Hot water will <u>sometimes</u> freeze faster than colder water.

James D. Brownridge

Ooooh!!! Yes!! It Is True!

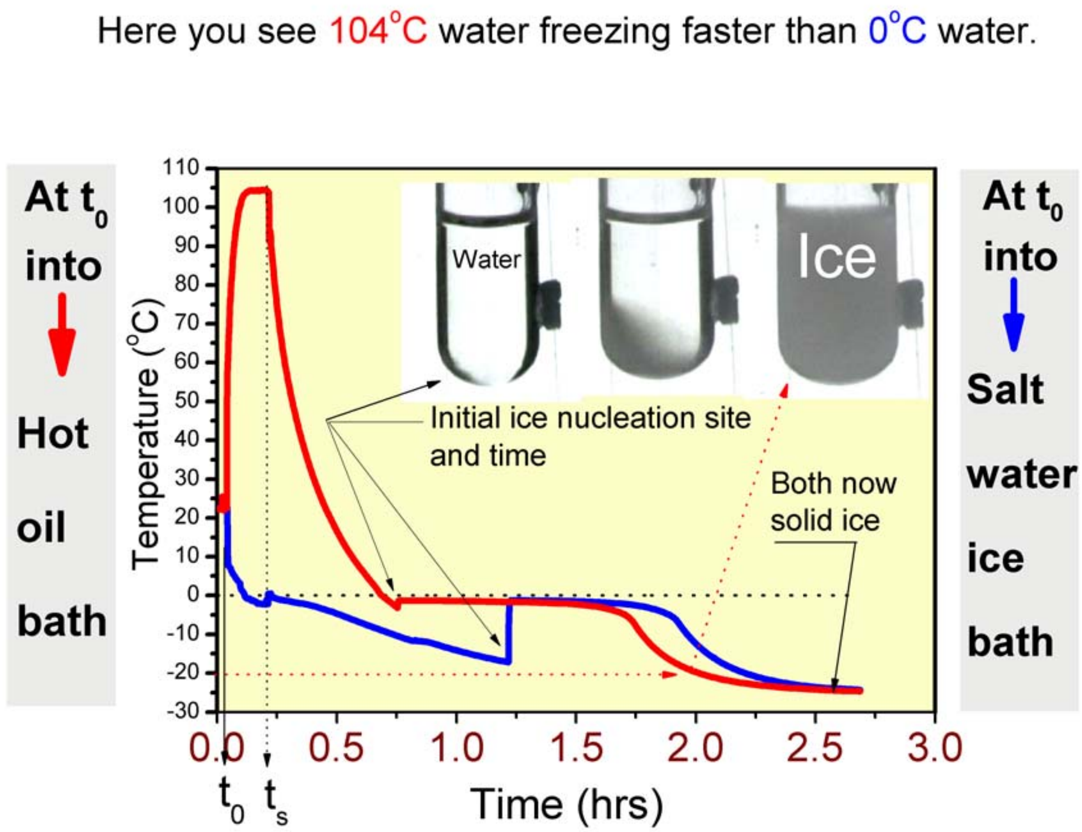

Fig. 1. In this experiment I chose two vials both at room temperature. At $\mathbf{t_0}$ one vial was inserted into a heating bath and other into a cooling bath. At $\mathbf{t_s}$ they were removed and suspended in a freezer to air cool. As you can see the hot vial froze first. Is this magic? Is this a trick? Let's try a different set of vials. As you can see in Fig. 2 below, in one case the hot vial froze first and in the other the cold vial froze first. What's going on here? The time-lapse photo inset of water freezing in a vial is a typical example of the freezing process.

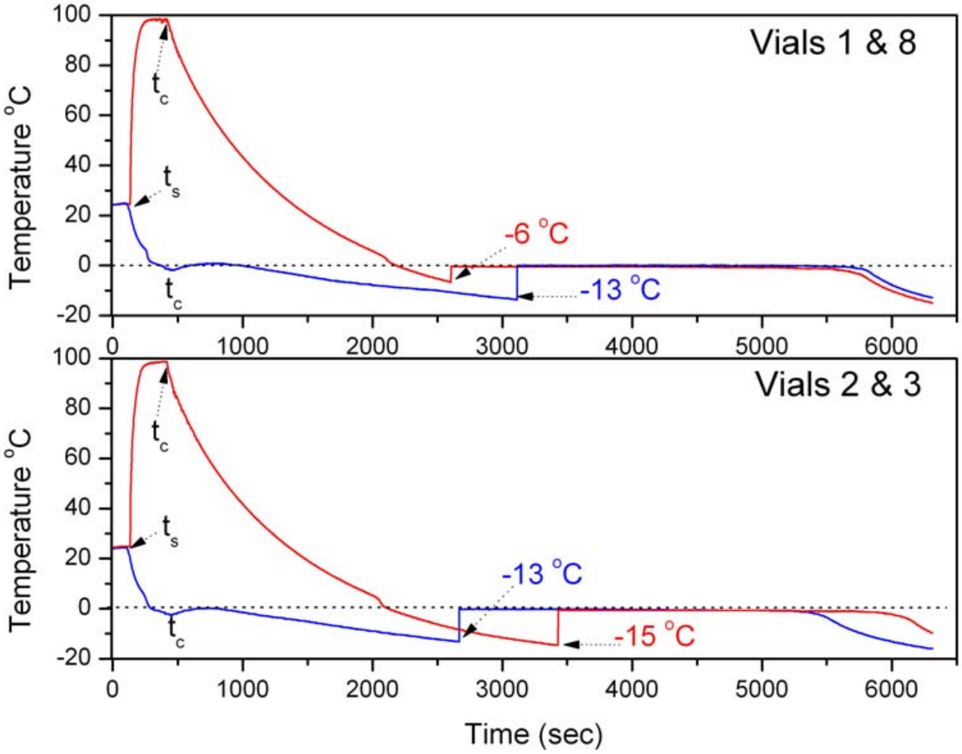

Fig. 2 The results presented in these figures have been repeated with many different "kinds" of water: hard tap water, soft tap water, double distilled water, ultra-pure water, and pond and river water. Unless samples are pre-selected* before testing, the results will be about 50-50 that the hot water will begin freezing first for a large number of tries with **closed or sealed** containers. **This is assuming that all physical conditions except initial temperature are the same for both samples.** *We will talk about pre-selection later.

Why does hot water freeze faster than cold water?

Introduction:

Assume that we have two containers that are identical with equal volumes of water from the same source: yes, **sometimes** the hotter one will freeze faster. **This occurrence is purely by chance.** Several unknown conditions must be met during the preparation of the containers and the selection of the water for this to happen.

When the temperature of frozen water is raised from a temperature that is less than 0^oC it will **always** begin melting when its temperature reaches 0^oC. However, when **still** water is cooled from a temperature above 0^oC it will **usually not** begin freezing when its temperature reaches 0^oC, it will continue cooling. This **asymmetry**, along with "**ice nucleation agents or sites"** (impurities) in water, is why hot water will sometimes freeze faster than cold water even when all known conditions are identical except the initial temperature. Only under very specific controlled conditions (described below) will hot water **always** freeze faster than cold water.

In the case of moving or running water, aggregation of water molecules is the catalyst that generates the open, crystal-like structure that forms the seed for **ice nucleation** and freezing at 0^oC. That is why when one shakes or pours supercooled water, its temperature spontaneously rises to 0^oC and the water begins freezing. In the case of **outdoor frost**, it is most likely biological **ice nucleation** agents, such as bacteria, that are the catalysts.[1] For open containers in a freezer it is most likely microscopic ice crystals (**freezer frost**) that is the catalyst.[2]

In order to observe hot water freezing **consistently** faster than cold water one needs to place equal volumes of water into 10-20 vials or containers, more may be needed. The water should come from a common source; tap or bottled water will do. Seal the vials or containers, and then heat them in a boiling water bath for about 30 minutes. This will **"fix"** the **"ice nucleation agents or sites**". After they cool, determine the temperature at which each vial or container will release latent heat and begin freezing.[2,4] See figs. 2 and 5 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf. Select the two vials or containers that show the largest temperature difference. If the difference is greater than 5^oC and you heat the one with the lowest "start of freezing" temperature it will freeze first. If the temperature difference is much less than 5^oC then the cold water will freezes first.

"Heating water may lower, raise or not change the spontaneous freezing temperature".[4] However, when heating does lower the "ice nucleation temperature" the hot water will most likely not freeze first. See fig. 19 on page 11 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf, for examples of how heating may change the start of freezing temperature. Notice that the temperature at which freezing began changed in some of the vials after heating. That is why I suggest heating the water samples first if the object is to observe hot water freezing first **consistently**.

When the conditions under which the water samples are cooled are not carefully controlled for an array of variables; I find that there are three secondary reasons and one primary reason why hot water will freeze faster. **Controlling variables cannot be overstated**; Jeng discusses variables in a review article.[3] The one variable that is virtually impossible to control for is the nature of the impurities in water. **Ultimately, it is impurities that determine at what temperature still water in a sealed or closed container will begin freezing**. In order to confirm that this is indeed the case I put 4 vials of tap water into a cold bath at -15^oC, one degree above the previously determined highest "start of freezing" temperature of any of the vials. Three of the vials remained unfrozen for 422 days.[2] The loss of (AC) power ended the experiment. Upon the return of

(AC) power the temperature of the bath was lowered to below -18°C. All four vials began freezing between about -15.5°C and -17°C.

Reasons:

Secondary reason 1: **Better thermal contact**

Better thermal contact can results in hot water loosing heat faster and therefore freezing before cold water under certain conditions.[4] The hot water containers will often make better thermal contact with the cooling environment because the hot container **melts more freezer frost than the cold container.** When the melted freezer frost re-freezes under the containers the results is often a faster flow of heat from the container that is in better thermal contact with the freezer, this will usually be the hot container. The so call "frost free freezers" are not truly frost free all of the time. See Fig. 4 in Am. J. Phys., Vol. **79**, 78-84 (2011) page 80. Also Fig. 9 on page 7 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf **. If all other physical conditions are equal, except temperature, a better thermal contact with a colder surface is the only reason that hot water will cool to 0°C before cooler water.**

Secondary reason 2: **Supercooling**

"On those occasions where the cold water supercools sufficiently more than the hot the Mpemba scenario is the following: The hot water supercools, but only slightly, before spontaneously freezing." **David Auerbach.** [5] This was confirmed conclusively.[2,4] See Fig. 4 below.

Newton's law of cooling tell us that if two containers of water are identical in every way except the initial temperature and are suspended in the same cooling environment the hot container **can not** cool to 0°C before the cold one does. (See Fig. 3) The hotter it is the longer it will take to cool to 0°C. See Fig. 3 in Am. J. Phys., **78**, page 79. See also Fig. 14 on page 38 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf .

If it is assumed, as I believe it is by many, that water necessarily begins freezing when its temperature is lowered to 0°C, then Newton's law of cooling tell us that hot water will never freeze first. My belief is in part based on a statement by Monwhea Jeng.[3] *"If the initially hotter water is at 99.9999 °C and the initially colder water is at 0.0001 °C, then the initially cold water is just seconds away from freezing, and the hot water cannot possible overtake it"*. **However, it is well documented that still water in a freezer will almost always supercool several degrees below 0°C before latent heat is released and the temperature of the water rises to 0°C and freezing begins**.[2,5,6,7] Therefore, in order to "get around" Newton's law of cooling and for the hot water to freeze first, the cold water **must** supercool. **This is assuming better thermal contact is not a factor.** The loss of water by evaporation does not play a detectable roll in the process.[4] However, it does add to the production of freezer frost. The key is how deeply the cold water supercools. See Figs. 11 and 13 on page 8 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf . Here hot water could and did evaporate as the waters cooled. The results were similar to results obtained in sealed containers.

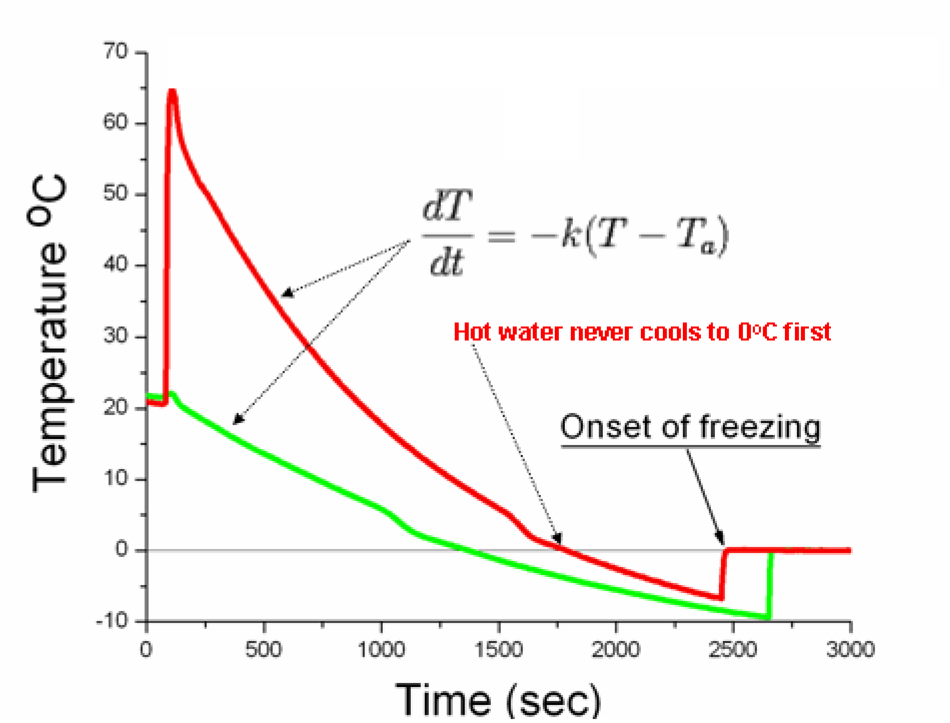

Fig. 3. Two containers of water were suspended in a cooling environment so that they would air cool and freeze. They were identical in every way except the initial temperature of the water. The result was as expected the coolest water cooled to 0°C first. The hot water can cool to 0°C first only if the physical conditions are not identical. (i.e. better thermal contact)

Secondary reason 3: **Impurities**

Impurities are found in all bulk water and bulk water containers, no matter how pure or clean the water is.[6] This is why bulk water can not be cooled to the heterogeneous nucleation temperature of approximately -40°C.[6,7] The agents are usually in the water while the sites may be affixed to the inside of the containers.[2,4,6,7] These sites or agents all have **unique** temperatures at which they will **interact** with water molecules causing them to change into a more open, crystalline like structure that becomes a seed for ice nucleation and freezing. **The site or agent with the highest "ice nucleation temperature" determines at what temperature a sample of**

still water in a closed container will begin freezing. See Figs. 9 and 10 on pages 35 and 36 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf . **Notice** how reproducible the **ice nucleation temperature** was until a **new** "ice nucleation site" was produced at a fracture site in the glass vial, Fig. 10. **Notice** also that this new site has a **higher** "ice nucleation temperature" and that the water begins the freezing process at this **higher temperature**. Figure 8 on page 34 in the same paper shows an example of ice nucleation occurring near the top of the water in a vial.

***Primary reason:** **Depth of supercooling of the colder water**

When hot water freezes faster than cold water, and all conditions are identical except initial temperature, the cold water always supercools to a much lower temperature than the hot water. Hot water will **consistently** freeze before cold water **only** when the cold water supercools to a much lower temperature than the hot water, at least ~5.5°C.

Conclusions:

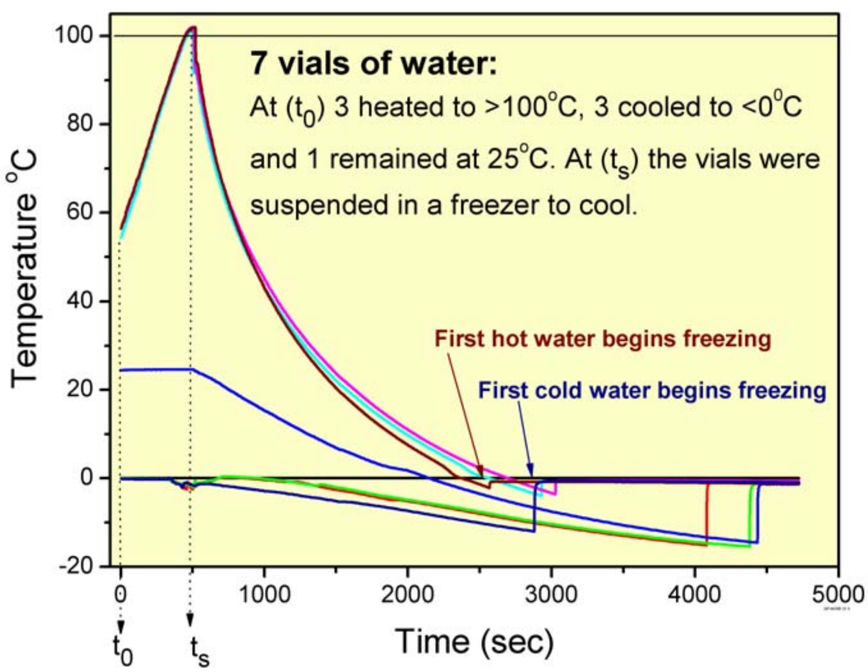

Fig. 4. Here we show that it is the depth of supercooling that determines which water sample freezes faster.

The fundamental property of water that permits hot water to **sometimes** freeze faster than cold water is supercooling.

Observing hot water freeze faster than cold water is usually a **chance occurrence** which until now could not be repeated on demand. That is why the mystery has survived for more than 2000 years.

I was able to succeed in observing hot water freeze faster than cold water 28 times, consecutively. This can only be observed when the water samples are in **closed** containers and pre-selected as discussed above.

If your object is to freeze a container of water quickly, then placing an **open container** of hot water on a bed of freezer frost is a very good idea. The hot water will most likely cool to 0^{o}C before a container of cooler water because of better thermal contact with the cold surface. Microscopic ice crystals (freezer frost) forming in the air and on the containers will be the seed crystals that starts the freezing process in the first water sample that cools to 0^{o}C. However, if both containers are placed on thermal insulators, then the colder water will freeze first because it will always cool to 0^{o}C first. Put a lid on the containers and it will be **seeds already in the water and or containers that will determine which freeze first not necessarily the first one to cool to** 0^{o}C. See figs 9 and 10 on page 7 in a paper posted at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf.

1. References:

1. B. C. Christner, C.E. Morris, C. M. Foreman, R. Cai, and D. C. Sands, "Ubiquity of biological ice nucleators in snowfall," Science **319**, 1214 (2008).

2. J. D. Brownridge, "When does hot water freeze faster then cold water: A search for the Mpemba effect," Am. J. Phys. **78**, 78-84 (2011). http://ajp.aapt.org/resource/1/ajpias/v79/i1/p78_s1?view=fulltext.

3. M. Jeng, "Hot water can freeze faster than cold," Am. J. Phys. **74**, 514-522 (2006). http://ajp.aapt.org/resource/1/ajpias/v74/i10

4. Supplementary information can be found at: http://arxiv.org/ftp/arxiv/papers/1003/1003.3185.pdf and http://www2.binghamton.edu/physics/people/james/index.html

5. D. Auerbach, "Supercooling and the Mpemba effect: When hot water freezes quicker than cold," Am. J. Phys. 63, 882-885 (1995). http://ajp.aapt.org/resource/1/ajpias/v63/i10

6. N. E. Dorsey, "The freezing of supercooled water." Trans. Am. Philosophical Society **38**, 247-328 (1948).

7. C. A. Angell, "Supercooling water," Am. Rev. Chem. **34**, 593-630 (1983).