A few lines after stating the Mpemba effect, Aristotle offers it as the explanation for rainstorms in hot climates often being torrential: "For the same reason in Arabia and Aethiopia rain falls in the summer and not in the winter, and falls with violence and many times on the day: for the clouds are cooled quickly by the reaction due to the great heat of the country" (Aristotle 1952). It is a wrong explanation for a real phenomenon. Source: Jessie Eastland, Wikimedia Commons.

The Rise and Fall of the Mpemba Effect

Hot fluids freeze faster than cold fluids. This was what high school student Erasto Mpemba reportedly discovered. However, his discovery turned out to be a misunderstanding—one with a long history.

MARTIN BIER

Thirteen-year-old Erasto Mpemba was in high school when he observed that a mixture of milk and sugar froze faster if placed in a freezer while it was hot. This happened in 1963 in what is now Tanzania.

When Mpemba followed up on what he had found, his physics teachers told him it was nonsense. Local street ice cream vendors, on the other hand, turned out to be very familiar with what Mpemba had observed.

A few years after Mpemba's discovery, prominent British physics professor and diplomat Denis Osborne visited Mpemba's school for a guest presentation. During the Q&A session after the presentation, young Mpemba again brought up his discovery, and again he was derided by his teachers and fellow students.

But the distinguished diplomat had become intrigued, and he carried out experiments—not with ice cream but with water—after his return to Dar es Salam. Eventually, in 1969, this led to the publication of an article in the journal *Physics Education* (Mpemba and Osborne 1969). Mpemba had finally been proven right! The article, authored by Mpemba and Osborne, is very readable and has become a classic.

That hot water freezes faster than cold water is today known as the Mpemba Effect. However, the idea has a history that goes back much further than the 1960s. In the fourth century BCE, Aristotle wrote in his treatise on meteorology: If the water has been previously heated, this contributes to the rapidity with which it freezes: for it cools more quickly (Aristotle 1952). At the beginning of the seventeenth century, Francis Bacon was among the first to articulate how scientific knowledge and insight can be obtained through a combination of observation and reason. In his *Novum Organum*, he wrote, "*aqua parum tepida facilius conglacietur quam omnino frigida* ("water a little warmed is more easily frozen than that which is quite cold"; Bacon 1902). The *Physics Education* article by Mpemba and Osborne refers to none of this history.

The article by Mpemba and Osborne describes in detail how the young, innocent Mpemba was misunderstood and scoffed at when recounting his discovery. None of his teachers took him seriously. Naturally, this engages the reader's sympathy for Mpemba. The picture painted is of an enthusiastic and incorruptible youngster colliding with a narrow-minded establishment. The story evokes the struggles of Galileo and Albert Einstein, ground-breaking scientists up against a ruling order that is persisting in dogma. Osborne's experiments and the article reporting the outcomes of these experiments are a heart-warming happy end fit for a Hollywood movie—one that puts the Cinderella story in a twentieth-century academic context.

Mpemba and Basic Principles

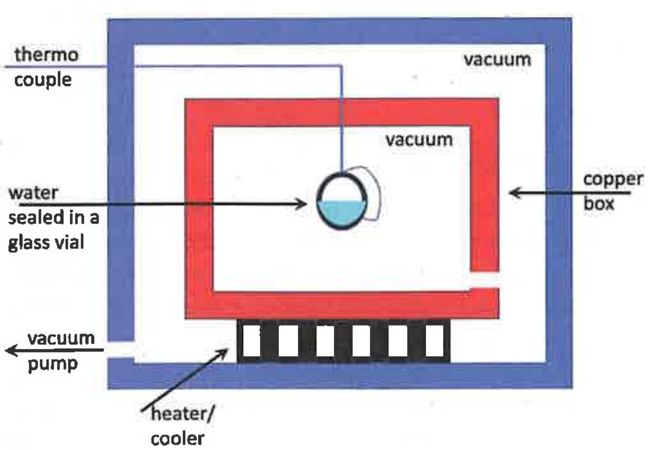
On a number of counts the article by Mpemba and Osborne gets it wrong. The derision Mpemba experienced was based on sound scientific intuition. The Mpemba Effect is an assault on the insight and understanding that one acquires over many years of studying physics.

In the nineteenth century, physicists came to the realization that heat is a form of energy. As a gallon of water cools down from the boiling point (100°C) to the freezing point (0°C), energy is released. This process is reversible, i.e., the same amount of energy must be added again when the water is returned from the freezing point to the boiling point. If the Mpemba Effect were real, it would mean that more energy is required to bring the water from the freezing point to 80°C than to 100°C. This is not consistent with the fact that a cup of water reaches a higher temperature if it is heated up in the microwave oven for a longer time.

The Mpemba Effect violates the First Law of Thermodynamics, which says that energy can neither be created nor destroyed; it can only be transferred from one form to another. The First Law of Thermodynamics is probably the most corroborated of all laws in physics and can be considered a universal principle. In breaching this law, the Mpemba Effect implies the possibility of constructing a perpetuum mobile (i.e., a car that does not require fuel).

But there's more: Assume we have two glasses of water at room temperature. The first glass has been at room temperature for a long time. The second glass has just been cooled down from a higher temperature. We put both glasses in a freezer. According to Aristotle, Bacon, and Mpemba, the second glass would freeze faster than the first glass, implying that the glasses of water somehow "remember" what happened in the past (i.e., whether or not they had been previously heated). This goes against everything we know about thermodynamics! In liquid water at room temperature, each molecule moves with a speed of about a quarter of a mile per second and collides on average around a trillion times per second with another molecule. This is known as Brownian motion. Temperature is merely a number that indicates the average energy of the Brownian motion of the molecules. Brownian motion makes it impossible for the molecules in a glass of water to maintain a structure; there is no mechanism to preserve a "memory."

Mpemba's story of different freezing speeds clashes with principles of elementary thermodynamics. In 1963, as now, physics teachers had a professional duty to say so and explain why. That the Mpemba Effect kept being a subject of wonder and debate for decades is mostly a result of physicists conceiving inept interpretations of poorly designed experiments.

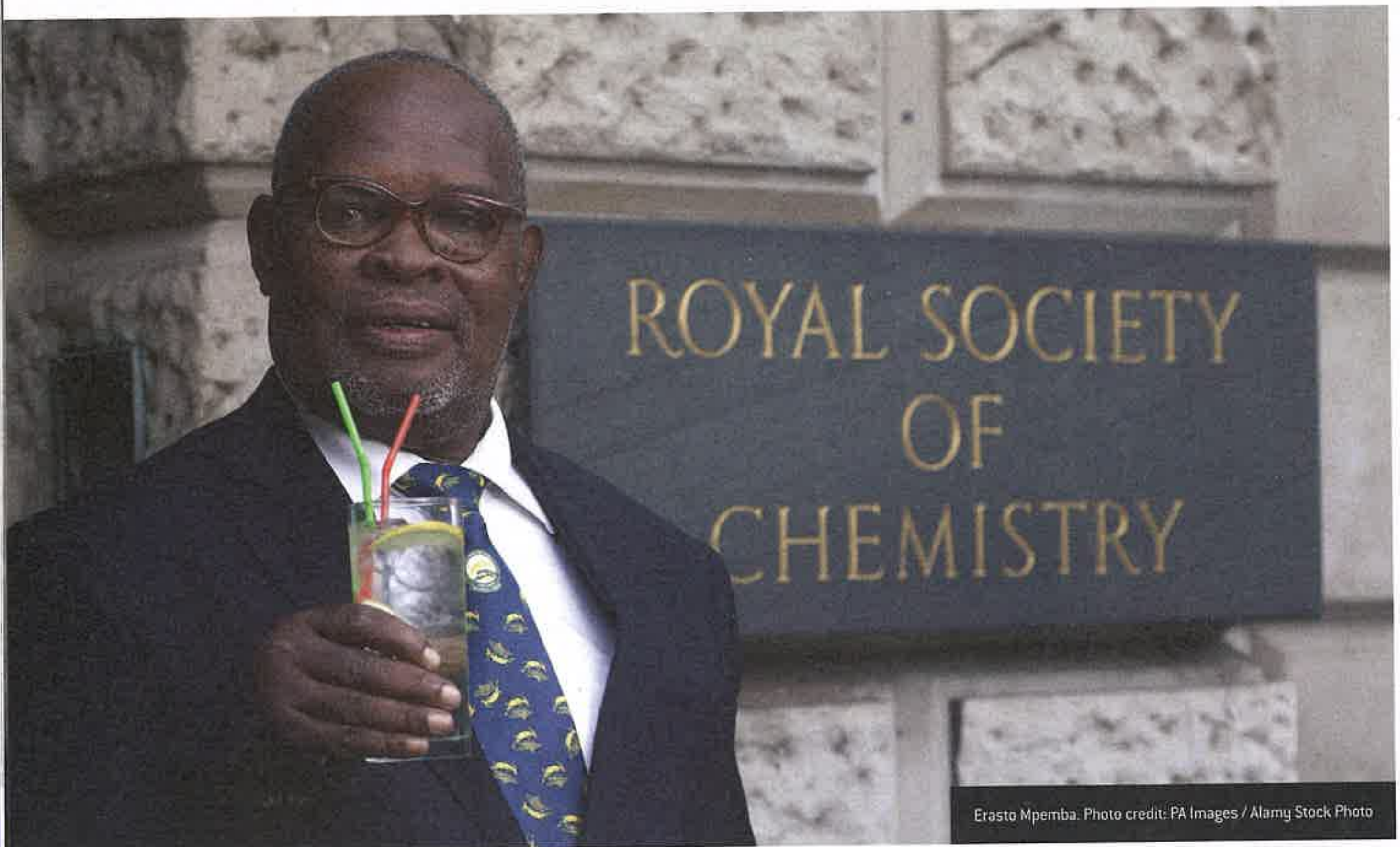


The setup that James Brownridge used to investigate the Mpemba Effect. By eliminating variables that are possibly beyond the control of the experimenter, Brownridge attempted to come to solid, reproducible results. Drawn by the author based on Figure 2 of the reference by Brownridge.

Brownridge's Experiment

In 2011, James Brownridge of the State University of New York in Binghamton published an article in the prestigious *American Journal of Physics* (Brownridge 2011). Brownridge's experiments were meticulous and well-described. The work was decisive.

Heat moves from hot to cold objects. There are three ways in which heat can be moved: (1) *Conduction* takes place inside solid material where molecules have fixed positions; it is the way a teaspoon in a hot cup of tea gets hot. (2) *Convection* occurs when a gas or liquid circulates between a hot and a cold object and transfers heat; it is what happens in a convection oven. (3) *Thermal radiation* is electromagnetic radiation that is emitted by every object. The higher the temperature of an object, the more radiation it emits. Sunlight, for instance, is thermal radiation that we receive from the Sun.



Erasto Mpemba. Photo credit: PA Images / Alamy Stock Photo

To properly test the Mpemba Effect in an experiment, all three forms of heat transfer need to be controlled as much as possible.

The schematic on p. 49 shows Brownridge's experimental setup. Distilled water is contained in a vial that is melted shut and hung from a wire in a vacuum. The vacuum has been created in a copper box. Copper is a good heat conductor, and this guarantees that the temperature around the vial is the same everywhere. The vial's temperature is measured continuously and accurately with an electronic device called a thermocouple. Note that thermal radiation is the only way the vial exchanges heat with the copper box. Conduction and convection have been ruled out because of the vacuum. Heat transfer through the wire is negligible.

However, even with Brownridge's setup, not everything is under control. Freezing always starts at a nucleation site and propagates from there. The nucleation site is generally a small dust-size particle. For tap water or water in a pond, the nucleation sites are generally the abundant dirt particles or other impurities. Freezing then readily occurs at the proper 0°C. But the pure, distilled water in Brownridge's experiments may stay liquid until well below 0°C. This is called "supercooling." It is actually possible to keep pure water liquid until -45°C. The distilled water in Brownridge's experiments tended to freeze at temperatures between -20°C and 0°C. The freezing temperature varied from one vial to the next but was always the same for one particular vial. This is likely because the nucleation sites in Brownridge's vials were small irregularities in the glass walls.

Brownridge found that for vials with the same shape and size, 0°C is always reached first in the vial that started with the lower temperature. It is in principle possible that the vial with the warmer water will freeze before the vial with the colder water. This can happen when the vial with the warmer water contains a microscopic irregularity in the glass wall that gives rise to a higher freezing temperature. That wall irregularities are responsible is evidenced by the fact that for one and the same vial, the freezing always occurs at the same temperature.

Details and Reproducibility

In a scientific experiment, it is important to consider all variables and their possible effects on the outcome of the experiment. Spontaneous generation—another idea that goes back to Aristotle—provides a good example of this. Until the late seventeenth century, it was believed that flies originate from cadaver tissue, that shells spontaneously form from sand, and that mice appear out of nothing in grain. Simple experiments in which cadavers, sand, and grain were isolated and observed demonstrate that these beliefs were wrong.

The fact that the Tanzanian ice cream vendors confirmed Mpemba's observations is not surprising. The vendors would probably have used freezers without a dehumidifier.

In the course of a day, a freezer is opened and shut many times, each time allowing an amount of hot, humid air in. Because cold air can contain less humidity than warm air, surplus humidity settles in the form of ice crystals inside the freezer and forms a layer of frost. Air is a good thermal insulator, and if a cup of water is put inside a freezer, most cooling will occur through the bottom of the freezer that the cup is standing on. However, if the cup is standing on a layer of frost, the cooling will be slower. This is because the frost is porous and contains a lot of air. The layer of frost effectively acts like a wool sweater between the cup and the cold surface. But now imagine that a hot cup of water is put on a thin layer of frost. It is then possible that the layer of frost is melted away and that the cup will ultimately make full contact with the bottom of the freezer. The subsequent cooling will then be faster, and it is possible that a cup that started at a colder temperature will be caught up with and overtaken on the race to freezing.

The claim that warm water freezes faster than cold water is too general to be considered scientific. Lake Michigan will not freeze over during one freezing night while a small container with hot water placed on the edge of Lake Michigan will readily freeze from top to bottom. So, scale is a factor. The material of the contact surface also plays a role. Water in a metal container will freeze faster than water in a wooden container of the same size and shape. This is because metal is a better heat conductor than wood. The shape of the container is also significant. Because of the larger contact surface, water on a flat tray will freeze faster than the same amount of water in a spherical container.

Scientific articles that give experimental results generally have a Materials and Methods section in which detailed descriptions are given of procedures and the equipment used. A good Materials and Methods section guarantees the reproducibility of the reported results. The one-liners of Aristotle and Francis Bacon are such that there is no way to ever find out again how the underlying observation of the Mpemba Effect came about. Aristotle implies it is common knowledge as he follows up the statement of the alleged effect with: "Therefore many people when they want to cool water quickly first put it in the sun" (Aristotle 1952). Bacon's assertion of the Mpemba Effect is a side remark amid an abstruse pharmacological account (Bacon 1902).

In the first few decades after the 1969 article by Mpemba and Osborne, much experimental work was done on the Mpemba Effect. Sometimes the effect was observed and sometimes it was not. Different researchers used different setups and only rarely did someone try to exactly reproduce the results of someone else. The large number of variables involved in the freezing of water, the lack of appropriate detail in the reporting, and the lack of a proper emphasis on reproducibility ultimately led to the Mpemba Effect myth lasting much longer than it should have.

The way in which the Mpemba Effect is written about has changed in the decade following the publication of the Brownridge article. Articles in which exotic mechanisms are postulated to explain the Mpemba Effect no longer abound.

In 2012, the British Royal Society of Chemistry organized a contest with a thousand English pounds in prize money for the best explanation of the Mpemba Effect. There were 22,000 entries, and Erasto Mpemba himself was there for the award ceremony. Nikola Bregović of the University of Zagreb prevailed. In the winning article, he described his own experiments and confined the analysis to elementary thermodynamics (Bregović 2012). He pointed to four factors as being of possible significance: evaporation, dissolved gases, convection, and supercooling. Bregović argued how supercooling is ultimately the significant factor and, in the conclusion, he quoted Brownridge's article: "Hot water will freeze before cooler water only when the cooler water supercools, and then, only if the nucleation temperature of the cooler water is several degrees lower than that of the hot water. Heating water may lower, raise or not change the spontaneous freezing temperature" (Bregović 2012).

In 2016, a long article by Henry Burridge and Paul Linden of Cambridge University appeared in *Nature: Scientific Reports* (Burridge and Linden 2016). The article gives a thorough overview of the confusion and the lack of reproduction of results that have characterized the discussion on the subject since 1969. The authors conducted their own experiments, and they excluded supercooling as a factor by just measuring how long it takes for water to cool down to 0°C. The Mpemba Effect then no longer occurs. The article's title sums it up well: "Questioning the Mpemba Effect: Hot Water Does Not Cool More Quickly Than Cold." ■

Note

In June 2022, a Dutch-language version of this article appeared on the blog kloptdatwel.nl at https://kloptdatwel.nl/2022/06/07/de-opkomst-en-ondergang-van-het-mpemba-effect/.

References

Aristotle. 1952. *Meteorologica*. Translated by H.D.P. Lee. Loeb Classical Library 397. Cambridge, MA: Harvard University Press. Book 1, Chapter 12. Free translation also online at http://classics.mit.edu/Aristotle/meteorology.1.i.html.

Bacon, F. 1902. *Novum Organum*. Translated by J. Devey. New York: P.F. Collier & Son. Book 2, Chapter 50, Section 4, p. 277. Also online at https://www.thelatinlibrary.com/bacon/bacon.liber2.shtml.

Bregović, N. 2012. Mpemba effect from a viewpoint of an experimental physical chemist. Online at https://www.rsc.org/images/nikola-bregovic-entry_tcm18-225169.pdf.

Brownridge, J.D. 2011. When does hot water freeze faster than cold water? A search for the Mpemba effect. *American Journal of Physics* 79: 78–84.

Burridge, H.C., and P.F. Linden. 2016. Questioning the Mpemba effect: Hot water does not cool more quickly than cold. *Scientific Reports* 6: 37665.

Mpemba, E.B., and D.G. Osborne. 1969. Cool? *Physics Education* 4: 172–75.

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