Freezing point depression and boiling point elevation: the effects of solutes and of pressure

Freezing point depression is the lowering of the equilibrium freezing or melting temperature by solutes in the liquid phase. Solutes in the liquid phase also raise the equilibrium boiling temperature. Pressure also affects freezing temperature (a little) and boiling temperatures (a lot).

This page gives a simple, non-mathematical explanation of all these effects. Although the phenomena are more general, water is given as the familiar example, because of questions such as:

- What happens to boiling and freezing when you add solutes (eg sugar or salt) to water?
- Why do they salt the roads when it snows?
- How does antifreeze work?
- How can living tissues survive subzero temperatures?
- Can you make good tea on a mountain top?
- Do skates work by depressing the melting temperature of ice?

(For those looking for formal treatments, these effects are analysed in standard second year physics courses under the headings phase equilibria and the Clausius-Clapeyron equation, which we quote here without derivation.)

- Why do substances melt and boil?
- The effects of solutes
- The effect of pressure
- When are the boiling temperature and freezing temperature equal? What happens then?
- Further complications - superheating and supercooling
- Mpemba effect: can hotter samples freeze faster than cold?


Why do substances melt and boil?

To oversimplify only a little, temperature is a measure of how much energy there is in molecular motion. To begin with an explicit example, let's consider water. When water molecules are cold enough, they don't have much heat energy so they don't jostle around too much. Consequently, they can pack together in a very organised structure, called ice. At high enough temperatures, they have so much energy that they can escape the attraction of their neighbours. So they form steam, in which the molecules fly all over the place in a very disordered way. At medium temperatures, which means that the molecules have moderate amounts of energy (and if the pressure is high enough*) they form liquid water. Here the molecules have enough energy to move around, but not enough to escape from their neighbours entirely. Molecules in liquid water are more ordered than in steam but less ordered than ice. (As an example of the order in a liquid, we can observe that the centre of each molecule is about one molecular diameter away from that of its nearest neighbours.)

Why is the change so sudden? At atmospheric pressure, water melts at 0°C and boils at 100°C. What determines the melting point and the boiling point?
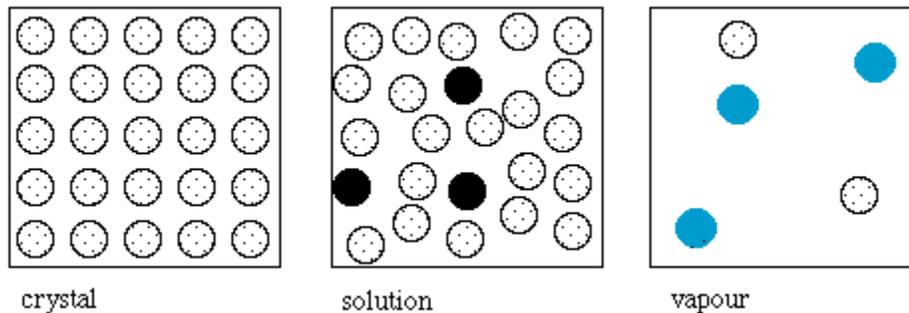
The answer is a trade-off between the molecular energy (which we notice as temperature) and the molecular order: the difference between highly organised structure in ice, rather close packing in liquid water, and nearly complete disorganisation in steam. At 0°C and 100°C, the order effect and the energy effect are exactly balanced, and so ice and water co-exist at 0°C, water and steam coexist at 100°C (at atmospheric pressure).

The crystalline structure of ice is rather difficult to show in two dimensions, so the sketches below show, schematically, a simpler crystal, liquid and vapour phase. The patterened circles represent simplistically the substance in whose melting and evaporation we are interested. The coloured circles represent molecules of the air, which is mainly nitrogen. The black circles (next picture) represent solutes. The sketches are not to scale.

crystal   liquid   vapour
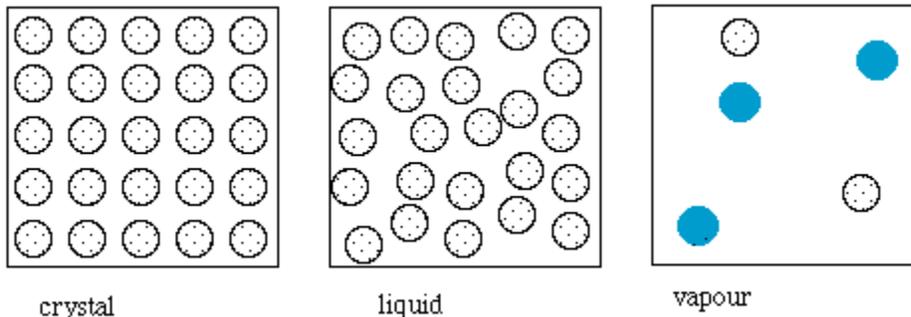
The effects of solutes

What happens if, instead of having pure liquid water, we put some salt or sugar in the water? In other words, what if our liquid phase is a solution? This makes the liquid state less organised, because the sugar molecules or salt ions are free to move about almost randomly. So the liquid water molecules are more disordered (less regimented) in a solution. The ice and the steam remain unaffected, however: sugar and salt hardly dissolve at all in ice, nor do they evaporate near 100°C.

crystal   solution   vapour

How does this affect the trade-off between the molecular energy and the molecular order? The gain in disorder on evaporation is now less, because the liquid water in solution is more disordered. The energy effect is hardly changed, so the energy effect now dominates over a

slightly larger range: the molecules of water in solution have to have slightly more energy (a slightly higher temperature) in order for the two effects to be in balance. So the boiling temperature is higher for a solution.

Conversely, when we look at melting, the disorder effect is greater for a solution: on melting into a solution, water molecules go from the high order of crystalline ice into an even more disordered state than pure liquid. So the disorder effect can dominate even at lower temperatures. So the freezing temperature is lower for a solution.

I mentioned the equilibrium freezing and boiling temperatures above. Time to explain. Imagine ice floating in pure water at 0°C. If we add a little heat, some ice melts. Remove a little heat and some water freezes. We call this the equilibrium freezing temperature: 0°C for water. However, when one cools reasonably pure water, it usually cools several degrees below 0°C – we say it supercools by several degrees – before the first ice crystal appears. That ice crystal then expands rapidly, giving up latent heat, which warms the nearby water back to about 0°C. More about supercooling and super heating below.

An aqueous solution has a higher boiling point and a lower freezing point than does pure water.

If the solution is not too concentrated, these two effects are approximately independent of what the dissolved substance is: a sugar molecule has much the same effect as a salt ion. So, provided you remember to count each ion separately, the effect of concentration on boiling point elevation or freezing point depression is much the same for all small solutes in water. (Macromolecules such as polymers behave differently because they have lots of neighbouring solvent molecules, and so affect the solvent much more than simple solutes.)

Antifreeze. So, you might expect that the antifreeze in a radiator not only stops it freezing, but also helps stop it from boiling. However, the real situation is more complicated: antifreeze has the disadvantage that it is not quite as good as water at transporting heat. Ethylene glycol is one antifreeze. Salt is used to melt snow and ice on roads in cold countries, but it is not used in radiators because it is corrosive and crystallises readily. Sugar is not used in some applications, because concentrated sugar solutions are viscous, and because they support bugs. However, many organisms use sugars and other small organic molecules as antifreeze. See cryobiology.

An interesting observation: The concentration of solutes in blood is less than that in sea water, so the equilibrium freezing temperature of blood is usually higher than that of sea water. Consequently, some Arctic and Antarctic fish live at temperatures below the equilibrium freezing temperature of normal blood. The bio-antifreeze in their blood is a protein that works in a way different from the anti-freeze used in car radiators: the antifreeze protein binds to freezing nuclei and so permits the blood to remain supercooled.

The effect of pressure

Notice that above I've included the proviso "at atmospheric pressure" a few times. The reason why the pressure is important is that, in the vapour phase, a given amount of a substance

occupies a much larger volume than it does as a liquid. Some of the energy required to vapourise it goes towards 'pushing the air out of the way' to make room for the amount evaporated. (The amount of work done is the product of the pressure P and the change in volume ΔV. Technically, there is a PΔV term in the latent heat.) So, at low pressure, it is easier to form the vapour phase and so the boiling point is lower. The dependence of the transition temperature on pressure is the Clausius-Clapeyron effect. (Again, being a bit technical, we note that this effect involves energy - the work done in displacing air - whereas the solute effect involves entropy - the disordering of the liquid phase.)

Water expands a lot when it boils: one kilogram of water is one litre of liquid water, but it becomes about 1700 litres of steam at atmospheric pressure. This means that even modest increases in altitude can measurably reduce the boiling temperature. Some people complain that this affects cooking and even the taste of tea at altitude.

It is also true that pressure changes the melting temperature. However, because the volume occupied by a kilogram of liquid is not much different from that occupied by a kilogram of solid, this effect is very small unless the pressures are very large. For most substances, the freezing point rises, though only very slightly, with increased pressure.

Water is one of the very rare substances that expands upon freezing (which is why ice floats). Consequently, its melting temperature *falls* very slightly if pressure is increased.

It is sometimes said that freezing point depression with pressure explains the low friction under an ice-skate. On its own, this story is not convincing. The Clausius-Clapeyron effect appears not large enough to make a noticeable difference. However, the skate story is so widely believed (outside of thermodynamics classes, anyway) that it's worth being quantitative. The Clausius-Clapeyron equation says that the ratio of the change in pressure times the change in specific volume to the latent heat of the phase change equals the ratio of the change in transition temperature to the (absolute) melting or boiling temperature. (It's often written as dP/dT = L/T*Δv, an equation that we might have guessed from dimensional considerations.)

The weight of the skater is say 1 kN. I'm not a skater, but let me guess at a lower bound for the skate-ice contact area of say 100 mm^2. (Say 200 mm long by 0.5 mm wide: skaters, is this reasonable?) So, with this value, the pressure is increased by (very roughly) 10 MPa. A kg of water (one litre) freezes to give about 1.1 litre of ice, so the change in specific volume is about 10^{-4} m^{3}kg^{-1}. The latent heat of fusion of ice is 330 kJ.kg^{-1}. So the proportional change in temperature is (10 MPa)(10^{-4} m^{3}kg^{-1})/(330 kJ.kg^{-1}), which is 0.3%. Multiply this by the melting temperature of ice (273 K) and we get an upper bound to the temperature change of around 1 K = 1 °C. So, with these values, the calculation shows that the pressure of an ice skate can reduce the melting temperature of ice by more than 1 °C. So, if this were the cause of the slipperiness, ice skating would be possible only at temperatures only one or a few degrees below freezing. From observation, it is possible to ice skate on ice at much lower temperatures than this. Unless we could argue that the area of contact of a skate is as small as 10 mm^2, this effect cannot explain why ice is slippery under a skate. On the other hand, it is easy to explain that the surface of ice is at least a little slippery. At the surface of ice, water molecules are only hydrogen bonded to their neighbours on one side. Consequently, their energy is not as low as in bulk ice. So, at equilibrium, they must have a higher entropy. So ice must have a thin water layer on the surface, whose thickness woud be expected to increase at temperatures close to melting.

The comparable calculation for boiling point change is a bit more complicated. The latent heat in this case is larger (2.3 MJ^{-1}) but the change in specific volume is much larger (typically a few times 10^{-2} m^{3}kg^{-1}). So changes in altitude can change the boiling temperature, and going up a mountain can reduce it by as much

as several degrees.

When are the boiling temperature and freezing temperature equal? What happens then?

For all substances, as we lower pressure, the boiling temperature falls much more rapidly than does the freezing temperature. (For water, the freezing temperature rises slightly at low pressure.) Hence the obvious question: Are the boiling temperature and freezing temperature ever equal?

The answer is yes. At the low pressure of 611 Pa (only 0.006 times atmospheric pressure), pure water boils at 0.01 °C, and it also freezes at 0.01 °C. The combination of conditions (P, T) = (611 Pa, 0.01 °C) is called the**triple point of water** because, at this pressure and temperature ice, liquid water and steam can coexist in equilibrium. This point is used to define our scale of temperature: by definition, the triple point of water occurs at 273.16 K, where K is the kelvin. 273.16 K = 0.01 °C

* This explains why, above, I wrote that liquid water only exists if the pressure is high enough. At pressures below 611 Pa, there are only two phases, and ice sublimes to form steam directly, without passing through a liquid phase. (In this context, the reverse of 'to sublime' is not, as one might have hoped, 'to ridicule'. At low pressures, steam condenses to form ice.)

Further complications - non-equilibrium phases

I've made a simplification above and it's time to look at it. At atmospheric pressure, pure water does not always boil at 100°C nor freeze at 0°C. **Superheating** is the term for raising the temperature of a liquid above its equilibrium boiling point. I have a page on superheating in microwave ovens because it is so dangerous.

Supercooling occurs when a liquid is cooled below its equilibrium freezing temperature. For example, water can sometimes be cooled as much as a few tens of degrees below 0°C without freezing. This phenomenon is important in cryobiology. See also What is 'unfreezable water'?

Cryobiology links

- Introduction to cellular cryobiology and some of our research in this area.
- Membranes: homeostasis and regulation of area and tension, and how this relates to survival of freeze-thaw cycles.

- Freezing in alpine forests. A collaborative study with Marilyn Ball of ANU.
- What is 'unfreezable water'?. A FAQ in cryobiology and anhydrobiology.
- What the Hydration Forces Explanation *doesn't* say. A warning about some prevalent misquotations in cellular cryobiology.
- Society for Cryobiology. The scientific society in this field.
- CryoLetters, the rapid communication journal in the field.