# Mpemba effect explanation

We use pure natural mineral water in salts; therefore, we can assume that the affection of the dissolved ions is negligible. Water molecules are V-shaped electric dipoles. Cold water has a rudimentary "structure," where in these dipoles are positioned and oriented next to one another such that their opposite charges are face to face. They are joined by hydrogen bonds:

Each water molecule can form two hydrogen bonds involving their hydrogen atoms plus two further hydrogen bonds utilizing the hydrogen atoms attached to neighboring water molecules. These four hydrogen bonds optimally arrange themselves tetrahedrally around each water molecule as found in ordinary ice. In liquid water, thermal energy bends and stretches and sometimes breaks these hydrogen bonds. However, the 'average' structure of a water molecule is similar to this tetrahedral arrangement [1].Today tetrahedrally-coordinated water seems most accepted, but the hydrogen bonded arrangement of most molecules is not such symmetrical. At room temperature, 80% of the molecules of liquid water have one strong hydrogen bonded O-H group and one non-, or only weakly, bonded O-H group at any instant, the remaining 20% of the molecules being made up of four-hydrogen-bonded tetrahedrally coordinated clusters. A typical 'average' cluster consists of five water molecules. In the ice this tetrahedral clustering is extensive, producing crystalline forms. In liquid water, the tetrahedral clustering is only locally found and reduces with increasing temperature. In bulk water at any instant, it is expected that strong tetrahedrally-placed hydrogen bonds form a network (mesh), plus a smaller amount of isolated pockets of weakly or broken hydrogen bonded water molecules [1].When water is heated, the hydrogen bonds break and the molecules move far away from each other and get randomly repositioned. As a result, the structure collapses. The percentage of water molecules joined by hydrogen bonds decreases [2].The breaking of the bonds and the resulting increase in the disorder of the water molecules leads to increased entropy (S).The increase in entropy (dS) after the water is heated from a lower temperature T_1 to a higher temperature T_2 can be calculated as:

$$dS = mc\ln(T_2/T_1), \qquad m = \text{water mass}, \quad c = \text{specific heat}$$

However, the structure does not reconstruct itself immediately upon cooling; the reconstruction needs time. If the water is cooled in a powerful freezer, water molecules do not get sufficient time for restructuring because the cooling process is too fast. In contrast, when the water is cooled in a fridge where a stable temperature of 5 ℃ is maintained, water molecules get sufficient time to rearrange in order. When the water is cooled to an initial low temperature, a structure does not instantaneously form, or in other words, its entropy does not immediately decrease. During the cooling process, water's structure does not instantaneously return to the ordered condition, as hydrogen bonds do not form instantly. The entropy reduction curve as a function of temperature S=f(T) appears to lag, relative to the entropy growth curve. At any temperature point T, the entropy during heating S_h is less than the entropy during cooling S_c.

T

0

S_h S_c S
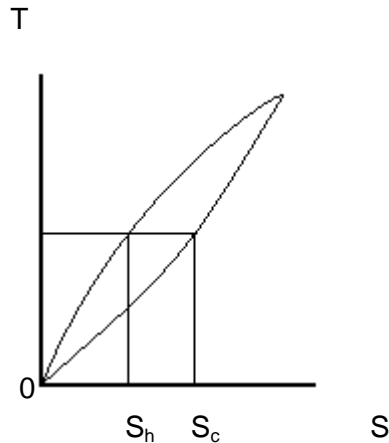
The water, having been heated and then cooled to the starting temperature, now has more entropy and fewer hydrogen bonds than it did immediately prior to heating, even though the temperature is now the same. At any temperature T, the heat capacity mc=S/lnT upon cooling is greater than it is upon heating. Thus, the specific heat coefficient is larger in the former case.

Consider two jars, A and B, each containing an identical quantity of water at the same temperature (T), but one (A) has more entropy than the other (B). This means that the water molecules of both jars have the same energy, but those of jar A are moving in all directions, whereas the thermal motion of those in jar B is restricted by the network mentioned above. Therefore, in the case of jar A, random collisions are more likely than in the case of jar B. Because of these random collisions, the water molecules lose more average kinetic energy (E), which results in a reduction in the temperature according to the relationship: $E=(3/2)bT$, b=Boltzmann constant. Therefore, water in jar A cools faster than the water in jar B.

According to Newton's Law of Cooling, during the cooling of a material body, the rate of temperature decrease is proportional to the temperature (T):

$$dT/dt = -kT \implies T=T_0 e^{-kt}$$

t=time, k=coefficient of temperature change, T_0=initial temperature

half time period (HTP) = ln2/k

In an experiment, we simultaneously put into a freezer three bottles, A, B, and Γ, each containing the same quantity of water. The temperature of the water in bottle A was 50 °C, and in B and Γ it was 25 °C. The water in bottle B was at ambient tem perature. The water in bottle Γ was heated to 50 °C and then cooled down to 25 °C. After 1.5 hour s, we observed that the water in bottles A and Γ simultaneously reached 2 °C earlier than B. A and Γ followed the same process. The coefficient k is the same for both A and Γ, and is larger than that of B. The halftime period is the same for both A and Γ, but lower than that of B.

The experiment was conducted at the laboratory of the Argolida Regional Quality Control Center. The lab meets the requirements of the standard ISO/IEC 17025:2005 since 2009(Accreditation Body: ESYD S.A., certificate number: 609).

Commercial PET bottles, of 500 mL volume, were filled with 500.00g of distilled water produced by the lab's distiller (Bibby Sterilin model D4000). The water of Γ was warmed up to 50 °C and left to cool down to 25 °C. Water A was warmed up to 50 °C. Immediately afterwards, the water was poured into the bottles. The bottles were then immediately put into a freezer and cooled to 2 °C. The procedure and results are shown in the table below:

sample	average weight (g)	freezing duration (min)	standard error (min)
Γ	500,006	82	1
B	500,001	90	2
A	500,003	81	3

Number of samples=10 per type (total 30).

The experimental results data are presented in more detail in the table below:

					data						average	sd
A	84	84	83	83	82	80	79	78	78	78	80,9	2,6
B	92	92	92	91	90	89	88	88	88	88	89,8	1,8
Γ	83	83	82	82	82	82	81	81	81	81	81,8	0,8

The averages were compared with the F test results. First, the B average (B_{av}) was compared with the A and Γ averages ($=(A_{av} + \Gamma_{av})/2$) to check whether the preheating affects the cooling duration. Afterwards, the averages of A_{av} and Γ_{av} were compared to check if they were equal.

For the first case, the F value F_1 was estimated to be 136,8 and the F tables with a significance level of 0.1% gave F=13.6 << F_1, showing that the prewarming of water strongly affects the cooling duration.

For the second case, F_2 was estimated to be 1.16, which is significantly less than 13.6 (F_1), which gives rise to the following: $A_{av} = \Gamma_{av}$.

Any dissolved salts present in the water can affect the structure of the water molecules, because the ions are hydrated. Consequently, the network is smaller, and the molecules are less organized than in pure water. Hence, the intensity of the phenomenon decreases.

REFERENCES

1. Chaplin. M., (2011) The water molecule, liquid water, hydrogen bonds and water networks, In *Water The forgotten biological molecule*, D. Le Bihan and H. Fukuyama, Ed. Pan Stanford Publishing Pte. Ltd., Singapore, pp. 3-19.
2. Pettersson LGM, Nilsson A, 2015, The structure of water; from ambient to deeply supercooled *Journal of Non-Crystalline Solids* **407** 399-417."

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