Section 15.2

Water Purification

Fresh water is an essential ingredient of modern life. Thought it's often available as the result of natural processes, there are times when it must be extracted from impure water, typically salt water. In some countries where rain water is scarce, desalinated sea water is the main source of drinking water. Any extraction process that purifies water must separate water molecules from contaminating liquids, solids, or gases. This section examines some of the techniques that make this molecular separation possible.

Questions To Think About: *Where does naturally occurring fresh water come from? Why does a can of soda go flat instantly if you open it after freezing it? How did minerals form in the earth's crust? Is sea ice salty? Why does swimming in salt water dry out your skin? Is distilled water always purer than non-distilled water?*

Experiments To Think About: *You can purify water in your own kitchen. If you boil salt water in a pot, you'll create steam and will see mist forming above the water as that steam condenses into water droplets in the air. If you place a cold surface in the steam, the steam will condense on that surface. The condensed steam is nearly pure water—distilled water. While the water in the pot contained salt, the distilled water does not. However, before you taste the distilled water, make sure that the water in the pot contained only non-toxic additives. Distillation isn't perfect at removing contaminants and it can even concentrate them in some situations. In a few minutes, you'll understand why.*

Distilling Water from Salt Water

One way to purify water is by distillation. **Distillation** is a general technique for separating various chemicals from one another. The chemicals are heated to form a vapor and that vapor is condensed to form a new mixture of chemicals. Because the various chemicals have different tendencies to form vapors at a particular temperature, the newly formed mixture has a different balance of the chemicals from the original mixture. In some cases, the condensed liquid contains primarily a single chemical—all of the other chemicals are left behind in the original liquid.

To understand how distillation can purify water, let's look at the phases of water. At any temperature above absolute zero, there's a possibility of finding gaseous water molecules above the surface of ice or water. These water molecules have acquired enough thermal energy to break free of the solid or liquid and become a gas.

If you place some water in an enclosed container, water molecules will evaporate until there are enough of them in the gas phase that they return to the liquid's surface as often as they leave it. At that point the two phases, liquid and gas, are in **phase equilibrium**. Although molecules constantly shift back and forth between the two phases, neither phase grows at the expense of the other. Overall, there's no net movement of molecules from one phase to the other.

At this phase equilibrium, the relative humidity is 100%—the water vapor has reached its saturated vapor pressure. But we have forgotten to pay attention to temperature. Since water's vapor pressure depends on temperature, the present balance of gas and liquid in the container is ideal only at its current temperature. If you warm up the container, more water molecules will enter the gas phase and the amount of liquid water will decrease. If you cool down the container, more water molecules will enter the liquid phase and the amount of gaseous water will decrease. This connection between temperature and vapor pressure is the central principle behind distillation.

What happens if there is air inside the container, along with the water and water vapor? Surprisingly, the air doesn't matter. The density of water molecules in the gas phase is the same, whether the air is there or not. This interesting observation makes it possible to perform distillation with or without air around, although air's presence affects the total pressure on the water and thus its boiling temperature. The desalination schemes we'll examine shortly operate most effectively at less than atmospheric pressure, so many distillation plants remove air from their equipment in order to reduce the gas pressure.

How much water vapor is there in the container? Water's vapor pressure at 20 °C, typical room temperature, is about 2,300 Pa or about 2% of atmospheric pressure. That means that when the humidity is 100% at room temperature, about 2% of the molecules in the air are water molecules. At 0 °C, the melting temperature of ice, water's vapor pressure is only about 600 Pa or about 0.6% of atmospheric pressure. That means that there is still quite a bit of moisture in the air even at freezing. And at 100 °C, water's vapor pressure is about 101,300 Pa or 100% of atmospheric pressure at sea level. That's why water boils at 100 °C at sea level.

The simultaneous presence of both water and water vapor in the container means that there is a **phase separation**. The two phases, liquid and gas, appear in separate regions of the container. The denser water phase sinks to the bottom of the container while the less dense water vapor phase floats to the top. These two phases can exist in phase equilibrium over a wide range of temperatures. There is actually one special temperature and pressure, water's **triple point**, at which water, water vapor, and ice can all exist together in a single container and in phase equilibrium with one another. This triple point occurs at about 0.01 °C.

Before going further into water distillation, let's consider the behaviors of a few other chemicals to see how they differ from water. After all, if they behaved exactly as water does, distillation wouldn't separate them from water.

❒ Although gaseous salt molecules are rarely found in air near room temperature, breaking waves fill the air with tiny salt water droplets. These droplets evaporate to leave minute salt grains, which are carried aloft by drag forces and account for the salty air near the ocean.

Table salt, sodium chloride, is a solid at room temperature. It doesn't even melt until 801 °C and its boiling temperature is about 1450 °C at atmospheric pressure. Salt's vapor pressure is almost negligible at any temperature below about 500 °C. So if you put a block of salt in a container at less than 500 °C, it will reach a phase equilibrium with almost all the salt molecules in the solid phase and only a tiny number in the gas phase. (For some interesting cases of materials in different phases, see ❒s.)

The situation is quite different for ethyl alcohol (grain alcohol). Ethyl alcohol melts at –112 °C and boils at only 78 °C near sea level. Although ethyl alcohol molecules are larger than water molecules, they don't form many hydrogen bonds and are relatively easy to separate from one another. As a result, ethyl alcohol is more likely than water to form a gas.

Distillation uses these differences in vapor pressures to separate chemicals. When you heat a mixture of chemicals to a particular temperature, the whole mixture tries to establish a phase equilibrium. The chemicals that tend to be gaseous at that temperature accumulate in the gaseous phase of the system. The chemicals that tend to be a liquid at that temperature accumulate in the liquid phase. When the phase equilibrium is finally reached after a minute or two, the balance of chemicals in the gaseous phase may be very different from that in the liquid phase.

❒ Nitrogen, oxygen, and argon are all gases at room temperature, regardless of pressure. Compressing them simply pushes their molecules closer together, without creating a separate liquid phase. They must be cooled to very low temperatures before they will liquefy.

The distillation process occurs when you insert a colder surface into the vapor. Molecules condense as a liquid on that surface and you can use a pump to remove them from the system. As you remove molecules from the gaseous phase,

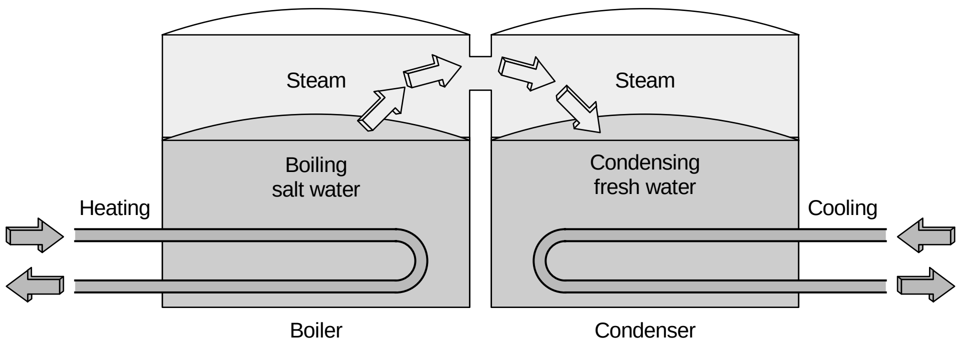

Fig. 15.2.1 - Fresh water can be obtained by distilling salt water. In this process, salt water in boiled in one region to form a vapor that is mostly pure steam. This steam is then condensed in a second, cooler region and becomes fresh water.

more molecules will shift from the liquid phase to the gaseous phase to maintain the phase equilibrium.

The condensed liquid contains molecules that evaporated most easily from the original liquid phase and that condensed most easily on the colder surface. These molecules are the ones that experienced the largest changes in vapor pressure between the two temperatures. They tended to become gaseous at the temperature of the liquid phase and liquid at the temperature of the colder surface.

We can now look at how to desalinating salt water by distillation. A simple distillation system appears in Fig. 15.2.1. Two separate liquid containers, a boiler containing the original salt water and a condenser containing fresh water, share a single region of vapor. Since salt molecules rarely enter the gas phase near room temperature, the vapor is virtually pure steam. The salt water boiler is kept hot so that its water molecules tend to evaporate into a gas. The fresh water condenser is kept cold so that its water molecules tend to condense into a liquid. Since the two regions share the same vapor, water molecules tend to move from the salt water to the fresh water.

With enough patience, only a small temperature difference is needed to separate fresh water from salt water. This temperature difference just has to be large enough to make sure that, on the average, water molecules leave the salt water as gas and arrive at the fresh water as liquid. Nature is very patient and it uses small temperature differences to produce fresh water. Rain, dew, and frost are all created by natural distillation. Salt water evaporates in warmer weather and the resulting water vapor condenses in colder weather.

It might seem as if even the tiniest temperature difference can perform distillation, but that’s not true. When you mix salt with water, you create disorder and entropy. Separating salt from water decreases entropy and the second law of thermodynamics comes into play. If you’re going to separate the two chemicals and reduce their entropy, you must create extra entropy elsewhere. In distillation, that extra entropy comes from letting heat flow from the hotter region to the colder region. The temperature difference between the two regions must be large enough so that the total entropy doesn’t decrease.

In real water distillation systems, the temperature difference is usually quite large. A large temperature difference doesn’t make purer water but it does speed up the process. Most systems boil the salt water, a step which dramatically increases the evaporation rate. They also condense the water vapor rapidly by bringing it into contact with a very cold surface. The water molecules move swiftly from the salt water side to the fresh water side so the facility produces fresh water much more rapidly than nature itself. In exchange, the facility consumes far more ordered energy per liter of fresh water than nature does.

Actually, large distillation-based desalination plants are a little more sophisticated than this. For the distillation to proceed quickly, they do have to boil the water. But they don’t boil it at atmospheric pressure—they pump the air out of the distilling chambers so that water boils at a much lower temperature. Everything proceeds as above, except they don't have to heat the salt water as much. While the facility can't produce quite as much fresh water per hour because the density of water molecules in the vapor is lower, a little patience saves a lot of energy.

However, distillation still uses more energy than anyone would like. The problem lies in water's huge latent heat of vaporization. Water vapor carries away lots of heat from the salt water as it evaporates and it gives that heat to the fresh water when it condenses. The salt water gets colder and the fresh water gets hotter, reducing the temperature difference and slowing the distillation process. To keep everything working quickly, the distillation plant must continuously add heat to the salt water and remove it from the fresh water. It's this heating and cooling that makes distillation so expensive.

The transfer of heat from the boiler to the condenser, due only to water's latent heat of vaporization, is unfortunate. The second law of thermodynamics doesn't require such a transfer in order to separate water from salt. It's just a side-effect of using the liquid / gas phase transition to separate two chemicals from one another. Fortunately there are tricks that a desalination plant can use to reduce this heat transfer.

The best trick is to reuse the heat. Most distillation plants use the same heat over and over again, operating several separate distillation systems with it. Because distillation units that operate at different pressures also operate at different temperatures, the waste heat leaving the condenser of a higher pressure distillation unit can be used to heat the boiler of a lower pressure distillation unit. Since water's boiling temperature depends on pressure, the two distillation units function properly at very different temperatures.

An example of such heat reuse appears in Fig. 15.2.2. The heat first distills water in a high pressure distillation unit and then in a low pressure distillation unit. In the high pressure unit, the heat travels from the boiler to the condenser in the steam and then leaves the condenser in its cooling water. This cooling water leaving the high pressure distillation unit is actually hot enough to be the heating

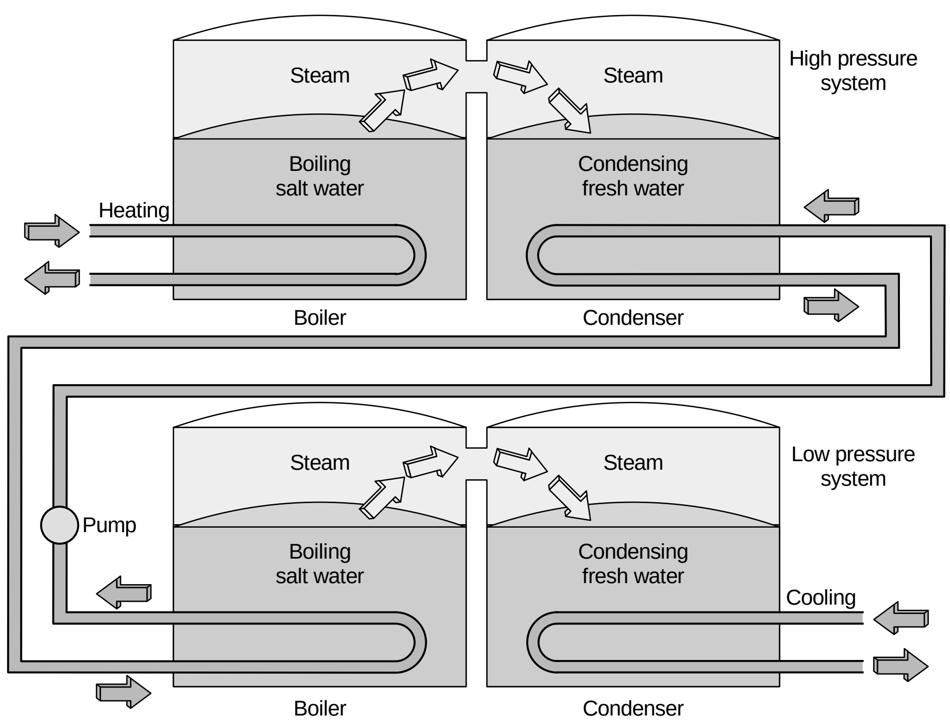

Fig. 15.2.2 - Distilling water at atmospheric pressure requires a large amount of heat. This heat is used to raise the temperature of the water to 100° C and then to separated the molecules into a vapor. When the steam condenses in the condenser, this heat is released and becomes waste heat in the cooling water. However, a more sophisticated distillation plant lowers the pressure in a second distillation unit and reuses heat from the first unit to operate the second unit.

water for the low pressure distillation unit. There, the heat travels from the boiler to the condenser and finally leaves the plant in a second cooling water system. This waste heat is dispersed into the great outdoors.

A desalination plant may reuse the same heat five or more times before sending it out into the ocean or the atmosphere. The heat may originate as solar energy or it may come from burning fuel or from a nuclear reactor. In some cases, it comes from waste heat released by an electric power plant.

This same process of distillation is used to create liquor. Natural fermentation can't produce liquids that are more than about 20% ethyl or grain alcohol because too much alcohol kills the yeast that causes the fermentation. However, the alcohol and water mixture can be distilled to create much more concentrated alcohol and water mixtures. Near room temperature, alcohol has a much higher vapor pressure than water and it boils at a lower temperature. When alcohol and water are heated together at atmospheric pressure until the mixture boils, the vapor above the mixture will be mostly alcohol. If this vapor is condensed, the new liquid is as much as 90% alcohol.

CHECK YOUR UNDERSTANDING #1: Keep It Clean
Household appliances such as steam irons and humidifiers work best with distilled water. What is the difference between normal tap water and distilled water?

Freezing Salt Water to Produce Fresh Water

Boiling isn't the only change of phase that's used to purify water. The ice that forms when sea water freezes is essentially pure fresh water, a phenomenon that Eskimos have use to obtain potable water for thousands of years. This purification effect results from a balance between energy and disorder.

Physical systems tend to minimize their potential energies. For example, a ball tends to roll down hill to minimize its gravitational potential energy. Similarly, a mixture of ice and water tends to minimize its potential energy by excluding contaminants from the ice and leaving them in the water.

Water is disordered already and having solids, liquids, or gases dissolved in it isn't a problem. Ice, on the other hand, is a highly ordered crystal that is seriously disrupted by the presence of dissolved chemicals. The water molecules in an ice crystal pack more neatly and obtain a lower overall potential energy when the ice contains no contaminants. So a contaminated mixture of water and ice reaches its lowest overall potential energy when all of the contaminants stay in the water and the ice contains only water molecules.

As long as the water freezes slowly, the ice crystal it forms will have very little contamination in it and the unfrozen water will end up with a relatively high concentration of contaminants (Fig. 15.2.3). By separating pure from impure water, this process reduces the water's disorder so that, to avoid violating the second law of thermodynamics, additional disorder must be created somewhere else. This additional disorder is created in the low temperature region that freezes the salt water. As the salt water freezes, which it does well below water's ordinary freezing temperature, the salt water releases heat to the low temperature region and introduces considerable disorder into that region. This rise in the low temperature region's entropy more than makes up for any decrease in entropy in the water as it freezes.

However, disorder appears whenever it can and so the ice crystals that form always contain imperfections. Even if there are no impurities around, the crystals will probably have minor defects. These defects include flaws in the stacking of molecules or empty spots in the otherwise orderly arrays of mole-

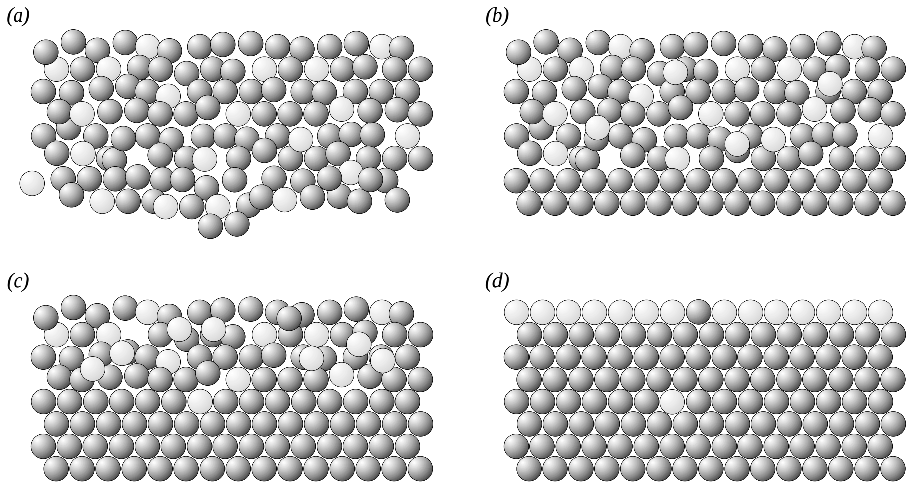

Fig. 15.2.3 - While water can incorporate many dissolved ions and molecules into its disordered structure (*a*), ice is too ordered to include such contaminants. As water freezes from the bottom up (*b*–*d*), the interface between solid ice and liquid water moves slowly upward through the container. The ice incorporates more and more of the water molecules (dark) and rejects almost all of the contaminant molecules (light). Eventually the contaminant molecules form solid, liquid, or gaseous regions of their own (*d*).

cules. Truly perfect crystals are extremely hard or even impossible to grow.

When you freeze a bucket of salt water, the ice that forms first contains very little salt. The salt is in the remaining salt water, which becomes more and more concentrated as additional water molecules are bound up in the ice. By the time there is only a small amount of water remaining, that salt water has a very high concentration of salt and salt crystals begin to form. These salt crystals can easily become trapped in the ice so care must be taken to remove the ice from the concentrated salt solution before salt crystals begin to form. In sea ice, the salt is carried away by the sea water so only pure ice is formed.

When you freeze ice cubes, the outer surface freezes first and the impurities become concentrated near the middle of the cube. One of the main impurities is dissolved air, which eventually comes out of solution and forms tiny air bubbles in the ice. These air bubbles appear as a white cloudy region inside the ice cube. One way to reduce this clouding is to boil the water before you freeze it. Boiling the water drives most of the air out of solution so that no air bubbles form in the resulting ice.

Freezing salt water to form pure ice works best in cold climates where low temperatures are available directly. Active refrigeration can also freeze salt water to obtain fresh water, but it's expensive. Because of water's latent heat of melting, you must remove a large amount of heat from salt water to freeze it. Although refrigerated water desalination plants have been built, they have proven to be less economical than distillation plants. (For another case of purification through freezing and melting, see ❐.)

CHECK YOUR UNDERSTANDING #2: The Flavor's All Gone!

Frozen juice is a popular dessert in hot weather and exists in countless variations at the grocery store or snack bar. If you suck on one of these treats, the sweet flavor comes out first, leaving clear ice behind. How do you manage to remove the flavor from the bar?

❐ Some of the purest materials on earth are made by zone refining. In this technique, a rod of semi-pure material passes slowly through a heater that creates a moving zone of molten material. As each portion of the rod melts and then solidifies, its impurities are carried away in the molten zone. The final rod is remarkably pure, with as few as one atom in a billion being an impurity.

Osmosis

Another way to desalinate water is by **reverse osmosis**, a process resembling filtration except that it takes place at the molecular scale. In effect, salt water is converted to fresh water by filtering the impurities out of it with an incredibly fine filter. However, because it operates at such a tiny size scale, reverse osmosis encounters some peculiar pressure effects that you don't see with larger filters. In

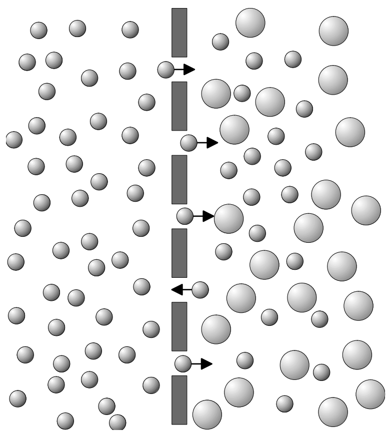

Fig. 15.2.4 - Osmosis occurs when two different fluids sit on opposite sides of a semipermeable membrane. Only the smaller, mobile molecules can flow through the pores in the membrane. On the average, these mobile molecules flow toward the side that has the largest concentration of immobile molecules.

order to describe these effects in reverse osmosis, let's first examine osmosis itself.

Osmosis occurs whenever two different fluids are placed on opposite sides of a semipermeable membrane. A **semipermeable membrane** is a surface that only allows certain molecules to pass through it. The molecules in the fluid jiggle about rapidly because they have thermal energy. They bounce and push off one another and off the membrane. Those molecules that can pass through the membrane often do, flowing back and forth until the two fluids reach a phase equilibrium. There is then no net flow of the mobile molecules through the membrane and the two fluids stop changing with time.

If the two fluids have the same pressure, phase equilibrium occurs when they have equal **concentrations** of the immobile molecules—equal numbers of those molecules per volume. At that point, it's just as likely for a mobile molecule to cross the membrane from one side as from the other. If you put a relatively concentrated solution of the immobile molecules on one side of the semipermeable membrane, it will have relatively few mobile molecules in it so mobile molecules will tend to flow through the membrane and into that concentrated solution (Fig. 15.2.4). This flow will dilute the concentrated solution and make it less concentrated. The fluid that loses its mobile molecules becomes more concentrated.

Some semipermeable membranes allow water to pass through them but don't pass salt. In solution, the salt exists as separated ions, wrapped up in water solvation shells. Although the ions themselves are very small, the solvation shells are huge and can't pass through the membranes. Since the salt ions are immobile, osmosis occurs between salt water and fresh water. If you put salt and fresh water on opposite sides of a semipermeable membrane, water molecules from the fresh water flow through the membrane to dilute the salt water. The total mass of fluid on the fresh water side decreases as water molecules flow over to the salt water side. Water molecules will continue to flow until the concentrations of immobile molecules on each side of the membrane are equal.

The only way to stop osmosis from diluting concentrated salt water is to increase the pressure of the salt water. Increasing that pressure tends to drive water molecules back out of the salt water and through the semipermeable membrane. The two fluids will still reach a phase equilibrium, but the salt water will retain a higher concentration of immobile molecules than the fresh water. Maintaining a large difference in concentrations between the two fluids require a huge pressure difference of many tens or hundreds of atmospheres.

Osmosis shows up in an enormous number of biological systems because most biological membranes are semipermeable. The mobile molecules, usually water, flow through these membranes and try to equalize the concentrations of immobile molecules in the two fluids. For example, your skin tends to lose moisture when it comes into contact with a concentrated solution of salt or other chemicals. Water molecules flow out of your skin as they act to dilute the concentrated solution. At the other extreme, your skin tends to absorb moisture from fresh water. Your skin cells contain immobile molecules and the fresh water enters them in order to dilute their contents.

Water flow of this sort, into or out of cells, is a very important issue for fresh and salt water animals, particularly microorganisms. These microorganisms must control osmosis or else suffer severe consequences. One way in which they handle osmosis is to maintain concentrations of immobile molecules inside their cells that are similar to those in the water around them. To do this, they must adapt specifically for salt or fresh water. Salt water can extract the moisture out of a fresh water microorganism while fresh water can swell and explode a salt water microorganism.

Plants use osmosis to attract water into their root hairs. The root hairs contain a relatively concentrated solution of immobile molecules and ground water flows into the root hairs to dilute the concentrated solution. In fact, water flows into the root hairs so aggressively that it raises the pressure inside the root hairs to many times atmospheric pressure. This high **osmotic pressure** is partly responsible for pushing water up toward the tops of trees.

CHECK YOUR UNDERSTANDING #3: Where Did All the Water Go?
Salt and sugar have been used for centuries to preserve foods. Why do concentrated salt or sugar solutions kill most spoilage bacteria?

Reverse Osmosis

We noted that you can use pressure to stop the flow of water molecules into a concentrated salt solution. Osmosis will only equalize the concentrations of immobile molecules when the pressures are equal on both sides of the membrane. If you exert extra pressure on the salt-water side, it will remain more concentrated than the fresh-water side. If the pressure on the salt-water side becomes high enough, it can actually make osmosis run backwards. Water molecules will flow from the salt-water side to the fresh-water side!

This reverse osmosis can be used to extract fresh water from salt water but it requires a lot of pressure. A typical reverse osmosis cell operates at about 1000 times atmospheric pressure. The semipermeable membrane must be able to withstand this imbalance of pressure between the low-pressure fresh-water side and the high-pressure salt-water side. Osmosis is also very slow, so that a desalination plant must use membranes that have very large surface areas.

To obtain such large surface areas, desalination is done by making a stack of several different materials and then rolling the stack into a long cylinder. The stack consists of a layer that carries in the salt water, a semipermeable membrane, and a layer that carries out the fresh water. The roll is arranged so that the membrane is well supported and doesn't explode when exposed to the high-pressure salt water.

Salt water flows into this rolled sandwich and fresh water flows out. Actually, the salt water also flows out of the sandwich through a separate tube. If the desalination plant tried to squeeze too much fresh water out of the same salt water, that salt water would become very concentrated. This increase in concentration would make further reverse osmosis even more difficult. To ease the extraction, only a small fraction of fresh water is extracted from any volume of salt water. The slightly concentrated salt water is then returned to the ocean and is replaced by new salt water.

Reverse osmosis is fairly energy efficient because it doesn't involve any change of phase. Thus there is no latent heat to provide or absorb. The only energy needed is that required to pump the salt water through the system at very high pressure. However, this energy is substantial and it comes in the form of mechanical work. Since heat is much easier to obtain than work, multi-stage distillation plants are still very competitive with reverse osmosis plants as ways to produce large quantities of fresh water from salt water.

CHECK YOUR UNDERSTANDING #4: Pushing Them Apart
Why does it take any energy at all to separate salt and water by reverse osmosis?