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Explanation for the Mpemba Effect

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Abstract

Water molecules are oriented dipoles joined by hydrogen bonds. When water is heated, this structure collapses (*i.e.*, the entropy increases). When water is re-cooled to a lower temperature, the previous structure is not re-formed immediately. Sometimes, when the re-cooling is performed within a freezer, there is not enough time for the structure to re-form because of the high cooling rate. The entropy reduction curve as a function of the temperature, $S = f(T)$, shows retardation (a lag) relative to the entropy growth curve. Water that has been heated and re-cooled to the initial temperature shows greater entropy than that before it was heated. This means that, while its molecules now have the same kinetic energy, their thermal motion after heating is less oriented with respect to the structure mentioned above. After re-cooling, random collisions are more likely, owing to this the temperature decreases more quickly.

Keywords

Entropy, Water, Specific Heat

1. Introduction

This case study proposes an explanation for the Mpemba effect, which is considered as the phenomenon wherein, under uncertain conditions, hot water freezes faster than cold water. The fact that the water has been warmed previously contributes to its rapid freezing. Hence many people, when they want to cool water quickly, begin by placing it in the sun. Named after Erasto Mpemba in 1963 [1], the Mpemba effect was reported by Aristotle, Bacon, and Descartes and has been discussed widely in both research as well as popular scientific journals [2]. Auerbach claims that it is different from the supercooling effect [2], but Brownridge argues that it is actually the same [3]. A latest study (2016) [4] totally disputes the phenomenon, although a more recent study [5] shows that the effect is present in granular fluids.

The explanations that have been suggested can be divided in two general categories. The first one, which for ease can called "physicals", includes theories like these: evaporation [6], frost [7], conduction [8], solutes [9], supercooling [10]. Second category, called for ease "chemicals", includes theories involving hydrogen bonds like these: crystallization [11] and hydrogen bonding [12]. But, the main query remains unanswered: Why does not the effect always occur?

In this study, this unique effect is defined as the phenomenon wherein, under certain conditions, hot water cools faster than cold water that is, it reaches faster a temperature point close to 0˚C: this perspective is adopted by Lasanta *et al.* [5], and described based on macroscopic parameters. Further, the underlying mechanism responsible for the effect is proposed and the randomness of the phenomenon is explained.

Let us consider two jars, A and B, with each containing an identical quantity of water at the same temperature (T), such that the water in A has more entropy than that in B. This means that the water molecules of both jars have the same energy; however, those in jar A are moving randomly in all directions, whereas the thermal motion of those in jar B is restricted by the structure mentioned above. Therefore, in the case of the water sample in jar A, random collisions are more likely to occur than in the case of the sample in jar B, resulting in the water molecules losing more kinetic energy (E) on average. This results in a reduction in the temperature according to the relationship $E = (3/2)bT$, where b is the Boltzmann constant. Therefore, the water in jar A cools faster than that in jar B.

Convection is the dominant form of heat transfer in liquids. According to Newton's law of cooling, during the cooling of a material body, the rate of temperature decrease (cooling rate = q) is proportional to the temperature (T):

$$q = \mathrm{d}T/\mathrm{d}t = -hT \Rightarrow T = T_0 \mathrm{e}^{-ht} \tag{1}$$

where t is the time, h is the heat transfer coefficient, and T_0 is the initial temperature. The half-time period (HTP) is equal to $\ln 2/h$. The greater the value of h, the higher is the cooling rate, so q is more likely to cause Mpemba effect: this is my aspect discussed below in Discussion Section. Heat transfer coefficient is dependent upon the physical properties of the water and the physical situation. However, h is affected by many factors such as the container's shape and material and the air circulation within the freezer, among others. For example, Equation (2) applies to a PET bottle assuming a planar geometry [13]:

$$h = \left(1/h_1 + \delta/k + 1/h_2\right)^{-1} \tag{2}$$

h: overall heat transfer coefficient;

h_1: heat transfer coefficient inside the bottle;

h_2: heat transfer coefficient outside the bottle;

δ: PET layer thickness;

k: PET thermal conductivity.

Thus, the Mpemba effect is hard to predict and is not observed in every instance.

2. Method

An experiment was performed to elucidate the effect of preheating on the cooling duration, wherein three bottles, A, B, and C, each containing the same quantity of water, were placed in a freezer with an internal temperature of −18˚C. The temperature of the water in bottle A was 50˚C while that of the water samples in B and C was 25˚C. The water in bottle C was first heated to 50˚C and then cooled to 25˚C. After 1.5 h, it was observed that the temperature of the water samples in bottles A and C reached 2˚C sooner than that for the water in B. It is likely that samples A and C followed the same cooling process; that is to say, the coefficient h was the same for both A and C, while it was larger for B. The HTP for both A and C was the same and lower than that of B. This experiment was conducted at the laboratory of the Nafplio Regional Quality Control Centre, which had met the requirements of the standard ISO/IEC 17,025: 2005 since 2009 (accreditation body: ESYD S.A., certificate number: 609).

Commercial PET bottles with a volume of 500 mL were filled with 500.00 g of distilled water produced by a distiller (Bibby Sterilin, model: A 4000D, conductivity of water: 1 - 2 μS/cm). The ambient temperature within the laboratory was adjusted to 25˚C. The water in bottle C was heated to 50˚C in a Pyrex glass using a hot plate and then left to cool to 25˚C. The water in bottle A was heated to 50˚C. The water was poured immediately into the bottles, which were at the ambient temperature. The sensors (pins) of the digital alert thermometers used for the temperature measurements were inserted from the top to the middle of the bottles. With no relaxation time, the bottles were capped then immediately placed in a freezer and cooled to 2˚C (Figure 1).

Digital alert timers were used to measure the duration time. Measurements were carried out under the plan one bottle per day. Initial conditions are kept

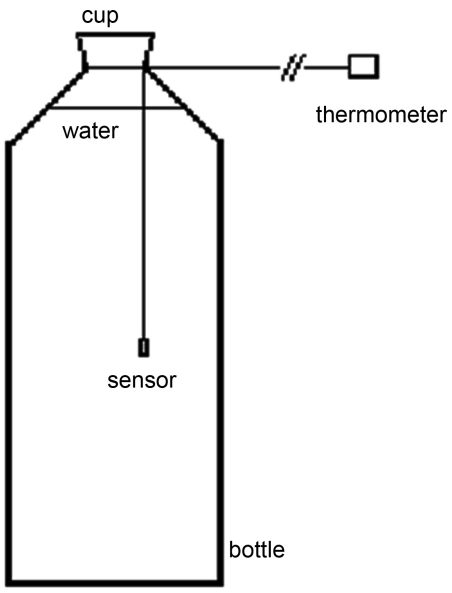

Figure 1. Experimental layout.

the same in the different repeated runs. The experimental results are shown in Table 1.

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

The experimental results are presented in more detail in Table 2 arranged in descending order.

Data are illustrated in Figure 2.

The average values were compared using the F test. First, the average value of the B samples (Bav) was compared with those of samples A and C ((Aav + Cav)/2), in order to check whether preheating affected the duration of cooling. Next, Aav and Cav were compared to determine whether they were equal within the limits of experimental uncertainty. In the first case, the F value, F1, was calculated to be 136.8. Further, the F tables with a significance level of 0.1% gave F = 13.6 ≪ F1, showing that the preheating of the water strongly affected the cooling duration. In the second case, F2 was calculated to be 1.16, which is significantly less than 13.6 (F1). This meant that Aav = Cav.

Table 1. Average weight and cooling duration.

Sample	Average weight (g)	Cooling duration (min)	Standard error (min)
C	500.006	82	1
B	500.001	90	2
A	500.003	81	3

Table 2. Cooling duration.

	Time (min)										Average	S.D.
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
C	83	83	82	82	82	82	81	81	81	81	81.8	0.8

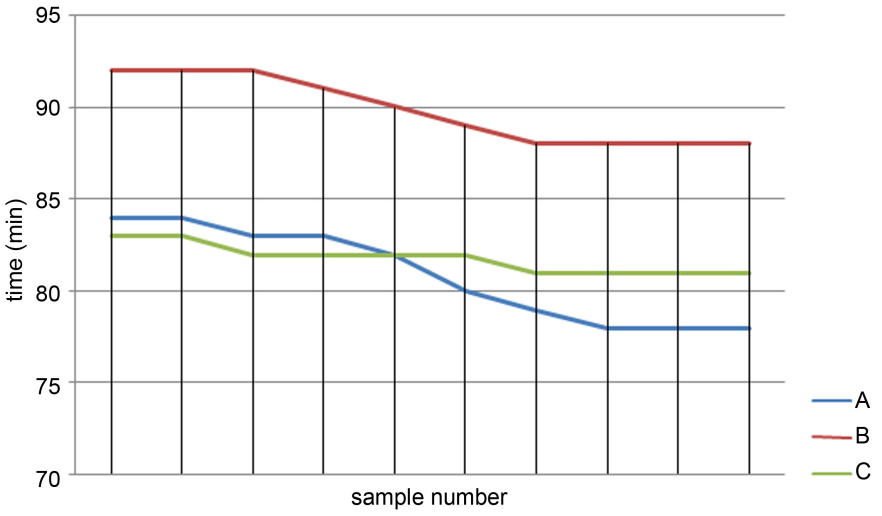

Figure 2. The three processes.

3. Discussion

Water molecules are V-shaped electric dipoles. Cold water has a rudimentary structure, hereinafter referred to as simply the "structure". The structure consists of intermolecular cyclic associates (clusters) of water with the general formula $(H_2O)n$ [14]. The ordering of water molecules into associates corresponds to a decrease in their entropy (randomness) [14]. 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 in a tetrahedral structure around each water molecule, as observed in ordinary ice [15]. In liquid water, thermal energy can cause these hydrogen bonds to bend and stretch and even break. However, the average structure of a water molecule is similar to this tetrahedral arrangement [15]. Today, this tetrahedrally coordinated water structure is generally accepted; however, the arrangement of most hydrogen-bonded molecules is not symmetrical. At room temperature, 80% of the molecules of liquid water have one strongly hydrogen-bonded O-H group and one non- or only weakly bonded O-H group at any instant. The remaining 20% of the molecules are made up of four-hydrogen-bonded tetrahedrally coordinated clusters [15]. The average energy of the hydrogen bonds between the H_2O molecules during the process of cluster formation is 0.1067 ± 0.0011 eV. As the energy of the hydrogen bonds between the H_2O molecules increases to 0.14 eV, the water clusters are destroyed [14]. A typical cluster consists of five water molecules. In ice, this tetrahedral clustering is extensive, producing crystalline structures [15]. In liquid water, tetrahedral clustering is only observed locally and its extent reduces with an increase in the temperature. In bulk water, at any instant, it is expected that strongly tetrahedrally oriented hydrogen bonds form a network (grid), with a small number of isolated pockets of water molecules with weak or broken hydrogen bonds also being present. Most of the interesting properties of water come from this three-dimensional hydrogen-bonding network [15]. The hydrogen bond energy is 5 - 10 kcal/mole, while the energy of O-H covalent bond in the H_2O molecule is 109 kcal/mole. The average energy (ΔE H…O) of the hydrogen H…O bonds between H_2O molecules is 0.1067 ± 0.0011 eV [14]. With fluctuations in the temperature of water, the average energy of the hydrogen H…O bonds in the water molecule clusters changes [14]. This is the reason that the hydrogen bonds in the liquid state are relatively weak and unstable: it is thought that they form and break readily with changes in the temperature. It is known that thermal oscillations (fluctuations) lead to the bending and breaking of hydrogen bonds [14]. When water is heated, the hydrogen bonds break, and the molecules move further apart and get repositioned randomly, resulting in extensive collapse of the structure. Hence, the fraction of water molecules joined by hydrogen bonds decreases. According to theoretical calculations, heating to 40˚C breaks approximately half the hydrogen bonds in water associates [14]. The breaking of these bonds and the resulting increase in the degree of disorder

of the water molecules leads to increased entropy (S). The increase in the entropy (dS) when water is heated from a lower temperature T_1 to a higher temperature T_2 can be calculated as follows:

$$dS = mc\ln\left(T_2/T_1\right) \tag{3}$$

where m is the mass of water and c is the specific heat. However, the structure does not extensively re-form immediately upon cooling, as the reconstruction process requires time. My aspect is that if the cooling process is very fast and performed using a freezer, the water molecules do not get sufficient time to re-structure. In contrast, when water remains for a long time in a fridge, wherein a stable temperature of 5˚C is maintained, the water molecules have sufficient time to reorder. When the water is cooled to an initial low temperature, the structure does not form instantaneously, that is, its entropy does not decrease immediately. During the cooling process, the water structure does not instantaneously return to the ordered state, as hydrogen bonds do not form instantly. This thermodynamic process or cycle can be visualized in a "temperature vs. entropy diagram" or T-S diagram [16]. In our case (**Figure 3**) the area enclosed by the circle is the energy consumed to deconstruct the "structure". The curve for entropy reduction as a function of the temperature, S = f(T), lags relative to the entropy growth curve. As we see in **Figure 3**, at any temperature T', the entropy during heating, S_h, is less than the entropy during cooling, S_c. After being heated and then cooled to the starting temperature, the water now has greater entropy and fewer hydrogen bonds than it did immediately prior to being heated, even though the temperature is now the same. At any temperature T, the heat capacity mc (=S/ln T) upon cooling is greater than that during heating. Thus, the specific heat is larger in the former case: $c_c > c_h$. Specific heat of water is not constant but it is a function of temperature [17] and it is in average 1 cal/gr ˚C =

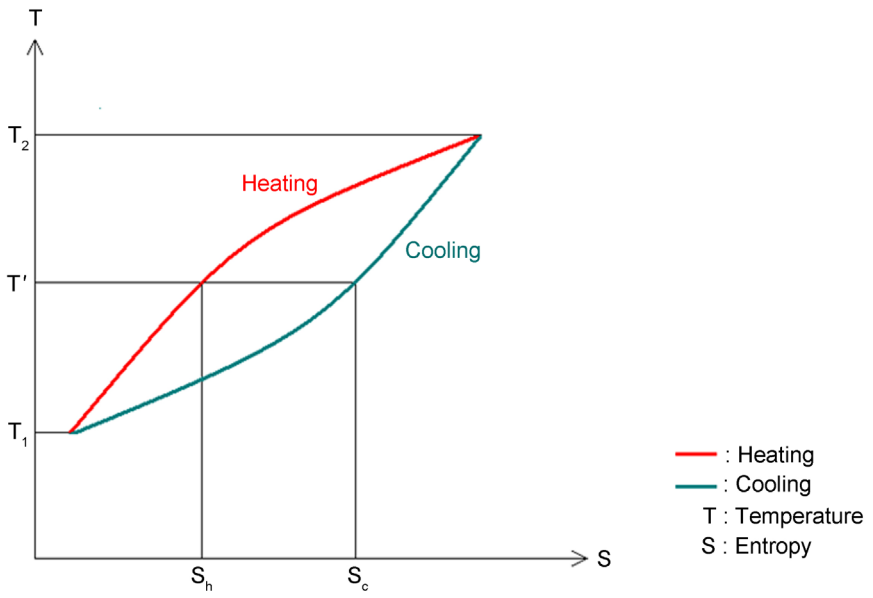

Figure 3. Curves of entropy as function of temperature.

4.18 J/gr ˚C in the range 25˚C - 60˚C:

$$c = 4.214 - 2.286\times10^{-3}T + 4.991\times10^{-5}T^2 - 4.519\times10^{-7}T^3 + 1.857\times10^{-9}T^4 \quad (4)$$

(T in Celcius, unit is J/gr ˚C).

Formula (4) is not an equation derived from physical laws but is just a polynomial best fitted to experimental measurements. Provided that it is produced by a FORTRAN code can be called "empirical". Therefore it is possible that the specific heat is furthermore affected from other unknown variables. Consequently the supposition: $c_c > c_h$ has a large possibility to be correct.

4. Conclusion

Warm water is cooling faster than cold because it contains more entropy when it comes to its temperature. The grid structure is more extended in cold water. Any dissolved salts present in the water affect the structure of the water molecules, as the ions are hydrated. Consequently, in the case of water containing dissolved ions, the water network is smaller, and the molecules are less organized than in pure water. Thereby, the effect of preheating is expected to be weaker.

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