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Mpemba Effect

Abstract

Water molecules are dipoles positioned and oriented joined by hydrogen bonds. When water is heated this structure collapses (increasing entropy). If after the water is recooled to a lower temperature the structure is not reconstructed immediately but needed some time. This time is not always available inside a freezer because the cooling process is fast. The entropy reduction curves function of temperature $S=f(T)$ appear retardation (lagging) relative to entropy growth curves. So, the water after was heated and recooled at the starting temperature, has more entropy than before it was heated. This means that molecules have now the same kinetic energy, but thermal motion before heating was more oriented by the structure mentioned above. So, after recooling random collisions are more possible leading to faster temperature’s reduction. The rate of temperature decrease is proportional to temperature.

Main Text

We use natural mineral water pure in salts, so we can assume that the effect of the dissolved ions is negligible. It is known that water molecules are electric dipoles. Cold water has a structure where these dipoles are positioned and oriented next to one another by their opposite charges face to face. They are joined by hydrogen bonds to form straight chains.

When water is heated bonds are broken and molecules are removed from each other and randomly repositioned, so the structure collapses. The hydrogen bonding percentage decreases. This is called increasing entropy ($S$). The increase of entropy ($dS$) after water is heated from a lower temperature $T_1$ to a higher $T_2$ is:

$$dS = m \ln \left( \frac{T_2}{T_1} \right) , \quad m = \text{water mass}, \quad c = \text{special heat}$$

If after the water is cooled to lower temperature the structure is not reconstructed immediately but it is needed some time in calm to be done. Sometimes this time is not available inside a freezer because the cooling process is fast. Inside a fridge when reaches and stabilize at the temperature of the refrigerator (5 °C) water will find the time to restore its structure. So, when the water is cooled at the initial low temperature its structure is not instantaneously fixed to the initial situation, or in other words, its entropy is not decreased immediately. During the cooling process, water’s structure is not momently returns to the neat condition. Hydrogen bonds are not reconnected at once. The entropy reduction curves function of temperature $S=f(T)$ appear retardation (lagging) relative to
entropy growth curves. At any temperature point entropy during heating $S_h$ is less than entropy during cooling $S_c$.

![Entropy Growth Curves](image.png)

Thereby now the water, after is heated and recooled at the starting temperature, has more entropy than which it has before it is heated. Also, the hydrogen bonding percentage is less than before it is heated.

Suppose that we have two jars contains the same quantity of water at the same temperature ($T$) but the one (A) has more entropy than the other (B). This means that molecules of both jars have the same energy, but inside A they are moving to all directions whereas inside B thermal motion is more oriented by the structure mentioned above. So, in the case of A random collisions are more possible than in the case of B. The random collisions cause molecules loosing average kinetic energy ($E$), which means temperature’s reduction: $E = (3/2)kT$, $k$ = Boltzmann constant. Therefore, water A is cooling faster than B.

It is known that during cooling of a material body the rate of temperature decrease is proportional to temperature ($T$):

$$\frac{dT}{dt} = -\varepsilon T \Rightarrow T = T_0 e^{-\varepsilon t}$$

$t$ = time, $\varepsilon$ = coefficient of temperature change, $T_0$ = starting temperature

Half time period (HTP) = $\ln 2/\varepsilon$

Now, let’s do an experiment. We simultaneously put in a freezer three bottles of water A, B and $\Gamma$ with exactly the same quantity in each of them. The temperature of A is at 50 °C, B and $\Gamma$ at 35 °C. B was taken at ambient temperature, the Greek summer. $\Gamma$ was heated to 50 °C before is cooled to 35 °C. After a time period we observe that A and $\Gamma$ simultaneously reaches 0°C earlier than B. A and $\Gamma$ followed the same process. Coefficient $\varepsilon$ is the same for A and $\Gamma$ and is bigger than that of B. Half time period is the same for A and $\Gamma$ but lower than that of B.

If there are many dissolved salts water’s structure differs because the ions are hydrated. Consequently chains are smaller and orientation of the molecules is less of pure water. So the phenomenon occurs reduced.