Ice cream making

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Answer to Question #56 ["Ice cream making," Sherwook R. Paul, Am . J. Phys. 65 (1), 11 (1997)]

Sherwood R. Paul asks for a simple explanation for the lowering of the freezing temperature of water when salt is added "in terms of familiar facts about entropy…". He also asks, if the effect is related to the fact that water expands upon freezing and, finally, if it is related to the elevation of the boiling point when adding another substance.

I shall propose a simple explanation of these phenomena but show at the same time, that an explanation only in terms of the "thermal variables" entropy and temperature is not possible.

What we need, are some facts and intuitive ideas about the chemical potential. A difference or gradient of the chemical potential μ can be understood to act as a driving force for a flow or a change of the amount of substance n. The chemical potential's role for substance currents, or n-currents, and for reactions of any kind is very similar to that of an electric potential gradient for electric currents, of a temperature gradient for entropy currents or of a velocity gradient for momentum currents.

We are concerned here with phase transitions. A substance in a phase A transforms into the same substance in phase B whenever μ_A is higher than μ_B. Sometimes a phase transition is strongly inhibited, the "reaction resistance" is very high. An example is the transition of diamond into graphite at normal pressure and temperature. In many other occasions the reaction resistance is so low, that only very slight potential differences can be sustained. Examples are the familiar phase transitions between the solid, the liquid and the gaseous phase.

Now, the existence of a well-defined phase transition temperature can be explained very simply in terms of the chemical potential. Let us take as an example the freezing and the melting of water. The chemical potentials of liquid and of solid water are both functions of the temperature, but since solid and liquid water are to be considered two different substances, these are different functions. For temperatures above the melting point

$\mu_{\text{solid}}(T) > \mu_{\text{liquid}}(T)$.

As a consequence, at such temperatures solid water will transform into liquid water. Liquid water is the stable phase. For temperatures below the melting point the contrary holds:

$\mu_{\text{liquid}}(T) > \mu_{\text{solid}}(T)$,

i.e. liquid water will transform into ice. Finally,

$\mu_{\text{liquid}}(T) = \mu_{\text{solid}}(T)$

is the condition for the coexistence of liquid and solid water, a state which chemists call chemical equilibrium. Since the “resistance” of these reactions is very low, it is not easy to realize solid water above or liquid water below the freezing temperature. There are, however well-known experiments which show that water can be “undercooled”.

To understand the lowering of the freezing temperature when adding salt to the water, we have to know in addition, that the chemical potential of any substance decreases when another substance is mixed to it. (As long as the concentration of the solute is low enough, the decrease of the chemical potential of the solvent is linear with the concentration of the solute and does not depend on its chemical nature[1].) This effect is easily seen in an osmotic cell: a container separated by a membrane into two parts. The membrane is permeable for the solvent, but not for a solute. Let us now put pure water into the left compartment, and a solution of sugar in water in the right. It is seen that the water slowly flows from the left into the right compartment, i. e. from the place where its chemical potential is high to the place where it is low.

Now, when adding salt to the liquid water of a mixture of ice and liquid water, the original quilibrium will be disturbed: the chemical potential of the liquid water decreases, that of the ice remains constant. As a consequence a potential difference builds up which drives the water from solid to liquid. In other words ice begins to melt. Only now the entropy comes into play. For the melting process entropy is needed. Since no entropy is supplied from outside, a cooling of the system results. How far does the decrease of the temperature proceed? As the temperature is decreasing, both chemical potentials, that of the liquid and that of the solid water, will increase. Since that of the liquid water increases more rapidly with the temperature than that of the solid, at a certain temperature both potentials will again be equal. The chemical equilibrium is restablished and both phases coexist again.

It is seen, that the crucial part of the phenomenon is a “chemical process”. Thus, it cannot be expected that the effect can be explained by means of thermal quantities alone. It is also seen, that the effect has the same direction for all substances. It is not related to the anomalous behaviour of water. The explanation of the elevation of the boiling point by adding salt to water is essentially the same.

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[1] H. U. Fuchs, *The Dynamics of Heat* (Springer-Verlag, New York 1996), p. 497.