The Changeable States of Matter

By Sarah Hansen

Almost all of the different kinds of "stuff" around you can be sorted into one of three categories: **solid, liquid, or gas**. Sometimes it is easy to tell which category something should belong to, but some materials aren't so obvious.

The first thing to do is to decide what defines each of the different states of matter.

Is it shape?

Weight?

Volume?

Color?

Can you tell just by looking, or do you have to touch something to determine which state of matter it is?

During this lab, we'll explore just what it is that makes a solid a solid, a liquid a liquid, and a gas a gas.

Your group will receive several balloons, each containing a different substance.

- In your lab notebook, write down:
  - two words for each balloon describing the substance it contains
  - whether each is a solid, liquid, or gas

- Compare your answers with those of the others in your group – did you all think that each material was in the same state?

Talk it over until you can all agree which state of matter is in which balloon.

Now for the harder part: *how* did you decide which state of matter each was?

- With your group, come up with a set of rules for deciding how to categorize substances by which state of matter they are.

For example, maybe all blue things are liquid. Or maybe all heavy things are solid. To test your rules, see if by following them you'd end up sorting out your set of balloons the same way you did before. If not, then either your rules need adjusting, or maybe you misclassified one of the balloons in the beginning!

- When you have your final set of rules decided, write them down in your lab notebook.

Changing States

What would happen if we left the balloons in the freezer overnight?

- In your lab notebook, write down your prediction of what the substance in each balloon would be like after a night in the freezer.
  - How would it feel?
  - What state of matter would it be?

- Share your answers with your group.

- Did you all think the same thing would happen?

It's ok if you don't agree – certainly scientists in the same research group don't always expect the same results of their experiments!

Once all the groups have predicted what the stuff in each balloon would be like, your lab instructor will give you balloons that have spent the night in the freezer.

- Were your hypotheses correct?
- Record in your lab notebooks:
  - whether (& how) the substances were different from when they were at room temperature
  - what state of matter each material is when cold

During the fall, we've already seen that **temperature affects which state of matter something is**. If you put an ice cube in a hot frying pan, the solid water will warm up until it reaches its melting point temperature, then melt, and then that puddle of liquid water will heat up until the boiling point is reached, and then the water will all turn to steam (gaseous water). The process works in reverse, too: cooling steam results in liquid water, and continued cooling would result in ice.

? What if I wanted to boil water, but couldn't heat it to 100° C?

? Is lukewarm boiling water an oxymoron, or is it possible?

? What if I wanted to melt ice but also keep it below 0° C?

There *is* something else we can change – besides the temperature – that will make phase changes happen.

Boiling Lukewarm Water

You will now get to watch an experiment demonstrating that lukewarm water can indeed boil. Your lab instructor will put a beaker of water with a thermometer in a bell jar. Attached to the bell jar is a pump. The pump will be turned on, and you will see what happens!

- In your lab notebook,
  - Draw a picture of the experiment setup.
  - Describe what happened during the experiment.

- Also record the following information:
  - What was the temperature of the water at the beginning?
  - What changes did you observe in the beaker of water?
  - What temperature was the water at the end?

You may have noticed that the bell jar got "all fogged up" near the end of the experiment.

- What caused that to happen?

Phase Diagrams

We've seen that both temperature and pressure can make phase changes happen. It can get complicated to remember just what temperature and pressure combination will make which phase change happen when! In order to keep track of what state a material is at different temperatures and pressures, we can use a plot called a "phase diagram." On a phase diagram, the horizontal axis represents temperature, with higher temperatures to the right. The vertical axis represents pressure, with higher pressures at the top. The different areas of the plot represent conditions under which the material is gaseous, liquid, or solid. The thick solid lines represent the transitions between these phases. For example, this is the phase diagram of water:

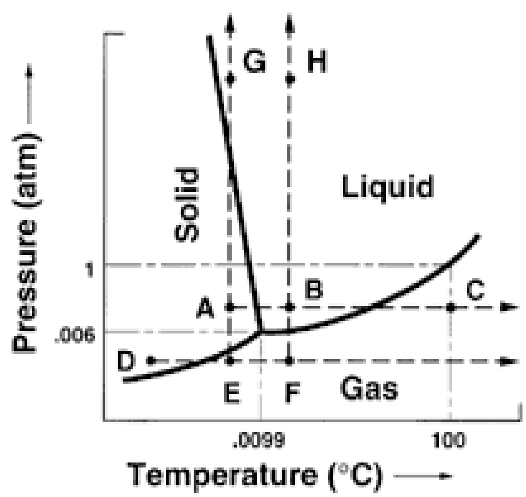

Figure 1: Phase Diagram of H_2O

At points 'A' and 'D', water is solid; at 'C', 'E', and 'F, gaseous; at 'B', liquid. The thick solid lines represent transitions between phases. Along these lines, two phases can exist together. At the triple point, where the lines intersect, the solid, liquid, and gas can all co-exist. For H_2O, the triple point falls at a temperature of 0.0099° C and a pressure of about 0.006 times the pressure of Earth's atmosphere at sea level. The heavy dashed lines represent sequences of heating (horizontal) or squeezing (vertical):

1. Start with the ice at 'A'. Keeping the pressure constant, warm it until it reaches the solid-liquid transition. At this point the ice melts. Further heating initially results in warmer liquid ('B'). If you warm the liquid enough, it reaches the liquid-gas transition and evaporates. Further heating results in warmer gas ('C').
2. Start with the ice at 'D'. Raising the temperature does not cause it to run into the solid-liquid transitions, but rather into the solid-gas transitions. The ice evaporates directly into the gas phase in a process called sublimation. Further heating warms the resulting gas ('E' and 'F').

3. Start with gas at 'E'. Holding the temperature constant, squeeze it until it reaches the solid-gas transition. At this point the gas condenses directly into a solid ('A'). For H2O, additional pressure pushes the solid to the solid-liquid transition, where it melts ('G' on left diagram). This behavior, liquification under increased pressure is a very unusual property of water. Most materials stay solid as the pressure is increased.
4. Start with gas at 'F'. Squeezing it pushes it to the solid-liquid transitions, where it condensed directly into liquid ('B').

The phase diagram represents what state the matter would "like" to be in at each temperature and pressure combination. Of course, taking an ice cube out of the freezer and putting it on the kitchen table doesn't make the ice instantly turn into liquid water! The ice warms up, eventually gets to the melting point, melts, and continues to warm until it is the same temperature as the surrounding air. This process is the H_2O "reaching equilibrium" with the air. The phase diagram tells you what state a material will be in *once it has reached equilibrium* with its surroundings. Sometimes a material will get "stuck" at a false equilibrium point, and may seem to exist in the "wrong" state, according to the phase diagram. In such a situation, the material just needs a little kick in the right direction and it will switch phases (often dramatically).

Let's compare water to a more 'typical' substance: here's the phase diagram for carbon dioxide (CO_2):

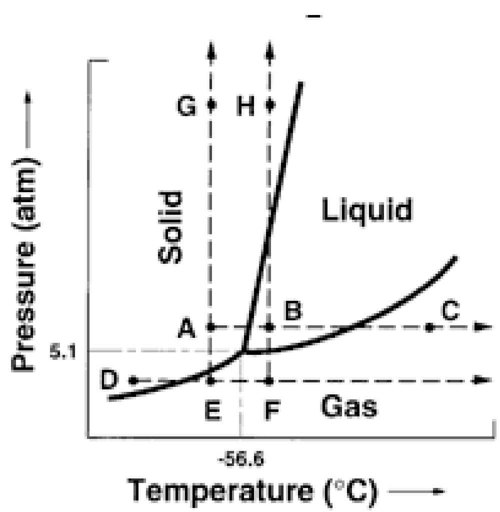

Figure 2: Phase Diagram of CO_2

There are a few important differences between the H_2O and the CO_2 phase diagrams. First, notice how different the temperature and pressure scales are! Room temperature and pressure would be at a point way to the right of point 'F', showing that carbon dioxide is a gas under "ordinary" conditions. The second big difference is the slope of the nearly vertical line between the solid and liquid phases. For CO_2, this line slopes upward and to the right - the normal behavior of almost all materials. However, for H_2O, the line slopes upward and to the *left*. This seemingly minor change reflects major differences in the behavior of H_2O under pressure.

What happens if we take gaseous CO_2, squash it at a temperature at which it will liquefy (above -56.6 degrees Celsius), and squeeze harder and harder? It will turn into a liquid and eventually into a solid. In Figure 2, this is represented by the line 'F' to 'B' to 'H'. If we crank up the pressure still further, nothing new happens; we move up the diagram, but CO_2 remains solid. Below -56.6 degrees Celsius, squeezing turns CO_2 gas directly into a solid without the liquid go-between ('E' to 'A' to 'G'). Thus, if you squeeze CO_2 and most other substances hard enough, they eventually solidify.

Water behaves very differently. If you start with water vapor hotter than 0.0099 degrees Celsius and squeeze, the gas condenses into liquid, just as CO_2 did. After this point, however, additional squeezing does not turn the liquid water into solid ice. It stays liquid. (Under extreme conditions, this is not exactly true.) In Figure 1, this process is represented by the line 'F' to 'B' to 'H'. Water also behaves differently at lower temperatures, below 0.0099 degrees Celsius. Applying pressure causes the gas to condense directly into a solid, as with CO_2. But if you apply more pressure, the H_2O ice melts. In Figure 1, this is represented by the line 'E' to 'A' to 'G'. This behavior is very different from that of CO_2, which stays solid no matter how hard you squeeze. If you squeeze H_2O hard enough, it eventually liquefies.

This peculiarity is associated with the fact that solid H_2O is less dense than liquid water. Water ice floats in water - a very unusual behavior. Dry ice, for example, sinks in liquid CO_2. Most solids are essentially as dense as those substances can possibly be, and further squeezing cannot make them significantly more compact. Yet when you squeeze H_2O ice, it can ease the squeeze by turning into a liquid, making itself smaller and denser.

This (almost) unique property is in part due to the water molecule's ability to form strong hydrogen bonds. In hydrogen bonding, the H atoms in H_2O form attachments to adjacent molecules. Such bonding is weaker than the covalent or ionic bonding that holds together molecules, but stronger than the normal intermolecular "van der Waals" forces. Hydrogen bonds are like the sticky portions of Post-It notes - stickier than just pushing two pieces of ordinary paper together, but less sticky than glue. It is hydrogen bonding between H_2O molecules that makes the folds in your wet shower curtain stick together. This ability to grab things firmly but not tightly is one of the reasons that H_2O is so very important for life. Because of it, liquid water can mediate much of the complex chemistry that occurs in living organisms.

Ice Can Be Welded

Based on this understanding of H_2O and its phase diagram, let's consider the physics of snowball manufacture. To make a snowball, you scoop up some snow and compress it between your cupped hands, after which you hopefully have a ball that hangs together. What makes the loose snow stick together?

Many people assume that the heat from their hands melts enough of the snow to make it cohere. However, if heat were responsible, a snowball would be made from the outside in, and you'd have to hold it long enough for sufficient heat to enter. But if you cut a snowball in half, it looks pretty much the same throughout; there's nothing special about its outer layers to indicate they were heated first. Moreover, snowballs can be compacted quickly.

If heat mattered, it would be easier to make a snowball with your bare hands than with gloves on. If you need further proof, try this: Drop two spoons in the snow and let them chill to snow temperature. Then pick the spoons up with gloved hands, so that you don't warm them, and use them to pack a snowball. You can make a perfectly good snowball this way, although the delay may cost you the snowball fight.

Alternatively, some people theorize that snowballs hang together because the intricate ice crystals in the snowflakes get tangled. If so, fluffy snow would make better snowballs than denser snow. In fact, the opposite is often the case.

The real explanation is revealed by the H_2O phase diagram (see Figure 3). Suppose you are strong enough that you can squeeze snow hard enough to raise its pressure from 'A' to 'C' or, equivalently, 'A´' to 'C´'. If the snow is warm enough, you can squeeze it sufficiently hard that it reaches the solid-liquid transition line. At this point, some of the ice crystals melt in order to take up less space. If you then release the pressure, the snow drops away from the solid-liquid transition line, and the ice that melted refreezes. In Figure 2, this amounts to moving from 'A' to 'B' and back to 'A'. The refreezing liquid bonds the ice crystals together. Voilà! A snowball.

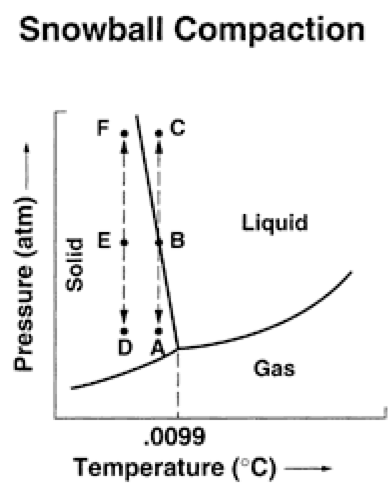

Figure 3. Making a snowball.

First, squeeze the snow hard enough that it moves vertically up the phase diagram to the solid-liquid transition ('A' to 'B'). Then release the pressure ('B' to 'A'). While at the solid-liquid transition ('B') some of the edges of the ice crystals melt. When you release the pressure, they refreeze, cementing the snow together. If you squeeze too hard, the snow goes all the way up to 'C' and the snowball melts completely away.

On a very cold day, the snow may start at location 'A´' and proceed up to 'B´' and 'C´'. At 'C´', you are squeezing as hard as you can, but the pressure is insufficient to reach the solid-liquid transition.

Because no melting occurs, when you release the pressure you are left with a loose handful of snow rather than a snowball. Diagram by Scott A. Sandford.

Now suppose you want to have a snowball fight on a very cold day. As you squeeze the snow it proceeds vertically up the phase diagram, but because of the low temperature, you can't squeeze hard enough to reach the solid-liquid transition. You're squeezing as hard as you can ('A′' to 'B′' to 'C′'), but you can't get any melting. When you release the pressure, you find that you are holding a loose handful of snow, rather than a snowball.

Feeling Cold?

So, how cold is too cold? It depends on how hard you can squeeze. Some quick-and-dirty measurements with scales in the laboratory indicate that my hand can apply a pressure of about 0.07 atmospheres (1 pound per square inch, or 7 kilopascals) without straining too much. I can get as high as 0.2 atmospheres if I use my arms to squeeze instead of my hands. Thus, squeezing a snowball only adds a minor pressure to the pressure that the air is already exerting on the snow (1 atmosphere). Consequently, you can't expect to make a snowball with your hands if the snow is more than a few degrees below freezing.

At lower temperatures, you would need Herculean pressures. At -25 degrees Celsius (-13 degrees Fahrenheit), a summer's day at the South Pole, it would take 2,000 atmospheres (30,000 pounds per square inch) to make a snowball. This would crush a submarine, let alone a handful of snow.

Prospects are even worse on deep-freeze worlds such as Ganymede, Pluto, and Mars. After Earth, Mars is the next warmest place in the solar system where there is any substantial amount of water ice. But with typical temperatures between -120 and -40 degrees Celsius (-180 and -40 degrees Fahrenheit, or 150 to 230 Kelvin), the snows of Mars are way too far to the left of the phase diagram to mold with our hands. Even the warmest temperature recorded by *Mars Pathfinder*, -9 degrees Celsius, would preclude snowballs.

But wait, you say, what if I were willing to drag around a hydraulic press? Could I make snowballs on Mars then? Sorry. So far, we have only considered the low-pressure part of the phase diagram. At very high pressures, H_2O gets weirder still. Figure 3 shows that H_2O can actually exist in a number of different solid forms depending on the temperature and pressure. The entire phase diagram shown in Figure 2 corresponds to a tiny horizontal strip near the bottom of Figure 3.

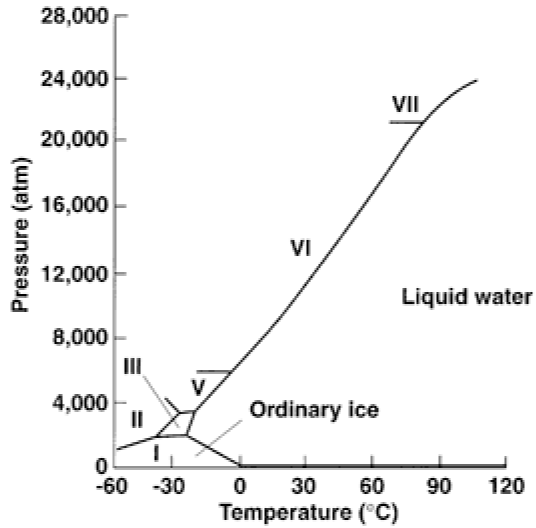

Figure 3. The high-pressure phase diagram of H_2O.

On this pressure scale, the entire area represented by Figure 1 or 2 - including the entire liquid-gas transition line - is an infinitesimal slice along the lower axis. At very high pressures, H_2O can exist in exotic solid forms: Ice II, Ice III, Ice IV, and so on. Everyday ice is Ice I.

Note that the solid-liquid transition line does not extend up and to the left forever. Instead it meets Ice III and then turns to the right, as for normal materials. For this reason, if you squeeze liquid H_2O *really* hard, it ultimately turns into one of the exotic solid phases. There is no region of stability for liquid water below -25 degrees Celsius (-13 degrees Fahrenheit). Crushing snow below this temperature does not cause any melting. Diagram by Scott A. Sandford, adapted from *General Chemistry* by Gordon Barrow, p. 311.

The everyday ice in our sodas is called *Ice I*. At extremely high pressures, H_2O ice can take on exotic crystalline forms: Ice II, Ice III, and so on. (Fortunately there isn't a form of ice called Ice IX which has the apocalyptic properties Kurt Vonnegut described in *Cat's Cradle*.) The solid-liquid transition line does not extend up and to the left forever. Instead it collides with the area of stability of Ice III and then turns and heads up and to the right, as for most other materials.

By the way, water also acts strangely at very low temperatures, off the left edge of Figure 3. When it is very cold - as in comets and interstellar molecular clouds - non-crystalline ice can form.

No Winter Olympics on Mars

The high-pressure ice phases and the reversal of solid-liquid transition line have several implications for the subject at hand. I stated earlier that if you started with H_2O gas or solid and squeezed, it would eventually turn into a liquid, and stay a liquid. That's not quite right. If you squeeze liquid water *really* hard (more than 4,000 atmospheres) it will ultimately transform into Ice V, VI, or VII, depending on the temperature.

More important, below -25 degrees Celsius, squashing snow (Ice I) doesn't result in any melting; it just turns Ice I into ices II, III, and so on. No melting, no snowball. If you were desperate for a snowball fight on Mars on any but the very warmest days, you'd need a heated hydraulic press.

Unfortunately, this behavior will also make it difficult to ice-skate on Mars. When you skate, you are gliding on a thin layer of water that forms between your blade and the ice. The weight of your body on the skate blades puts pressure on the ice, which helps to form the water layer. To be sure, the formation of the water layer is more complicated than a simple pressure effect. (See Samuel Colbeck's article in the October 1995 issue of the *American Journal of Physics*.)

So, snowball fights in our solar system are out, except on Earth. How about "snowball" fights using something other than frozen H_2O, say, methane or carbon monoxide on Pluto or carbon dioxide on Mars? Alas, those other compounds have unfavorable phase diagrams. No amount of compression will get them to melt and pack into snowballs. It makes you appreciate how special Earth really is.

Now, if you're like me, you are already wondering whether there aren't any other materials that behave like water - with solid-liquid transition lines that slope up and to the left. There are, but only under pressure and temperature conditions in which humans couldn't survive. For example, plutonium can exist in a form that melts when squeezed. If you had plutonium dust at 640 degrees Celsius (1184 degrees Fahrenheit) you might be able to squeeze it hard enough between your hands to get it to melt. Thus, if you were capable of surviving in a high-pressure blast furnace and had a strong grip, you could make a plutonium snowball out of plutonium snow. Of course, you would have to be extremely careful about it. If you made it too big, above critical mass, the resulting explosion would end the snowball fight for good.