

When hot water freezes before cold

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Abstract

I suggest that the origin of the Mpemba effect (the freezing of hot water before cold) is freezing-point depression by solutes, either gaseous or solid, whose solubility decreases with increasing temperature so that they are removed when water is heated. They are concentrated ahead of the freezing front by zone refining in water that has not been heated, reduce the temperature of the freezing front, and thereby reduce the temperature gradient and heat flux, slowing the progress of the freezing front. I present a simple calculation of this effect, and suggest experiments to test this hypothesis.

In a sub-freezing environment initially hot water often freezes before initially cold water. This observation is counter-intuitive because one naïvely expects the hot water first to cool to the temperature of the initially cold water, and then to follow the cooling history of the initially cold water. However, the effect has been observed many times and is folk-wisdom in many cultures; the earliest known reference is by Aristotle. It was brought to the attention of modern science by the Tanzanian high school student for whom it is now named; with admirable persistence in the face of disbelief on the part of his teachers, he insisted on the primacy of empirical evidence over theory. The history and literature are summarized by Auerbach [1].

No generally accepted explanation of the Mpemba effect exists. Apparently, pre-heating water affects its properties in a manner that accelerates its freezing. A number of mechanisms have been considered, including loss of mass by evaporation [2], the loss of dissolved gases (whose solubility in hot water is much less than in cold water) and supercooling [1].

Wojciechowski, *et al.* [3] report what appear to be the only systematic quantitative measurements of the Mpemba effect. Following a suggestion of Freeman [4], they also measured the freezing of water saturated with CO₂. Unfortunately, they did not describe the ionic content of their water, which is likely to be essential.

Auerbach [1] found substantial (several degrees) but non-reproducible supercooling in both preheated and non-preheated samples. As a result, some of his data showed an Mpemba effect while some did not. His experiments were performed on distilled and de-gassed water, and may therefore not be applicable to observations of the Mpemba effect in tap water or environmental water (Mpemba's observations were on sugared milk he was freezing to make ice cream!).

The observations clearly point to some change in water when heated. As has been remarked before, heating water removes dissolved air (chiefly nitrogen) because its solubility decreases rapidly with increasing temperature. The problem is to find a mechanism by which the removal of a small quantity of dissolved material (the solubility of nitrogen in water at room temperature is only about 0.7 mmolar/bar) can produce a Mpemba effect.

Gases are not the only substances whose solubility in water decreases with increasing temperature. Most natural waters are "hard", containing a variety of dissolved mineral salts, most importantly calcium bicarbonate Ca(HCO₃)₂. This is introduced into ground water that has been acidified by atmospheric carbon dioxide by the reaction in limestone

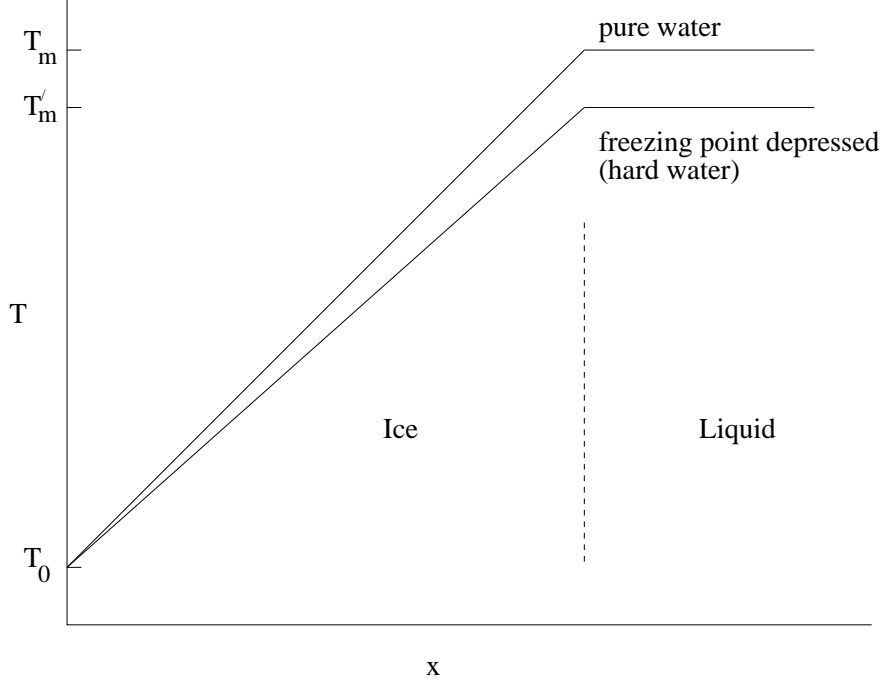


FIG. 1: Temperature profiles, neglecting specific heat in comparison to latent heat. T_m is the freezing point of pure water, $T'_m < T_m$ that of hard water, lowered by freezing point depression. Its temperature gradient and heat flux are reduced, so the freezing front advances more slowly than in water purified by heating.

rock [5]



Because the solubility of gases in liquids decreases rapidly with increasing temperature, heating shifts the equilibrium to the left, resulting in the precipitation of limestone deposits known as “boiler scale” or “kettle fur”. For this reason, hardness resulting from bicarbonates is known as “temporary hardness” [5]. Hard water that has been heated loses much of its dissolved calcium. Hence the freezing point T'_m of never-heated hard water is lower, because of the depression of freezing points by solutes [6], than the freezing point T_m of hard water that has been heated. For the same thickness of the ice layer, the temperature gradient and heat flux are less in the never-heated water, so it takes longer to lose the latent heat of freezing and freezes more slowly. This is illustrated in Fig. 1.

The concentration of dissolved calcium in moderately hard tap water is about 100 ppm, or 2.5 mmolar, but values several times greater or less are found. Each Ca^{++} ion corresponds to a total of three dissolved ions, so such a solution has a total ion concentration of 7.5 mmolar.

The freezing point depression of ideal dilute aqueous solutions [6] is $\Delta T_m = RT_m^2/H_m = 1.86^\circ\text{C}/\text{molar}$, where R is the gas constant and H_m the enthalpy of melting. The effect of hardness is typically ten times greater than that of dissolved air, but still rather small without further concentration.

The equilibrium ratio of the concentration of a solute in a solid to that in its melt is the Nernst equilibrium distribution coefficient k_0 [6]. For most solutes in water and ice $k_0 \ll 1$; they are almost completely excluded from the solid. As a freezing front advances into water the solutes are pushed ahead of it, and their concentration close to the front is enhanced over its initial value in the liquid, a process known as zone refining [7].

The conventional theory of zone refining [8] assumes a stationary state with a boundary condition that the concentration of solute equals its initial concentration in the liquid at a finite distance from the freezing front. This latter condition is appropriate when there is driven fluid circulation outside a viscous boundary layer of thickness δ . In the present problem there is no circulation and $\delta \rightarrow \infty$. Worse, in the limits $k_0 \rightarrow 0$ and $\delta \rightarrow \infty$ this solution becomes singular because in steady state the solute from an infinite volume of fluid must accumulate in a finite region of enhanced concentration.

Our problem corresponds to the low concentration limit of the theory of the freezing of binary melts [9], in which the progress of the freezing front is controlled by diffusion of heat. Mathematically, it is a ‘‘Stefan problem’’ in which the boundary condition is moving. We neglect the specific heats of the liquid and solid in comparison to the latent heat of the phase transition. Then the liquid is isothermal and there is no thermal diffusion of the solute within it.

The freezing front advances at a nonsteady speed $v_f(t) = \sqrt{(T_m - T_0)\kappa/(2H_m\rho_i t)}$ [10], where T_m is the melting temperature, $T_0 < T_m$ is the subfreezing boundary temperature, κ is the thermal conductivity and ρ_i the density of ice, and t is the time elapsed since freezing began. The equation for the conservation of solute concentration $C(x, t)$ in the liquid, in a frame moving with the freezing front, is

$$\frac{\partial C(x, t)}{\partial t} + v(t)\frac{\partial C(x, t)}{\partial x} - D\frac{\partial^2 C(x, t)}{\partial x^2} = 0, \quad (2)$$

where $v(t) = -v_f(t)\rho_i/\rho_l$ is the velocity at which liquid flows to the freezing front and D is the diffusion coefficient of solute in the liquid.

Both the diffusion length \sqrt{Dt} and the frozen layer thickness $\int v_f(t) dt$ are proportional

to $t^{1/2}$. Hence the solution is stationary in suitable variables. Defining $\zeta \equiv x/\sqrt{Dt}$ [11], we obtain the separable equation

$$t \frac{\partial C(\zeta, t)}{\partial t} - (K_M + \frac{\zeta}{2}) \frac{\partial C(\zeta, t)}{\partial \zeta} - \frac{\partial^2 C(\zeta, t)}{\partial \zeta^2} = 0, \quad (3)$$

where the dimensionless parameter $K_M \equiv \sqrt{(T_m - T_0)\kappa\rho_i/(2H_m\rho_l^2 D)}$. The value of D for $\text{Ca}(\text{HCO}_3)_2$ in water is not readily available, so we take the values [12, 13] for CaCl_2 as estimates and extrapolate to 0°C , giving $D \approx 0.6 \times 10^{-5} \text{ cm}^2/\text{sec}$. Then $K_M \approx 7\sqrt{(T_m - T_0)/10^\circ\text{C}}$.

Writing $C(\zeta, t) = C_\zeta(\zeta)C_t(t)$, we find ordinary differential equations for $C_\zeta(\zeta)$ and $C_t(t)$ with a separation constant A :

$$\frac{d \ln C_t(t)}{d \ln t} = A \quad (4)$$

$$\frac{d^2 C_\zeta(\zeta)}{d\zeta^2} + (K_M + \frac{\zeta}{2}) \frac{dC_\zeta(\zeta)}{d\zeta} - AC_\zeta(\zeta) = 0. \quad (5)$$

For $K_M \gg 1$ and $\zeta = \mathcal{O}(1)$ we can neglect the $\zeta/2$ term and the solution is elementary. From the conservation of solute (and $k_0 \rightarrow 0$) we find $A = 0$. The equation for $C_\zeta(\zeta)$ has solutions $C_\zeta(\zeta) \propto \exp(\gamma\zeta)$ with $\gamma = 0, -K_M$. The root $\gamma = 0$ gives the uniform solute density far from the freezing front, while the root $\gamma = -K_M$ gives the enhanced concentration of solute close to the front:

$$C_\zeta(\zeta) = C_0[1 + 2K_M^2 \frac{\rho_l}{\rho_i} \exp(-K_M\zeta)]. \quad (6)$$

This justifies the neglect of the $\zeta/2$ term to $\mathcal{O}(K_M^{-2})$.

The concentration at the freezing front is enhanced by a factor $\approx 100(T_m - T_0)/10^\circ\text{C}$. The fractional freezing point depression

$$\frac{\Delta T}{T_m - T_0} = \frac{RT_m^2 \kappa}{H_m^2 \rho_l D} C_0, \quad (7)$$

where C_0 is the concentration in moles/cm³, independent of time and of T_0 . For $\text{Ca}(\text{HCO}_3)_2$ in water the coefficient of C_0 is 20/molar so an ion concentration of 5 mmolar (67 ppm calcium) produces a 10% reduction in freezing rates compared to pure (once heated) water.

Wojciechowski, *et al.* [3] reported an apparent increase of H_m of CO_2 -saturated water of $10 \pm 4 \text{ cal/gm}$. This is not likely to be an actual change in H_m , but may reflect a reduction of the freezing point at the freezing front of $10 \pm 4^\circ\text{C}$, requiring the removal of additional internal energy before freezing begins. Application of the theory presented here predicts

that for water saturated with respect to CO_2 at 1 bar pressure at room temperature (33 mmolar CO_2) and $T_m - T_0 = 23^\circ\text{C}$ [3] the freezing point depression at the front is 10°C , consistent with the apparent increase in H_m . These authors found an Mpemba effect only in water that had not been degassed by boiling, which is consistent with the removal of temporary hardness, even though dissolved air itself is predicted to produce only a small Mpemba effect.

Our model makes readily testable predictions for the dependence of a Mpemba effect on the concentration of solutes whose solubility decreases with increasing temperature. It also predicts no Mpemba effect, but a dependence of freezing time on concentration, for solutes whose solubility does not decrease with increasing temperature. It predicts that the magnitude of freezing point depression and of the effect (having subtracted the time required for the solutions to cool to the freezing point) should be independent of the thickness of ice formed. In this model an Mpemba effect occurs in the time required for formation of an ice layer of any thickness, and hence is found for the onset of freezing as well as for complete solidification. Fully quantitative predictions require modeling of heat transfer through the air boundary layer.

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