Lecture 9: Properties of (Sea)water

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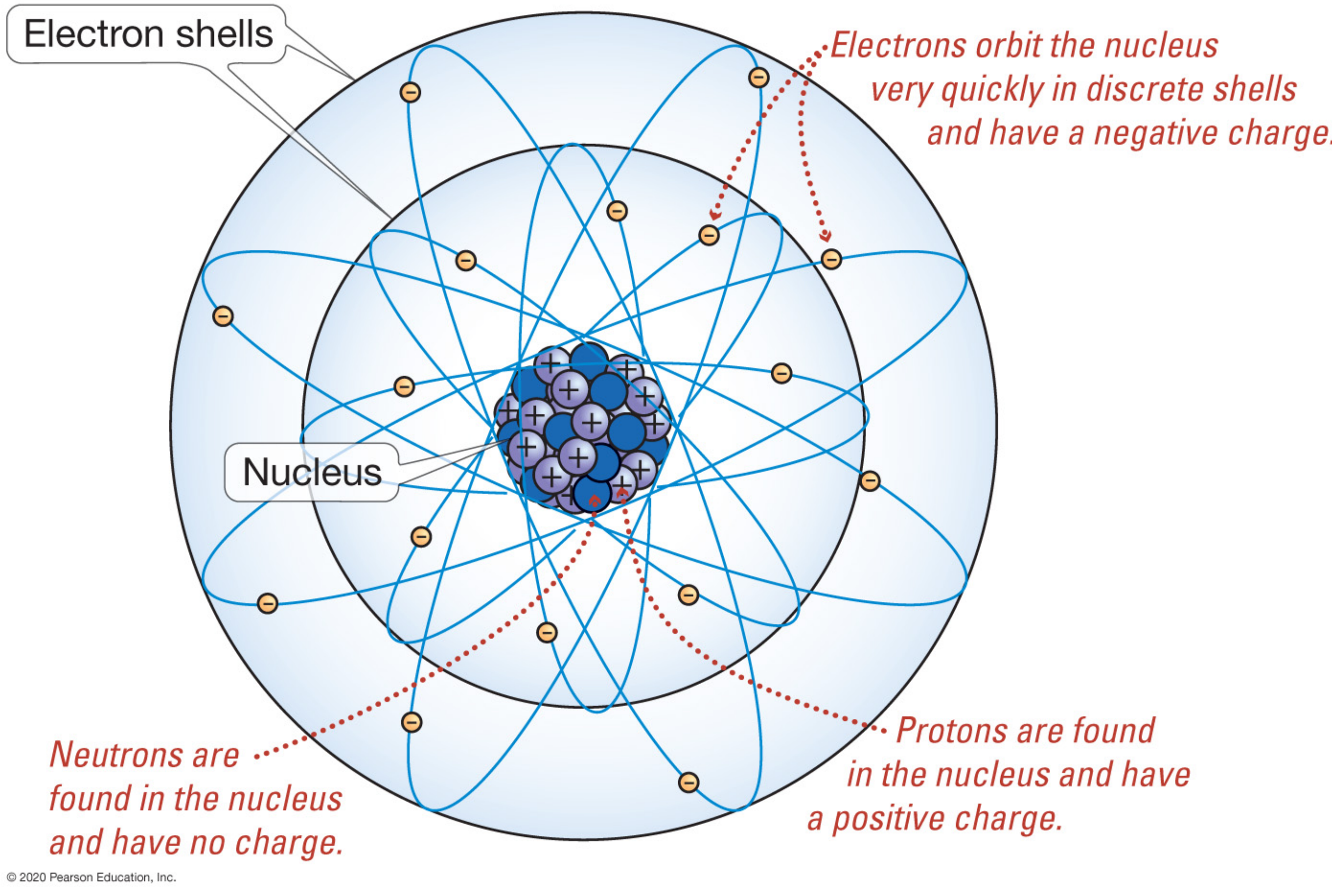
We live on a water planet.

The water on Earth is one of the fundamental reasons life has evolved on this planet and water is critical to life as we know it. All life on Earth requires the chemical elements carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus as well as numerous other elements in smaller amounts; it also requires water as the solvent in which biochemical reactions take place. A solvent is a usually (but not always) a liquid in which other substances can dissolve. If you look at the amount of water in the life that we have on Earth, there is a dazzling range from 65% water in humans, to 90% in plants plants, all the way to 95% in jellyfish. We have already discussed the water found on Mars and in the oceans under ice caps on Jupiter's moon Europa. Water is everywhere, and incredibly important, so let's focus in on this most remarkable molecule that is water.

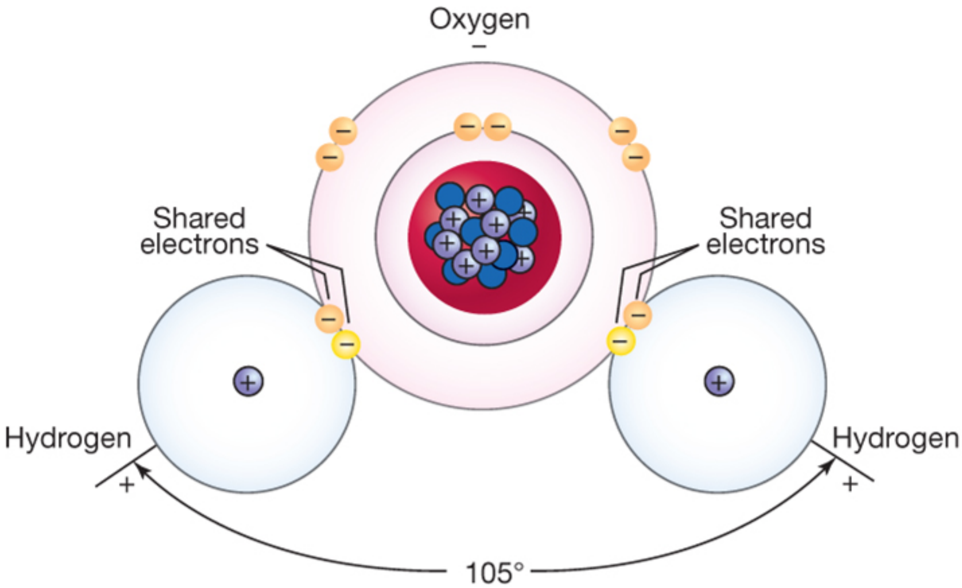
What makes the molecule 'water' so special? It all comes down to it's unique physical and chemical properties. We will first discuss those super-special chemical properties, then we will discuss how those properties allow ice to float, how it moderates global temperature, how it creates stratification, and how it plays a role in light penetration into the ocean.

the non-chemists in the class, let's do a quick review of chemistry. Atoms are the building blocks of all ter. Atoms themselves are made up of smaller particles called subatomic particles that are composed of even smaller particles that include quarks, leptons and bosons. Basically, as science advances and we become better at examining atomic particles, we are finding new and interesting things about the components they are made of. Without getting too far into the technical 'weeds', for our purposes, you can think of an atom as having a dense center (we call this the nucleus), and a relatively diffuse outer cloud of electrons. See the figure below. The nucleus of the atom is composed of protons and neutrons. Protons have a strong positive electrical charge and the neutrons have no electrical charge (they are neutral). Surrounding the nucleus are small particles called electrons that have about 1/2000 the mass of the protons & neutrons, and have a negative electrical charge. Ok – so we have neutral particles (neutrons), positive (protons) particles, and negative (electron) particles. What happens when you have positive and negative charges (think about magnets…) – they attract one another. The same thing happens in an atom, with the attraction between protons and electrons holding the electrons in layers around the dense nucleus known as shells.

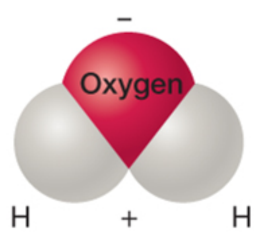


Overall for a single atom, the electrical charge is balanced because of the equal number of electrons and protons. The number of protons in an atom is what distinguishes it as a chemical element – oxygen (the chemical symbol for oxygen is O) for example has 8 protons, whereas hydrogen (the chemical symbol for hydrogen is H) only has one. In some cases an atom might lose or gain an electron and thus have an overall electrical charge (we call these charged atoms ions).

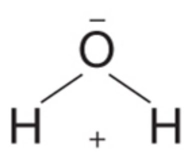
Now let's move on from an atom, to a molecule. A molecule is a group of two or more atoms held together by shared electrons. When atoms combine with other atoms to form molecules, they share or trade electrons and establish chemical bonds. The chemical formula for water, H_2O, indicates that a water molecule is composed of two hydrogen (H_2) atoms chemically bonded to one oxygen (O) atom. Some key aspects to consider about the nature of a molecule is the geometry, polarity, and connections between molecules. Let's look in detail at the geometry, polarity and connections to other molecules for our favorite molecule – water!



(a) Geometry of a water molecule. The oxygen end of the molecule is negatively charged, and the hydrogen regions exhibit a positive charge. Covalent bonds occur between the oxygen and the two hydrogen atoms as electrons are shared.



(b) A three-dimensional representation of the water molecule.



(c) The water molecule represented by letters (*H* = hydrogen, *O* = oxygen).

Geometry: Atoms are described as spheres of various sizes. The more electrons the molecule contains, the larger the sphere. Oxygen is about twice the size of an hydrogen atom. A water molecule consists of a central oxygen atom that is bonded to two hydrogen atoms that are separated by about 104.5 degrees. The bonds between the hydrogen and oxygen atoms are strong bonds called covalent bonds, which means that the atoms are shared between the atoms. A unique feature for oxygen is that both hydrogen atoms are on the same side of the oxygen, and this unique shape (sometimes called ‘mickey mouse’ shape) is a key to the unique properties of water.

Polarity: The bend in the water molecule results in the molecule having a slight negative charge on the oxygen side of the molecule and a slightly positive charge on the hydrogen side of the molecule. The separation of charges gives the molecule an electrical polarity. This slight polarity may be weak, but essentially they behave as tiny magnets.

<u>Connections of molecules</u>: From your experience with magnets, you know that magnets tend to orient themselves with the positive region of one magnet aligning with the negative region of another. In water the positive charge on the hydrogen side of the molecule is attracted to the negatively charged oxygen side of another molecule. These interactions between the positive and negative sides of two molecules form what is called a *hydrogen bond*. The hydrogen bonds are not as strong as the bonds between the oxygen and hydrogen atoms within a water molecule. Despite the fact that they are relatively weak bonds, they cause water molecules to stick to one another – a property called *cohesion*. The cohesive properties of water cause it to "bead up" on a waxed surface, or form itself into a drop as it falls from a dripping tap. This tendency is known as surface tension. Have you ever filled a water glass so full that the water is slightly higher than the top of the glass, but the water doesn't acutally spill over the side? That is because the surface tension (the hydrogen bonds among the water molecules at the surface of the water) is actually pulling together to hold that surface in place rather than letting it spill over. Water's ability to form hydrogen bonds causes it to have the highest surface tension of any liquid on Earth (except for mercury).

These unique chemical properties are very important. The water molecules stick not only to each other but they also stick to other polar chemical compounds. When this occurs, water reduces the attraction between ions of opposite charges by a lot (~80x!). A great example is table salt, which is made of sodium (Na) and chloride (Cl). Salt (NaCl) consists of positively charged Na and negatively charged Cl. When solid NaCl is placed into water, the charges in the water molecules weakens the attraction between the Na and Cl by ~80x. This makes it easier to separate the salt molecule, and then the positive ends of Na are attracted to the negative charged atoms of the water, and the Cl are attracted to the positive sides of the water molecule. The process by which water molecules surround other molecules is known as hydration. The result of this is that almost all polar molecules are able to dissolve in water. This is why water is known as the "universal solvent". Since the ocean is composed of water, this unique chemistry results in an amazing amount of dissolved material being present in the ocean (50 quadrillion tons of salt!).

Check out this video to recap some of these polar properties and the bonds that they create.

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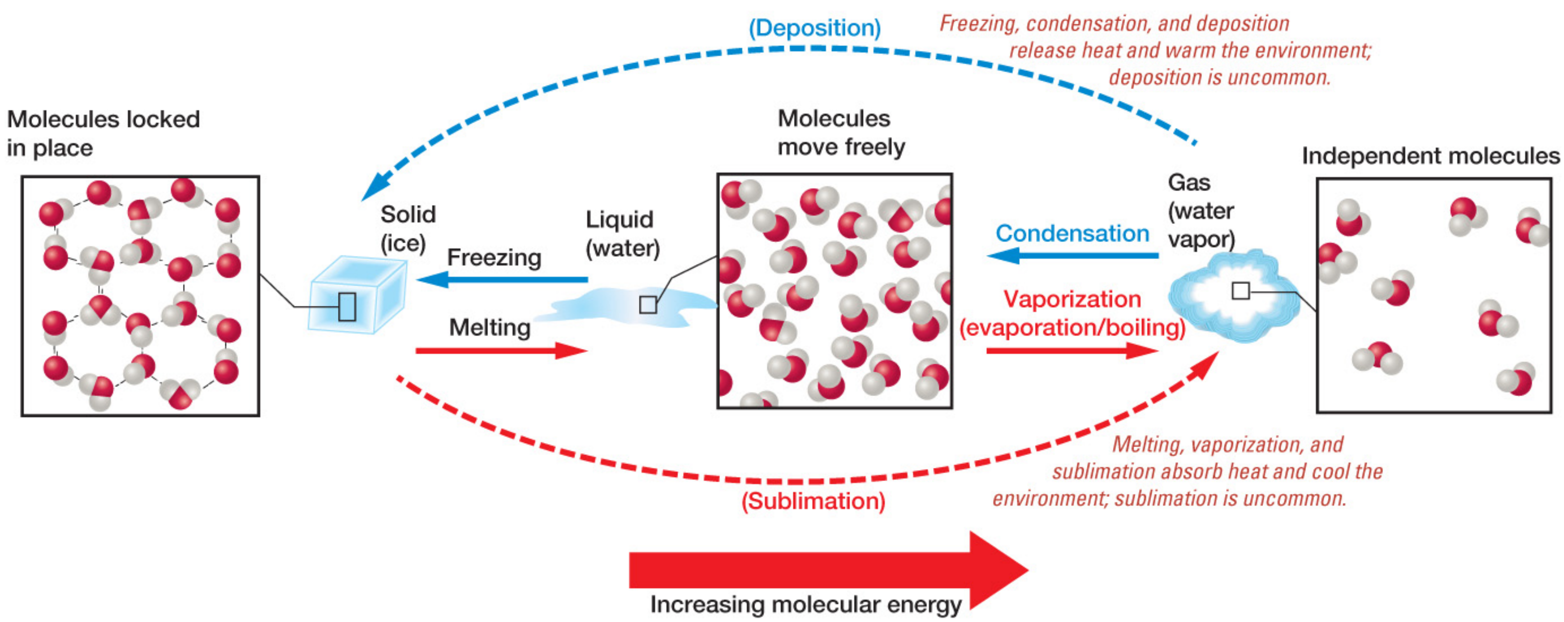
(https://youtu.be/ASLUY2U1M-8)

Water also has unique thermal properties.

Water has unique properties that can dramatically influence the temperature of our planet. Matter generally exists in one of three states, gas, liquid, and solid. The attractive forces between molecules (or ions) in a substance must be overcome if the state of a substance is changed from a solid to a liquid or from a liquid to a gas. These attractions that must be overcome include the hydrogen bonds that we discussed above and the van der Waals forces, named for a Dutch physicist, are weak interactions that are only important when the molecules are close together as in a solid or as liquid.   It takes energy to overcome these forces and break molecules apart. Adding or removing heat is the energy that separates molecules and allows them to change among states.

It is important to understand the difference between heat or temperature. Heat is the transfer of energy from one body to another due to a difference in temperature. Heat is proportional to the energy level of moving molecules and thus is the total energy (both kinetic and potential energy) which is transferred from one body to another. Heat is generated by combustion, by friction, or from radioactivity. It is transferred by conduction, convection, or radiation. One calorie is the amount of heat required to raise the temperature of 1 gram of water by one degree of centigrade. Temperature is a direct *measure* of the average kinetic energy of the molecules that make up a substance. The greater the temperature, the greater the kinetic energy of the substance. Temperature changes when heat energy is added or removed from a substance. So, for example, a candle flame can have a high temperature but not much heat; whereas a bath full of warm water can have a lower temperature but a lot more heat.

Ok – back to states of matter. Water in the *solid* state has a rigid structure and does not flow, at least over short time scales. Intermolecular bonds are constantly being broken and reformed in the solid state, but the molecules remain firmly attached to each other. In the *liquid* state water molecules still interact with each other but they have enough kinetic energy to flow past each other. The intermolecular bonds are being formed and broken at a much greater rate in liquid than in the solid state. In the *gaseous* state, water molecules no longer interact with one another except during random collisions. Water molecules in vapor or gas form flow very freely.



Water's freezing and boiling points. If you add enough heat to a solid you will melt it to a liquid. The temperature at which this occurs is known as the melting point of a substance. The temperature at which the substance transitions from a liquid to solid is known as the freezing point of a substance. The temperature at which a liquid transitions to a gas phase is known as the vaporization (or boiling) point. The temperature at which a substance moves from gas to liquid phase is known as the condensation point. Water is unique as the freezing and boiling points are unusually high. We are lucky because of this. If water was a normal substance, water would melt at -90 C and would boil at -68 C!!! This would mean no life on this planet because all of the water would be boiled away. This unique melting and boiling point is again because of that weird geometry of the water molecule. Recall the angle between hydrogen atoms that makes it polar and allows hydrogen bonds. The hydrogen bonds mean that water molecules wants to hold onto one another and therefore it takes more energy to break them apart.

Water's heat capacity and specific heat. Heat capacity is the amount of heat energy required to raise the temperature of a substance by 1 degree centigrade. If a substance has a high heat capacity, it can absorb large quantities of heat with only a small change in temperature. Substances that change temperature rapidly when heat is applied (oils or metals) have low heat capacity. The heat capacity per unit mass of a body is called the specific heat capacity (sometimes called specific heat). Water has an extremely high specific heat, which is fortunate for us. The specific heat for water is 10 times higher than the specific heat of oil and metals. If this was not the case the Earth would freeze every night. Why does water have such a high specific heat capacity? The reason is it takes more energy to increase the kinetic energy of hydrogen-bonded water molecules than it does for substances where the dominant intermolecular interaction is the much weaker van der Waals forces. As a result, water gains or loses much more heat than other common substances while undergoing an equal temperature change. If you think about it, your pool probably doesn't warm up much on a hot sunny day, but your exposed concrete sidewalk sure does – that is an example of the differences in heat capacity of the two materials. They are both getting the same heat, but one doesn't change much in temperature, while the other changes a lot.

The latent heat of water. When water undergoes a change of state, when ice melts or water boils or when vapor condenses – a large amount of heat is absorbed or released. An example: as your sweat evaporates your skin cools dramatically because the liquid water molecules take up a lot of heat to make the state transition to vapor.

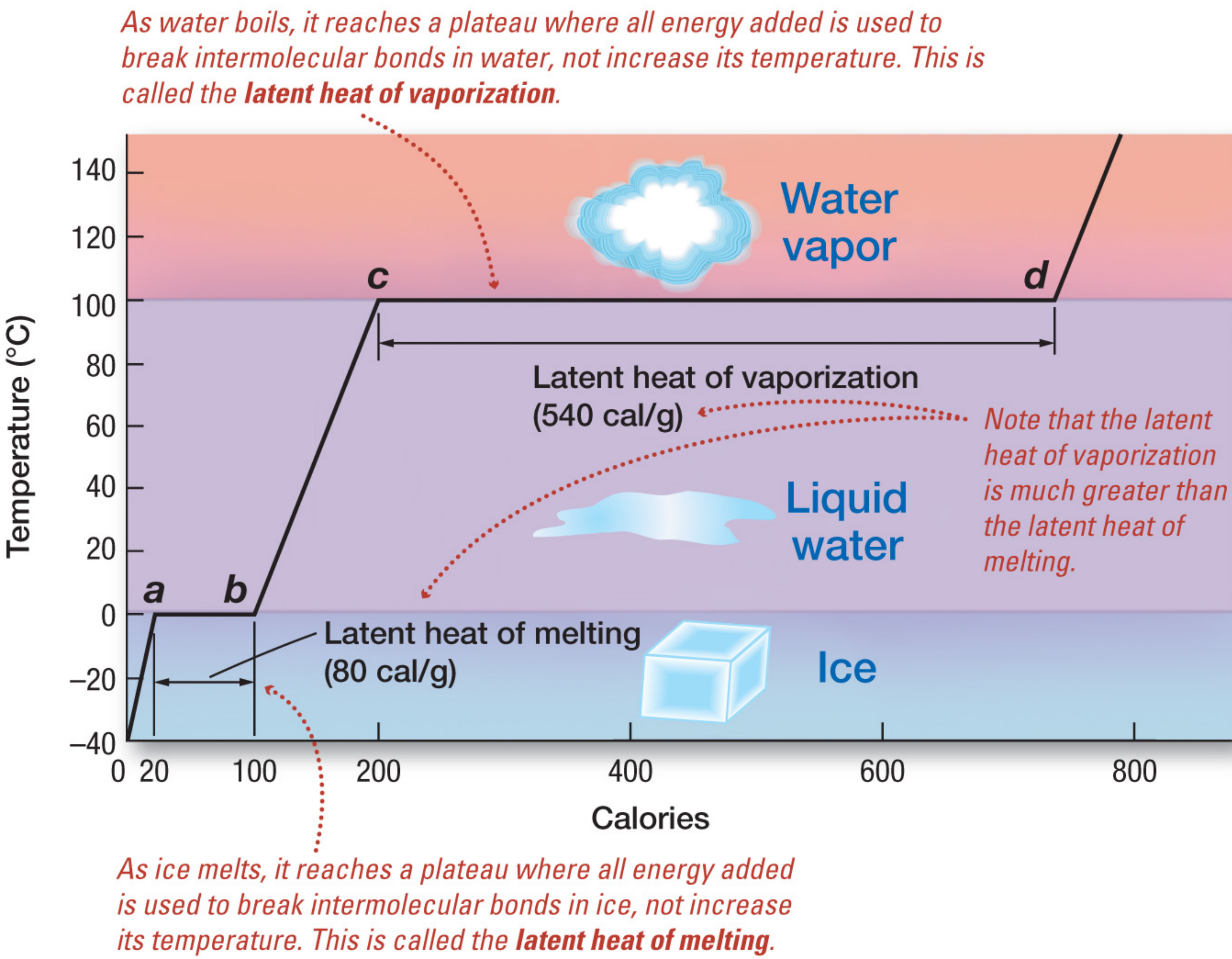
<u>*Latent heat of melting*</u>. The latent heat of melting is the energy needed to break the intermolecular bonds that hold water molecules rigidly in place in ice crystals (solid) and allow them to move as liquid water. The temperature remains unchanged until most of the bonds are broken. This means that the additional heat added to ice will not raise the temperature above 0 celcius until the transition to water occurs. For water this latent heat is very high.

<u>*Latent heat of vaporization*</u>. For water to go from liquid to gas (vaporization), all the individual hydrogen bonds must be broken. This occurs at 100 celcius, and means that water will remain at 100 celcius as more heat is added because that heat is being used to break hydrogen bongs and not to increase temperature. Once the bonds are all broken and the water is fully vaporized to gas, the gas will then increase in temperature.

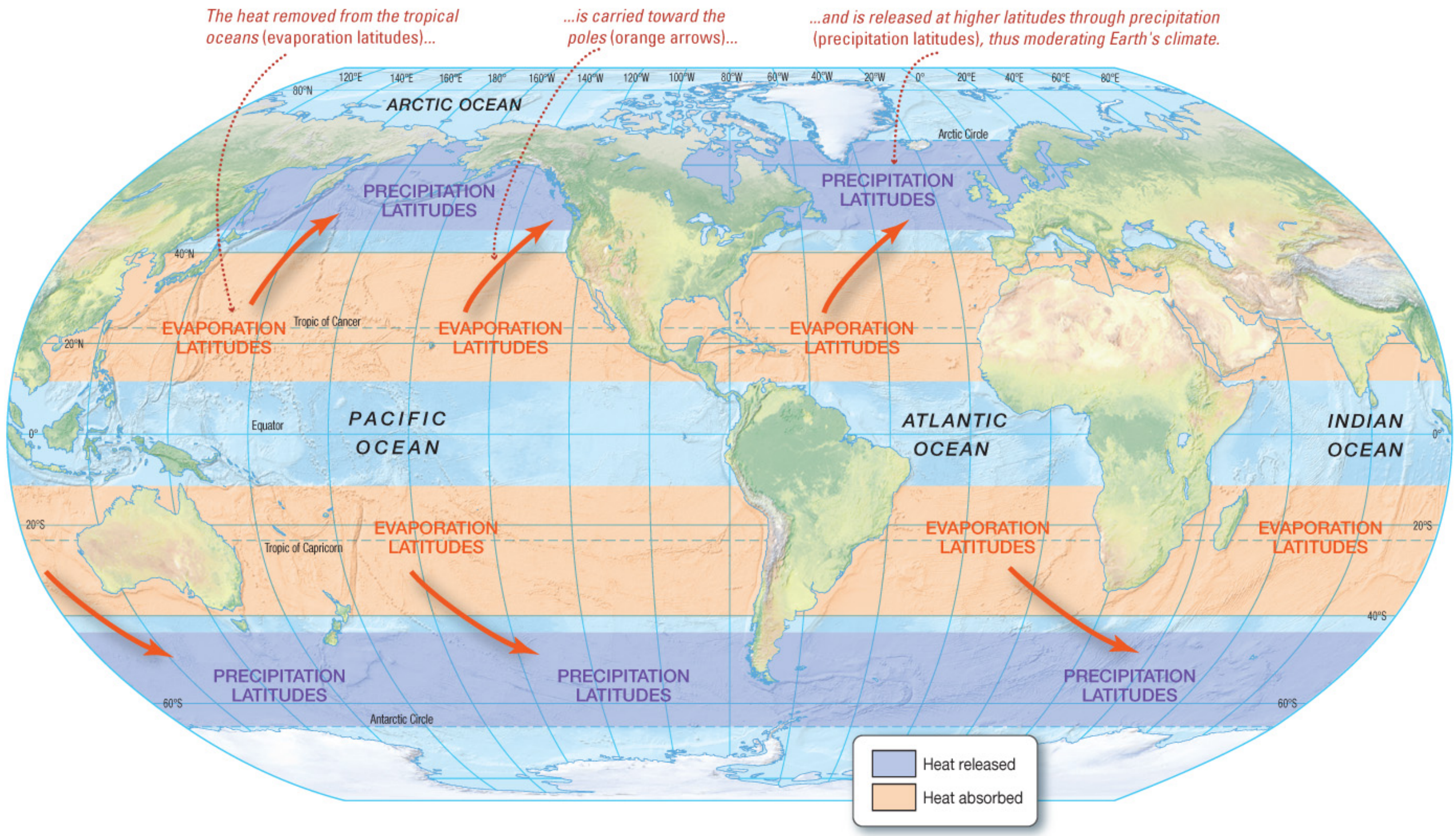
<u>*Latent heat of evaporation*</u>. If you leave a glass of water on your desk in your dorm room for weeks, you will notice that the amount of liquid water goes down over time. But how can this happen if your room isn't 100 celcius? The conversion of liquid water to a gas below the boiling point is called evaporation. In evaporation the water molecules at the surface must absorb energy to break free from its neighboring water molecules. This process takes energy from neighboring water molecules to give sufficient energy for the water molecule that is breaking free to a vapor to escape the liquid form, which explains the cooling effects of evaporation.

<u>*Latent heat of condensation*</u>. When water vapor is cooled sufficiently, it condenses to a liquid and releases its latent heat of condensation into the surrounding air. You utilize this property to cook food or steam milk for your morning latte. This energy also powers thunderstorms and hurricanes. Think about it, awesome power!

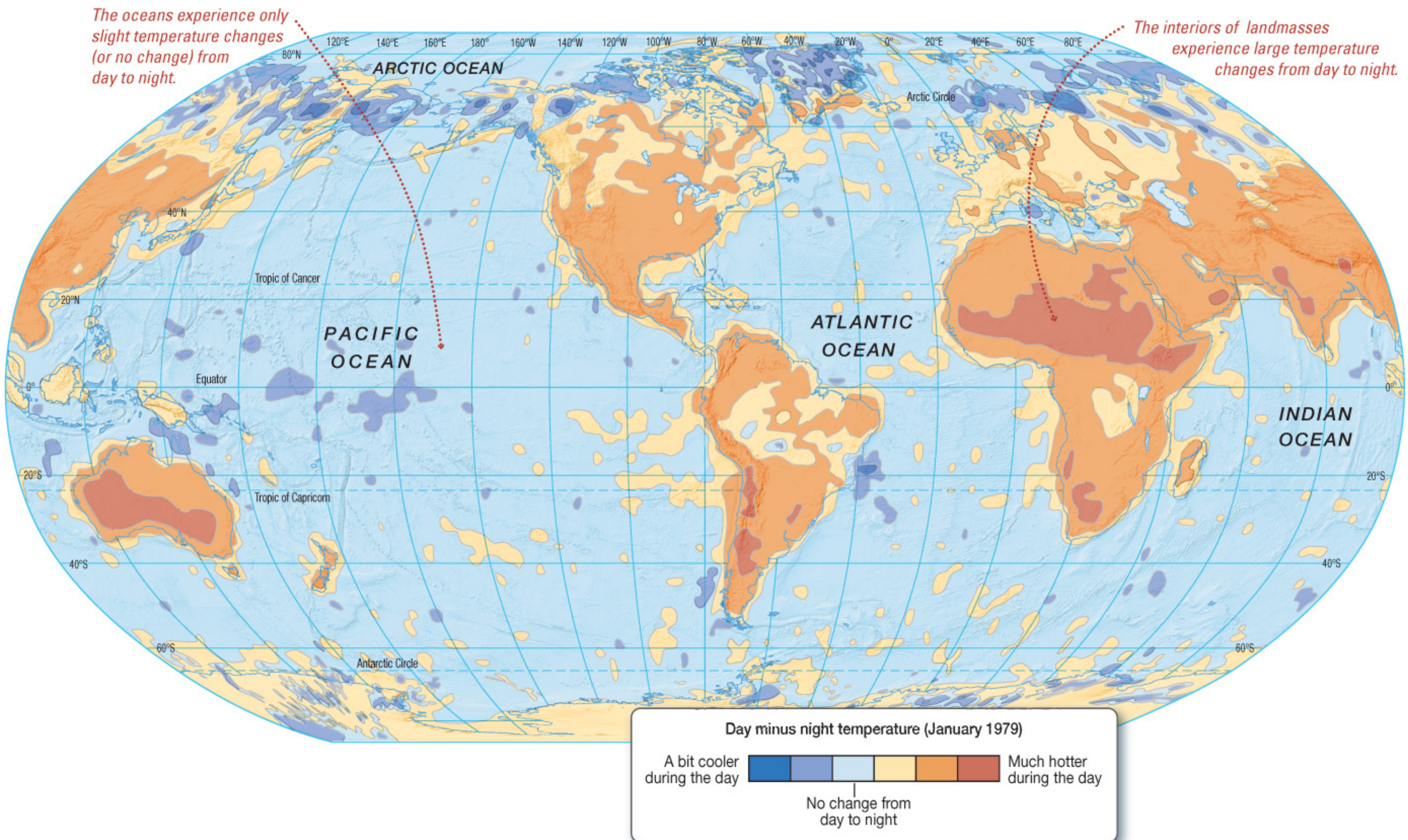
Latent heat of freezing. Heat is also released when water freezes (goes from liquid to solid). The amount of heat released is the same as the heat that was absorbed when ice melts. The ability of water to take in and releasing of energy is a process that is essential for weather and temperature on Earth. Ice can melt in one location (absorbing heat) then flow to a new location where it can freeze and release that heat. So the water itself has moved from one place to another, and it has moved the heat (energy) along with it!



Global Thermostatic effects. You love water more than you know. This is illustrated nicely by the thermostatic effects of water on Earth. Water's thermostatic properties moderate the world's temperatures, kind of like how a thermostat in a house keeps the temperatures in the house steady and comfortable. The sun radiates energy to the Earth and it is absorbed by the ocean. Evaporation removes the heat from the ocean and moves it to the atmosphere. In the upper atmosphere the cool temperatures condense the water vapor into clouds, which drives precipitation, and releases the latent heat of condensation. The exchange of latent heat between ocean and atmosphere is very efficient: for every gram of water that condenses in cooler latitudes, that same amount of heat was removed from the tropical ocean when that gram of water was previously evaporated elsewhere (most of it in the tropics). Check out the figure below to see the global patterns of how this all works. The unique chemistry of the water drives the climate cycle of our planet, and the life we know thrives because of these unique water properties.



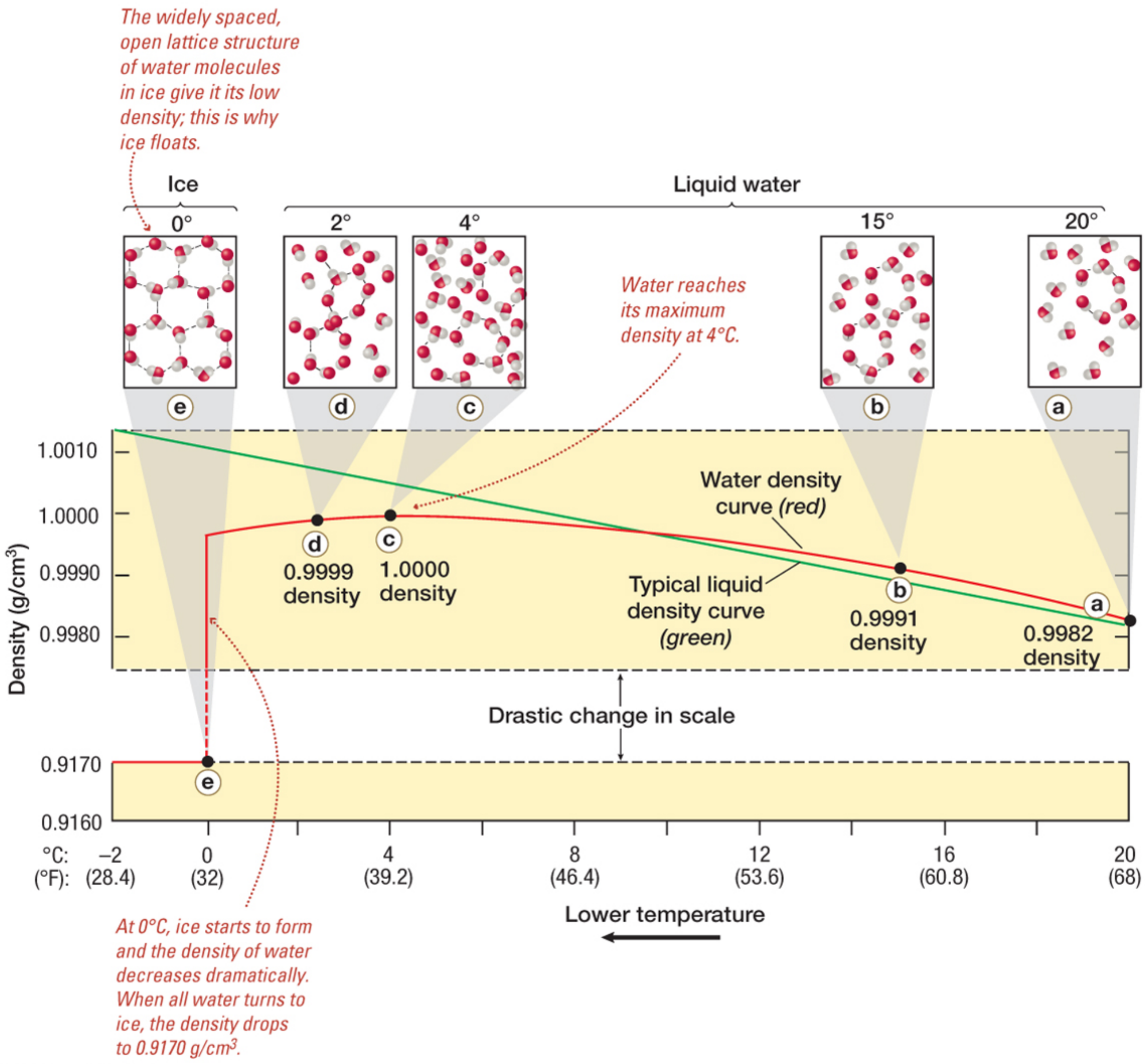
The thermostatic effects of water can also been seen in how the ocean is able to modulate the changes in temperature you see between day and night. Have you ever noticed how stable the temperature is in a coastal town, compared to a town further from the ocean. That is the thermostatic effect of the ocean at work (known as the marine effect). See the figure below to see how this looks globally. The map shows that the ocean is very stable (no big changes in temperature from day to night), but land masses have big changes with (mostly) hotter temperatures during the day due to the heating of land and soil and the inability of those materials to retain that heat at night.



Water Density. We have talked about density already - remember density is mass per unit volume. Density is controlled by how tightly packed molecules are. Many things change the density of water, including temperature, dissolved salt (salinity), and pressure. For example if water is warm it is less dense than if it is cold, because the water molecules in warm water are moving around a lot more and are more spaced out than in cold water. The denser the water, the heavier it is, and heavy fluid will sink. This concept is the basis of ocean currents – more on that in a bit.

Density increases as temperature decreases for most substances because it reflects the decrease in kinetic energy of the molecules that are packed increasingly close to each other. So, for most substances, as their temperature decreases the substance gets heavier. If that were true for water, why does ice float? As pure water cools to 4 degrees, its density increases (as expected); however, from 4 degrees to 0 degrees the density decreases! The result is that solid water (ice) is less dense than the cold liquid water. This happens because from 4 to 0 degrees, the molecular orientation due to the hydrogen bonding makes the water molecules space out regularly and they take up more space when locked into that regular (orderly) formation. This explains why a sealed water bottle thrown into the freezer eventually bursts. The orderly crystal formation of solid water is also why snowflakes have such a unique and hexagonal shape (see the figure below – the formation of the crystals take on a hexagonal pattern).

In the ocean, deeper water is under pressure (it has the weight of all of the water above it pressing down on it) which increases it’s density, and it is also cold (close to 2 degrees). So this means that deep ocean water is more dense than the warmer water above it (look at the graph below to convince yourself this is the case). All in all, this whole ‘ice is less dense than cold liquid water’ is a good thing - because if ice sank, it would crush everything in the ocean. Yet another reason to praise the unique chemistry of water.



To recap – some important properties of (sea)water that moderate and control changes in temperature. It has a *high heat capacity* which means it can hold onto a lot of heat. It also has *high latent heat* which means that as it changes state (among solid, liquid and vapour) it absorbs or releases a lot of heat on those transitions. And it has high thermal intertia which means that it tends to want to retain the energy it stores. All of this is realated to its chemical make-up and the fact that it is a polar molecule that can make and break hydrogen bonds. Pretty amazing!!

Since we have been thinking in depth about water melting and freezing – here is a video about a researcher who spends her time watching and thinking about just that.

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