Quantitative Analysis of the "Mpemba Effect"

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Abstract: A quantitative analysis is conducted on the "Mpemba effect" where hot water freezes faster than cold water. Specific calculation formulas and discriminant conditions are provided, and the causes of the "Mpemba effect" are revealed.

1、Introduction

The Mpemba Effect: The seemingly common yet strange natural phenomenon that hot water freezes faster than cold water in winter remains unsolved by science as a natural mystery. It is said that the ancient Greeks once discovered this interesting natural phenomenon but failed to find the answer to the problem. In 1969, Erasto Mpemba, a Tanzanian university student, formally put forward this question to the world—why does hot water freeze faster than cold water in winter? Since then, this problem has attracted the attention of scientists all over the world. It is said that Erasto Mpemba conducted many hot water freezing experiments and wrote many research reports, but none of them could give a correct answer. This magical natural phenomenon is called the "Mpemba Effect" in the scientific community[1].

To solve this natural mystery, scientific organizations such as the Royal Society of Chemistry have publicly offered rewards for answers to this question on multiple occasions, yet a scientific solution remains elusive[2].

Regarding the "Mpemba effect", some scholars believe that it does not exist at all, while others argue that there is an as-yet-unrecognized mechanism in the freezing process of hot water that causes this effect. The author has studied this effect using the principle of thermal energy exchange of water in different environments, and has basically clarified the problem theoretically. It is believed that:

(1) The occurrence of the "Mpemba effect" is conditional, and it is not the case that hot water freezes faster than cold water under all conditions.

(2) When environmental conditions change, during the cooling and freezing process of water, there are also phenomena where hot water freezes slower than cold water, and hot water and cold water freeze at the same speed.

(3) The "Mpemba effect" should exist in other liquids in nature, such as mercury, milk, gasoline, etc.

2、Theoretical Derivation

Principle: Water at 0 degrees Celsius (hereinafter referred to as "degree") and ice at 0 degrees are two different phases of water. Under the condition of constant pressure, there exists a latent heat of fusion (phase change heat) when water at 0 degrees turns into ice at 0 degrees. When the external ambient temperature of the thermal container is different, according to Fourier's theorem and Newton's law of cooling for fluids, the speed of heat exchange between the heat in the container and the external environment varies. Under specific conditions, the natural phenomenon that hot water freezes faster than cold water will occur.

This thermal energy exchange process can be theoretically derived: For the convenience of research, the basic units are taken as calorie, gram, second, centimeter, and degree Celsius (abbreviated as "degree"). The calculation formula for the latent heat of fusion of water is:

（1） $$\Delta H = Q/M$$

Where ΔH represents the heat of fusion, Q represents the heat released or absorbed when the solute dissolves, and M represents the number of moles of the solute. The heat of fusion of water (i.e., the phase change heat when ice melts into water or water turns into ice) is 331 J/g. The heat of fusion for 1 gram of water turning into ice is $331 J/g \times 0.239 \text{cal/J} = 79.1 \text{cal}$, which, when substituted into equation (1), gives us:

（2） $$\Delta H = Q/M \approx 79.1\mathrm{cal}/g$$

Assume that the container holding water is adiabatic with only one opening, allowing heat exchange between the water and the outside. Let the area of this heat-dissipating opening be S, the temperature of the water be T_1, the mass be m, the released heat be Q, and the rate of heat outflow be V. The temperature of the air outside the container is $T_2 < 0$. According to the formula for specific heat capacity, the total heat released when m grams of water cools from temperature T_1 to ice at 0°C is:

（3） $$Q = mc\Delta T = mc\Delta T_1 + \Delta H m$$

Wherein, ΔT_1 represents the temperature difference (a positive value) when the temperature of water drops from T_1 to 0°C; $c = 4.2J/(g.^0C) \approx 1\mathrm{cal}/(g.^0C)$ denotes the specific heat capacity of water under constant pressure; $\Delta H = 79.1\mathrm{col}/g$ stands for the heat of fusion (phase change heat) of water. By normalizing the heat unit, equation (3) can be simplified as:

（4） $$Q = mT_1 + 79.1m$$

The heat Q is exchanged through S into the air outside the thermal container, and the rate of heat outflow is

（5） $$v_0 = ks(T_1 - T_2)$$

Wherein, k represents the convective heat exchange rate of air per unit area, S denotes the heat dissipation area of water, T_1 stands for the initial temperature of water, and T_2 indicates the initial temperature of the air surrounding the thermal container.

（6）
$$k = q / t$$

Where q represents the heat flux of air and t represents time. When the temperature of water drops from T_1 to 0°C, the average rate of heat outflow is:

(7)
$$v_2 = \frac{v_0 + v_1}{2} = \frac{ks(T_1 - 2T_2)}{2}$$

The time required for water to cool from temperature T_1 to ice at temperature 0°C is

(8)
$$t = \frac{Q}{v_2} = \frac{2m(T_1 + 79.1)}{\mathrm{ks}(\mathrm{T}_1 - 2\mathrm{T}_2)}$$

Formula (8) indicates that the time t required for a fixed quantity of water to cool from temperature T_1 to ice at 0°C is proportional to the mass m of the water and inversely proportional to the heat dissipation area S. When m, S, and k remain constant, the freezing rate of water is determined by the factor $((T_1 + 79.1) / (T_1 - 2T_2))$. Let

（9）
$$F = \frac{T_1 + 79.1}{\mathrm{T}_1 - 2\mathrm{T}_2}$$

Wherein, T_1 is the temperature of water, and T_2 is the temperature of the external air. It is obvious that when T_2 =-39.55°C,F= 1; when T_2 > -39.55°C , F > 1; and when T_2< -39.55°C , F < 1. With M, S, K remaining unchanged, the following conclusions can be drawn according to equation (9):

1) When condition $T_2 = -39.55^0 C$ is met, the freezing time of water has nothing to do with the water temperature T_1. Whether $T_1 = 10$ or $T_1 = 50$, the freezing time of water is the same.

2) When condition $T_2 \in (0^0 C, -39.55^0 C)$ is met, F is proportional to T_1, meaning that the higher the temperature T_1 of the water, the shorter the time it takes for the water to freeze. For example, the value of F when $T_1 = 50$ is greater than that when $T_1 = 10$, indicating that water with a higher temperature freezes faster, while water with a lower temperature freezes slower.

3) When condition $T_2 \in (-39.55^0 C, -\infty)$ is met, F is inversely proportional to T_1, that is, the higher the temperature T_1 of the water, the longer the time it takes for the water to freeze. For example, the value of F when $T_1 = 50$ is greater than that when $T_1 = 10$, which indicates that water with a higher temperature freezes slower, while water with a lower temperature freezes faster.

4) From the above results, it can be concluded that the "Mpemba effect" occurs only when the air ambient temperature is $T_2 \in (0^0 C, -39.55^0 C)$.

5) Some scholars have observed the above results in laboratories, but the explanations they provided are not scientific[3].

3、Experimental Observation

It is a difficult task to experimentally verify the "Mpemba effect". The difficulty lies in the fact that the value of k, which represents the heat exchange rate between water vapor and air per unit area in equation (8), is determined by the heat flux q of the air. According to Fourier's theorem for fluids and Newton's law of cooling, the value of q changes with the variation of air temperature.Another difficulty is the need for specialized refrigeration equipment and observation devices. Without these conditions, it is challenging to obtain accurate experimental observation data. The data provided here by the author were observed in a natural outdoor environment in winter, which are relatively rough, and some only present theoretical data. It is hoped that readers will not be overly critical. Of course, it is also hoped that readers with access to experimental equipment will conduct experimental verification to improve the accuracy of the experimental verification data for this project.In the natural outdoor environment, the convective heat transfer coefficient of air at low temperatures is on the order of 5-25 ($W/m^2·K$). When converted to a unified unit ($cal/cm^2·°C·s$), it is on the order of $4.1×10^{-3}$ - $20.2×10^{-3}$ ($cal/cm·°C·s$).

Taking 100 grams of water (m = 100g) and a heat-dissipating area of the thermal container S = 50 cm^2, a comparison between the theoretical calculations and the observational data from field experiments is presented in the table below:

Table of Comparison Between Theoretical Calculations and Field Observation Data on Water Freezing Time												
Project Name	Unit	temperature										Remarks
Air temperature T_2	^{0}C	-20		-25		-30		-39.55		-50		
Water temperature T_1	^{0}C	100	10	80	10	60	10	100	10	100	10	
Theoretical freezing time t	S	1248	1738	858	1042	635	697	493	493	369	334	
Observation of freezing time t	S	1350	1920	960	1140	780	870	*	*	*	*	
Air-water heat exchange rate k	Cal/cm^{2}s	4.1*10^{-3}		5.7*10^{-3}		7.3*10^{-3}		8.1*10^{-3}		9..7*10^{-3}		

Note: There is a significant error between the observed freezing time and the theoretical freezing time in the table. This is mainly caused by errors in the k value, air flow in the observation environment, temperature fluctuations, and other factors, and there is room for improvement. The freezing time is calculated in seconds. The data marked with an asterisk (*) cannot be provided temporarily due to limitations in observation conditions and need to be obtained through relevant laboratories. The observation data are basically consistent with the inference in (9).

4、Application Prospects

The "Mpemba effect" of water truly exists in nature. Although this phenomenon has been observed and studied by many scientists, the reasons behind it have not yet been clarified, and this issue has not attracted much attention in the scientific community. Through formula (8), we have clarified the cause of the "Mpemba effect" in water and proved that the "Mpemba effect" is universally present in nature.For example, the "Mpemba effect" has also been observed when making ice cream with milk, sugar water, salt water, etc., which is consistent with the conclusion of formula (8). It is hoped that this article can play a role in throwing a sprat to catch a herring in promoting the research on the "Mpemba effect".From (8), we know that as long as a liquid material has phase change heat, liquids such as gasoline, alcohol, mercury, blood, and hydrochloric acid all exhibit the "Mpemba effect". Obviously, this is a very interesting field. If we can figure out the "Mpemba effect" of liquid materials, it will be of great significance to the research on the phase change theory of liquids.Therefore, the research on the "Mpemba effect" is a Nobel Prize-level issue and should receive attention from the scientific community. It is hoped that this article can play a role in throwing a brick to attract jade (i.e., serving as a modest spur to induce others to come up with more valuable ideas) in promoting the research on the "Mpemba effect".

References:

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