4) as well as other salts that are not precipitated by boiling. Permanent hard water may only be softened by the use of chemical softeners. Hard water exhibits less cleaning effectiveness than soft water due to the formation of insoluble calcium and magnesium salts with soap, which could be prevented by the use of detergents.

Water has a pH of 7 or neutral; tap water displays a variance on either side of neutral. It may be slightly alkaline or slightly acidic depending on the source and so forth. Hard water has a pH of up to 8.5. Chlorinated water is that which has had chlorine added to kill or inhibit the growth of microorganisms. Manufacturing or processing plants may require chemically pure water to prevent turbidity, off-color, and off-flavor. Tap water may not be sufficiently pure for use in food products.

Beverage Consumption Ranking

Drinking water was ranked as the preferred beverage to fulfill daily water needs and was followed in decreasing value by tea and coffee, low-fat (1.5 % or 1 %) and skim (nonfat) milk and soy beverages, noncalorically sweetened beverages, beverages

Conclusion

Water is essential for life and makes up the major part of living tissue. The nature of hydrogen bonds allows water to bond with other water molecules as well as with sugar, starches, pectins, and proteins. Water absorbs energy as it changes from frozen to liquid to vapor state, and is an effective cooling medium. If water is easily extracted from foods by squeezing, or pressing, it is known as free water. Inversely, water that is not easily removed from foods and that is not free to act as a solvent is known as bound water; water in foods imparts freshness. A measure of water activity is the ratio of the vapor pressure of water in a solution to the vapor pressure of pure water. If water is unavailable for pathogenic or spoilage-causing bacteria to multiply, food is better preserved and has a longer shelf life.

Notes

CULINARY ALERT!

Glossary

Bound water Water that cannot be extracted easily; it is bound to polar and ionic groups in the food.

Colloidal dispersion Molecules, larger than those in solution, dispersed in the surrounding medium.

Covalent bonds Strong bonds that hold the two hydrogen atoms and one oxygen atom together in a water molecule.

Free water Water that can be extracted easily from foods by squeezing, cutting, or pressing.

Freeze drying A food processing method that converts ice to vapor without going through the liquid phase (sublimation).

Gel Elastic solid; a two-phase system that contains a solid continuous phase and a liquid dispersed phase.

Hard water Contains 11–20 grains per gallon. Hardness is due to calcium and magnesium bicarbonates or sulfates, which results in less effective cleaning.

Hydrogen bonds Weak bonds between polar compounds where a hydrogen atom of one molecule is attracted to an electronegative atom of another molecule.

Latent heat of fusion The energy required to convert 1 g of ice to water at 0 °C—requires 80 cal.

Latent heat of vaporization The energy required to convert 1 g of water to vapor at 100 °C—requires 540 cal.

Sol A two-phase system with a solid dispersed in a liquid continuous phase; pourable.

Soft water Contains one to four grains per gallon, no mineral salts, some organic matter.

Solution (Ionic or molecular) Small molecules dissolved in water.

Sublimation When ice is subjected to vacuum and then heated, it gets converted to vapor without going through the liquid phase; basis for freeze drying; occurs in freezer burn.

Specific heat The energy required to raise the temperature of 1 g of water by 1 °C whether heating water or ice; requires 1 cal/g/°C.

Suspension Molecules larger than those in a solution or dispersion that are mixed with the surrounding medium. A *temporary* suspension settles upon standing.

Vapor pressure The pressure vapor molecules exert on the liquid.

Water activity (A_w) The ratio of the vapor pressure of water in a solution to the vapor pressure of pure water.

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