Can hot water freeze before cold water?: An answer to a 2300-year-old question

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“If there is magic on this planet, it is contained in water.”
(Loren Eiseley, The Immense Journey, 1957)
It all began

In the 4th Century BCE

Aristotle observed that “,,, water has
previously been warmed contributes to it's freezing quickly……”:

Roger Bacon in the 13th Century wrote that "slightly tepid
water freezes more easily than that which is utterly cold".

And many others
Then in 1963 the question was raised again

By
Erasto Mpemba
(Tanzanian school boy)

In 1968 he asked Physics Prof. Dennis Osborne how can a cup of boiling water at 100°C freeze faster than a cup of water at 35°C?

Published 1969
The Mpemba effect

Hot water freezing before cold water
26 June 2012
Press Release
by
Royal Society of Chemistry (UK)

Why does hot water freeze faster than cold water?

“……best and most creative explanation of the phenomenon, known today as

The Mpemba Effect.”
The 2300 year old question
Why does hot water sometimes freeze faster than cold water?

In most cases it is because “ALL” conditions are not equal and “identical” for both samples

\begin{align*}
\text{Temperature } ^\circ\text{C} & \\
\text{Time (min)} & \\
0 & 30 \quad 60 \quad 90 \quad 120 \quad 150 \quad 180 \quad 210
\end{align*}

\begin{align*}
& \sim 76 ^\circ\text{C} \\
& \sim 4 ^\circ\text{C} \\
\text{Hot and Cold tap water add to glass vials} \ \text{Latent heat is released} \\
\text{(Water begin freezing)}
\end{align*}

\begin{align*}
\text{Temperature } ^\circ\text{C} & \\
\text{Time (min)} & \\
0 & 60 \quad 120 \quad 180 \quad 240 \quad 300 \quad 360
\end{align*}

\begin{align*}
& \sim 83 ^\circ\text{C} \\
\text{Hot and Cold tap water add to glass vials} \ \text{Latent heat is released} \\
\text{(Water begin freezing)}
\end{align*}
Here all conditions are equal and “identical” and the colder water samples freezes first.

(But ---- not necessarily because they were cold)
NOMENCLATURE

Ice nucleation
Ice nucleation sites
Ice nucleation agents
Ice nucleation temperature
Fixed
Supercooling
Explanations

(Of ten sited but not correct)

- Hot water cools faster
- Evaporation
- Convection
- Gas concentration
- Dissolved gases and Minerals
- Nanobubbles
- Many others
Typical experimental set-up

Up to 8 vials

DAQ
How long does it take hot water to freeze?
For 1 ml of DD Water

Time to the onset of freezing

Number of freezing cycles

Start cooling Temperature (°C)

Freezing Temp.

Avg. = -11.8 ± 0.5°C (sd) for 138 cycles
Here “ALL” conditions are equal and “identical”
Can we do anything to change the time it takes to cool to $0^\circ \text{C}$?

Yes.--- Add a solute and **not mix**.

Adding $\text{D}_2\text{O}$ to $\text{H}_2\text{O}$
Time to cool to 0°C is longer

For D₂O not mixed (a) vs. mixed (c)
When conditions are not equal

Hot water will often freeze first as shown here.
Major problems

Conditions not equal.
How do you define frozen?
When did the waters freeze?
Eight 30ml samples of cool tap water from the same source

Although conditions may appear equal, they are not.

Notice: Difference. Time to cool to 0°C and time to -5°C.
Hot and cold water

Notice: Difference. Time to cool to 0°C and time to -10°C

Conditions not equal
When did the water freeze?
Maybe $t_f, t_b, t_s$ or some other time.

Open container in a freezer with 8 thermocouples
Water to ice $\rightarrow$ vol increase $\sim$9%

Martin Chaplin on 22 June, 2008

http://www.lsbu.ac.uk/water/history.html

Dense cluster $\rightarrow$ Low-density cluster
When did the water begin freezing?

Here ~3 seconds
Where *in the water* did the water begin freezing?

Here at a nucleation site

Temperature probe
How is it possible for hot water to freeze faster than cold water?

When all known conditions are equal except temperature.
Asymmetry and supercooling

Frozen water (ice) **always** begin melting at (0°C)

Liquid water will **not always** begin freezing at (0°C)
How long will water remain unfrozen (liquid) at -15°C?

We held water at -15°C for 422 days. Re-checked --1 year later -- it stilled cooled to <-15°C before freezing.
Reproducibility of latent heat release temperature

and

ice nucleation sites
Water 1 will freeze 1st **hot** or **cold**

**Ice nucleation sites in water**

**Water 1**
- Nucleation temperature: -5°C
- Fixed at -5°C
- -13°C
- -16°C

**Water 2**
- Nucleation temperature: -12°C
- Fixed at -12°C
- -13°C
- -15°C
The one that cools to its nucleation temperature first will freeze first.

\[ \frac{dT}{dt} = -k(T - T_a) \]

Hot water never cools to 0°C first.
Ice nucleation sites in water

Here the cold water will **always** freeze first

Water 1

Fixed at -13°C

Water 2

Fixed at -12°C
Reproducibility of latent heat release temperatures

Glass Vial # 8 with 2ml of tap water

Latent heat released

-11.2±0.2

~70hrs
Listen

nature may be trying to tell you something.
A sudden change in the nucleation temperature.
(Here nature told me something)

Glass Vial # 7 with 2ml of tap water

Temperature °C

-14.3 °C the vial was cracked by the ice doing the 1st freeze cycle

-5.3 °C

-6.4±0.1(11)

Latent heat released

Loss of water apparent

~70 hrs.
It is nucleation agents that determine at what temperature water will freeze; not its initial temperature.

Here I add:
- 3 vials with AgI crystals, a known nucleation agent
- 3 vials with unknown nucleation agents

Air temp.
Biological nucleation agents in rain water

Before heating

After heating

C> Not heated
H> Heated
A> Drop of not heated rain water added
Conclusion

All things being equal:

Yes, **hot water** will sometimes freeze faster than **cold water**. However, this will only occur **consistently** when an ‘ice nucleation sites’ in the hot water, **initiates** freezing at a higher temperature than any of those in cold water and **simultaneously**, the cold water supercools to a much lower temperature than the hot water.

(At least 5°C lower)
The answer to the 2300 year old question

supercooling and nucleation agents or sites

The hot water did not freeze first because it was heated.

Offset because TC on outside of vials

Start cooling

Ice at -20°C
Some magic

that you may not have seen
Heat flowing down is magical

Heat

$\Delta T \sim 0$

Out

magic

Heat

$\Delta T \sim 0$

Out
Input at top ~400 mW

Cooling bath

ΔT = 0.75°C

32.5°C

40.4°C

245 mW

24.4°C

7.9°C

0.8°C

-6.4°C

-10

-5

0

5

10

15

20

25

30

35

40

45

0 2000 4000 6000 8000 10000 12000 14000 16000 18000

Seconds

magic
Heat flow “up/down” can be turn “on/off“

Heater on at ~400mW

Top at ~46°C

~1°C

-7.8°C

Latent heat released

Insulation

Heater

TC

TC

H₂O

TC

Cooling bath
Thermal oscillations in a column of water
More magic

-6.0°C

Bath temperature

-6.0°C

-7.4°C
Vertical velocity up the column = \(~1\text{cm/hr}\)
Thank you
Table-top work published

Reduced heat flow in light water (H$_2$O) due to heavy water (D$_2$O),

Vertical movement of isothermal lines in water,

When does hot water freeze faster then cold water? A search for the Mpemba effect,
James D. Brownridge, A, J. Phys. 79, 78 (2011) (The 4th most downloaded paper for this issuer)

Anomalous Effects in Air While Cooling Water,

Electrical Indicator of Imminent Freezing in Supercooled Water