

The triple point of water and its use in thermometry

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1 Introduction

The triple point of water is a unique physical state of water in which all the three phases (solid, liquid and vapor) coexist at thermodynamic equilibrium. Due to the fact that it provides a way to reproduce exactly the same temperature (within 50 microkelvin), it is the cornerstone of modern thermometry. The Thermodynamic Temperature Scale is in fact defined by assigning a numerical value (273.16 K) to the temperature of the water triple point. As direct measurements of the thermodynamic temperature are very complex and time-consuming, a new quantity (the so-called international temperature) was introduced that can be used for all practical purposes and is a close representation of the thermodynamic temperature. Again the water triple point is also the basis for the International Temperature Scale, as any international temperature is calculated with reference to the water triple point temperature.

The national standards for the water triple point temperature, maintained at 20 National Metrology Institutes worldwide, were compared in a recent international comparison, coordinated by the International Bureau of Weights and Measures (BIPM, Sevres, Paris). The results showed significant discrepancies between the water triple point temperatures realized by different countries. These differences were attributed to various effects influencing the triple point temperature, the most principle one being the mixing character of pure water with respect to its isotope composition.

The results of the international comparison prompted the thermometry community to refine the definition of the water triple point temperature in order to take into account isotope effects and, as part of a wider move to redefine the units of the SI in terms of fundamental constants, to propose the re-definition of the kelvin in terms of the Boltzmann constant for the year 2011.

In this paper we summarize the basic facts related to the isotope effect on the water triple point temperature and the implications of a future redefinition of the Kelvin through the Boltzmann constant.

2 The triple point of water

Everybody knows that water, as most substances, can exist in three different phases: the solid phase (ice), the liquid phase (simply water) and the vapor phase (water vapor).

Most of the people is also familiar with the fact that, under certain circumstances, two different phases of water can coexist at equilibrium: for example, freezing water and melting ice (but also liquid water and water vapor above the liquid surface) can coexist in an isothermal container without exchanging heat between each other.

It is not very well known that, there is a very special case in which all the three phases of water exist at equilibrium: the triple point of water.

The pressure-temperature (p - T) phase diagram is a very useful tool to understand how this unique state of water is possible and can be realized. In the p - T phase diagram (see fig. 1), any state of equilibrium of water is represented by a point in the 2D pressure-temperature space. The three boundary lines for the existence of a single phase (the so-called two-phase equilibrium lines) join at a single point: the triple point of water.

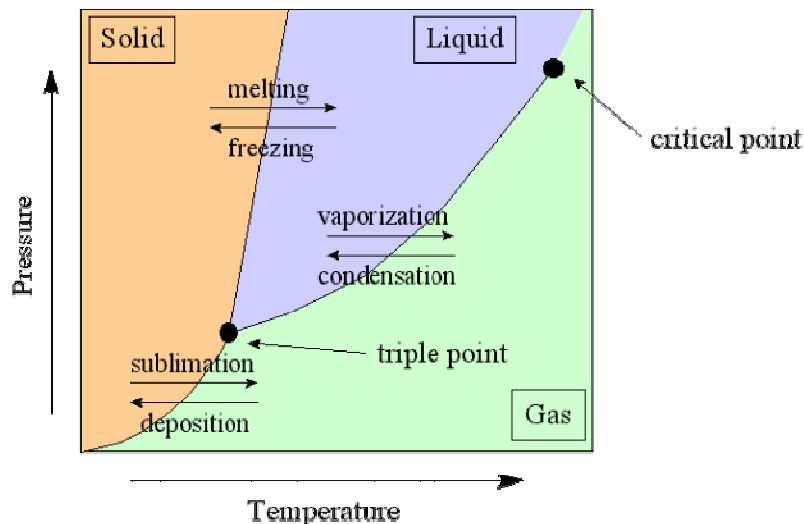


Figure 1: Phase diagram of water. Each point represents a physical state of equilibrium of water. The three boundary lines divide the plane into regions in which only one single phase exists (solid, liquid or gas). The points lying along the boundary lines represent states of coexistence of 2 phases (solid-liquid, liquid-gas, solid-gas). The boundary lines join at a single point, the triple point of water, in which all the three phases coexist at equilibrium.

3 Reference points for thermometry

Phase transitions have always been appealing to thermometrists because of the use as temperature reference points that can be made of them. The basic idea was that a phase transition always reproduces the same temperature (to be refined in the following: chemical and isotope compositions). For example, water always freezes at 0 °C and always boils at 100 °C. Unfortunately this is not true as can be easily seen from the phase diagram: any point along the solid-liquid equilibrium line (any point along the liquid-vapour equilibrium line) is a freezing point (boiling point) at a different temperature.

In other words, water freezes at 0 °C (and boils at 100 °C) only under "normal" pressure (101325 Pa). So if we want to use melting ice (and boiling water) as a temperature reference point at 0 °C (100 °C), we have to take care to keep the pressure at exactly 101325 Pa.

4 The water triple point as temperature reference point

The water triple point is the ideal temperature reference point because, once established, its temperature is uniquely defined and there is no need to control (or measure) the pressure (because also the pressure is uniquely defined).

Moreover the triple point is intrinsically stable in the sense that an external perturbation (for example an heat injection to the system) does not induce any temperature (or pressure) change. The perturbation will just re-adjust the relative amount of solid, liquid and vapor (for example a heat injection will melt some ice and will evaporate some liquid water) without changing the thermodynamic state.

The last highly desired self-controlling behavior of the water triple point is common to all first order thermodynamic transitions (every time a latent heat is associated to the transition).

5 The water triple point, the thermodynamic temperature scale and the international temperature scale

Temperature is one of the seven fundamental physical quantities. The scale of thermodynamic temperature is defined by assigning to the triple point of water a temperature of 273.16 K. The SI unit of temperature (kelvin) is then simply defined as 1/273.16 the temperature of the water triple point.

As direct measurements of the thermodynamic temperature T are very complex and time consuming, for practical reasons an empirical scale was introduced (International Temperature Scale of 1990, ITS-90) which allows to identify instead an International Temperature T_{90} in an easier, more precise and more reproducible way.

In defining the ITS-90 we give the definition of a new quantity T_{90} that can be used for all practical purposes and is a close representation of thermodynamic temperature.

The ITS-90 has been constructed in such a way that, for any given temperature, the numerical value of T_{90} is a very close approximation to the numerical value of T (according to best estimates at the time the ITS-90 was adopted).

Nevertheless, in some temperature ranges, the definition of T_{90} is the result of a trade off between simplicity and closest approximation to T and a detectable difference between the numerical values of T_{90} and T exists (see Figure).

In the range 13.8033 K to 961.78 K, any temperature T_{90} is determined in terms of the ratio $W(T_{90})$ of two resistances of a standard thermometer, the resistance $R(T_{90})$ at the temperature T_{90} and the resistance $R(273.16)$ at the triple point of water:

$$W(T_{90}) = R(T_{90})/R(273.16)$$

Clearly the measurement at the triple point of water is crucial for thermometry as it pops up inexorably at any temperature.

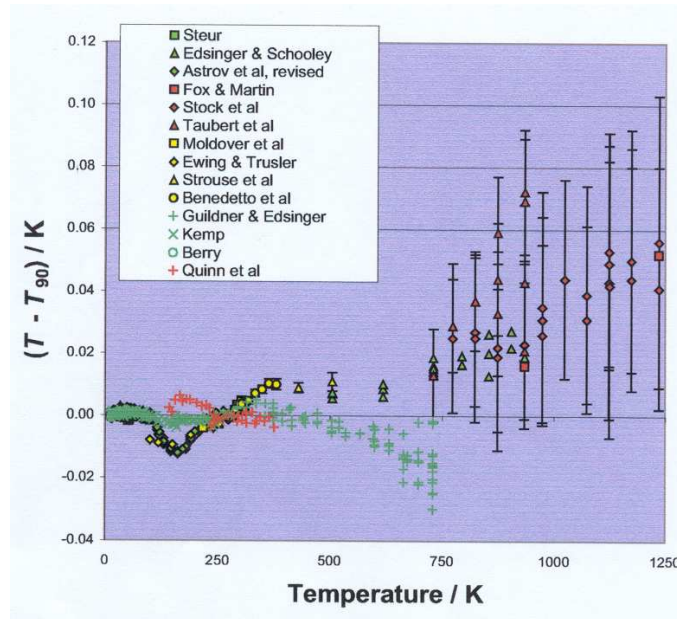


Figure 2: Difference between the Thermodynamic Temperature T and the International Temperature T_{90} , as obtained by absolute measurements of different scientists.

6 The water triple point cells

In practice the triple point of water is realized by using sealed glass (or quartz) cells (WTPCs, water triple point cells, see picture) containing high-purity water. A re-entrant well, located along the axis of the cell, allows for insertion of the thermometer to be calibrated.

By cooling the re-entrant well (with liquid nitrogen, carbon dioxide or other techniques) an ice mantle is produced around the re-entrant well. When the cell is accommodated in a water bath controlled at a temperature close to 0.01 °C, the equilibrium between the three phases is automatically established.

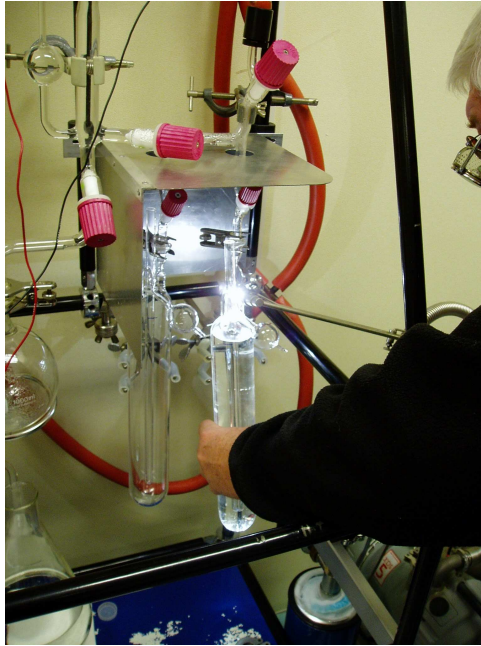


Figure 3: Manufacture of a water triple point cell at NMI VSL. The glass blower is sealing off a new water triple point cell from the distillation system.

7 The last international comparison of water triple point cells

The national standards for the water triple point temperature, maintained at 20 National Metrology Institutes worldwide, were compared in a recent international key comparison of water triple point cells, coordinated by the International Bureau of Weights and Measures (BIPM, Sevres, Paris).

The results (see fig. 4) showed significant discrepancies between the water triple point temperatures realized by different countries. For example, it is clear that the triple point temperatures of South Africa, New Zealand and Canada are “hotter” than the rest of the countries.

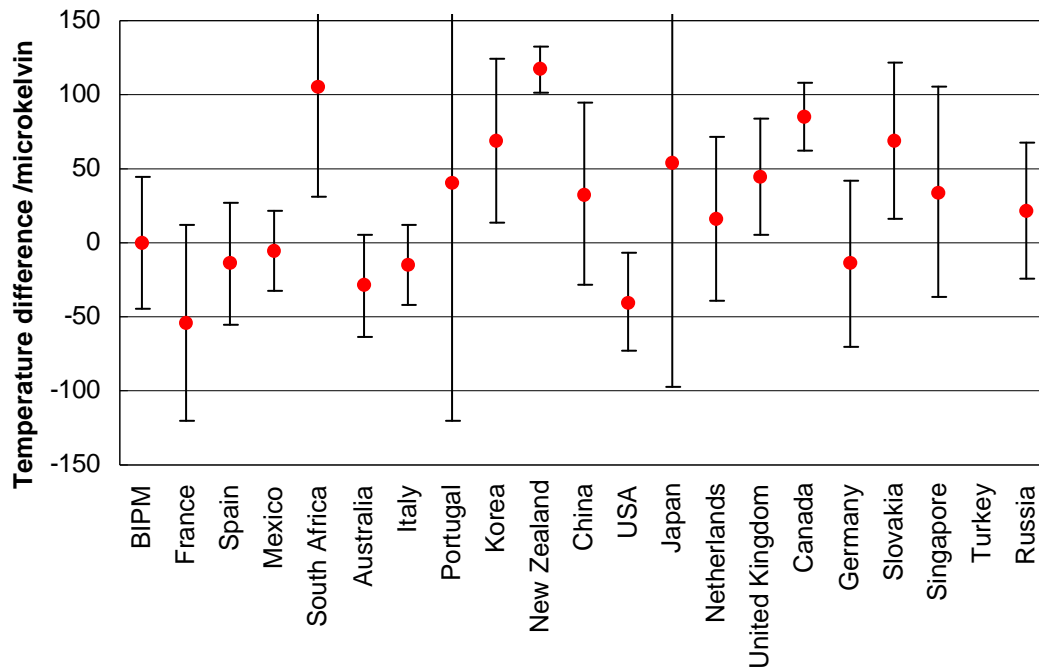


Figure 4: Temperature differences observed between the water triple point realized by different countries during the recent international comparison coordinated by the International Bureau of Weight and Measures (BIPM), Paris. Uncertainties are K=1.

These differences were attributed to various effects influencing the triple point temperature realized by a water sample, the most principle one being the mixing character of pure water with respect to its isotopic composition that will be discussed in the next chapter.

8 Isotope effects on the temperature of the water triple point

The physical explanation of why the isotope composition affects the triple point temperature of a water sample is very straightforward.

A molecule of water is made of two atoms of hydrogen and one atom of oxygen. Not all the atoms of hydrogen are identical. Most of the atoms of hydrogen are protium (^1H , simply one proton in the nucleus) but a small fraction (around one over 6700) of the atoms is deuterium (^2H , one proton and one neutron in the nucleus). The same applies to the atoms of oxygen. Most of them are ^{16}O , but one out of 2900 is ^{17}O and one out of 500 is ^{18}O .

Not all the combinations of different hydrogen and oxygen isotopes occur in natural water. The most abundant combination is $^1\text{H}^1\text{H}^{16}\text{O}$ but also a non-negligible fraction of $^2\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}^1\text{H}^{17}\text{O}$ and $^1\text{H}^1\text{H}^{18}\text{O}$ is present.

Each one of the above-mentioned 4 main isotopologues has a different triple point temperature (see table 1) and the triple point temperature of any sample of natural water depends on the relative concentration ratios of the component isotopologues.

<i>Isotopologue</i>	<i>Triple point temperature /K</i>
$^1\text{H}^1\text{H}^{16}\text{O}$	273.1587 (estimate)
$^1\text{H}^1\text{H}^{17}\text{O}$	273.31 (estimate)
$^1\text{H}^1\text{H}^{18}\text{O}$	273.46
$^2\text{H}^2\text{H}^{16}\text{O}$	276.97

9 The global meteoric water cycle: light water and heavy water

Due to various natural processes, isotope abundances of meteoric waters vary over place and time on earth. On a global scale, the most important natural processes affecting isotope composition of meteoric waters are evaporation and condensation.

Most water vapor on earth is produced by evaporation in the tropics for two simple reasons:

1. That is where it is warmest.
2. Because of the spherical shape of the earth there is a very large surface area at low latitudes.

Much of this water vapor rains out again close to the equator (it is not called tropical rain forest for nothing). But if we look at the net transport of water vapor on a global scale, we see that water vapor is traveling from the subtropical region towards the poles, losing continuously part of the total amount of water vapor due to repeated precipitations (condensation of water vapor into rain and snow) at higher latitudes. Only a very small fraction of the total water vapor makes it to the poles.

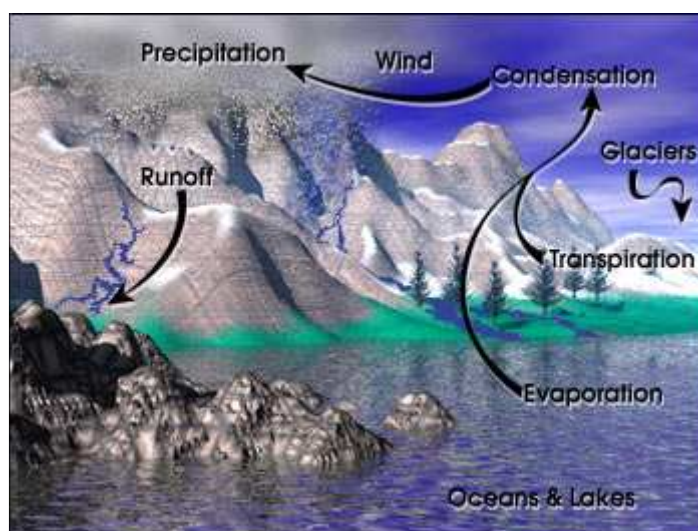


Figure 5: Pictorial view of the global water cycle.

But why is the isotope composition of water changing during these processes of evaporation and condensation?

The answer to this question is a physical phenomenon called isotope fractionation. When water evaporates, the lighter isotopes of water are more likely to leave the liquid than the heavier isotopes. On the contrary, when water condenses, the heavier isotopes have a slightly higher probability to do so than the lighter isotopes.

Looking at the global meteoric water cycle in light of isotope fractionation, it should be clear that evaporated water is poorer in heavier isotopes (depleted, in the language of isotopes) and condensed water is richer in heavier isotopes (enriched, in the language of isotopes). As water vapor travels from the tropics towards the poles, it becomes more and more depleted because of condensation and subsequent precipitation of heavier isotopes.

That's why the lightest natural water on earth is polar snow and the heaviest water can be found in the lakes of central Africa.

10 Vienna Standard Mean Ocean Water (VSMOW)

The isotope content of a water sample is defined by the concentration ratios of the component isotopes. As absolute concentration ratios cannot be measured with sufficient accuracy, concentration ratios are expressed as relative to a reference isotopic composition. For water the internationally accepted standard is Vienna Standard Mean Ocean Water (VSMOW) reference material of International Atomic Energy Agency (IAEA).

The isotope composition of VSMOW is:

$$\begin{aligned}\left({}^2\text{H}/{}^1\text{H}\right)_{\text{VSMOW}} &= 0.00015576 \\ \left({}^{18}\text{O}/{}^{16}\text{O}\right)_{\text{VSMOW}} &= 0.00200520 \\ \left({}^{17}\text{O}/{}^{16}\text{O}\right)_{\text{VSMOW}} &= 0.0003799\end{aligned}$$

The isotope composition of natural water is described in terms of departure from VSMOW composition:

$$\delta^2\text{H} = \frac{\left({}^2\text{H}/{}^1\text{H}\right)_{\text{sample}} - \left({}^2\text{H}/{}^1\text{H}\right)_{\text{VSMOW}}}{\left({}^2\text{H}/{}^1\text{H}\right)_{\text{VSMOW}}}$$

and analog expressions for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$.

11 Refining the definition of the water triple point temperature

In the original ITS-90 definition of the water triple point temperature, attention was paid to the isotope-mixed character of natural water by requiring the water being “substantially of the same isotopic composition of ocean water”.

In fact the isotopic composition of ocean water is surprisingly uniform all around the earth and its variability would produce a spread in the water triple point temperature of only 2 μK (provided that the water is sampled properly away from river deltas and more than 2 meters deep).

Unfortunately the manufacturer of water triple point cells did not take very seriously the ITS-90 recommendation about the isotopic composition and the water used to manufacture the cells has been invariably continental fresh water.

As consequence the isotope effect is presently one of the major sources of the observed variability between different realizations of the water triple point.

The CCT has recently clarified the definition of the Kelvin by specifying that:

- The definition of the Kelvin refers to water of a specified isotope composition.
- This composition is that of the Vienna Standard Mean Ocean Water of IAEA.

12 Towards a new definition of the Kelvin through the Boltzmann constant

For over 50 years, the unit of thermodynamic temperature, the Kelvin, has been based on an assigned value for the thermodynamic temperature of a particular state of matter, the triple point of water, 273.16 K.

However, this definition is arbitrary and the value was adopted for consistency with previous practice, in which the size of the unit was fixed by assigning 0 C to the melting point of ice and 100 C to the boiling point of water.

The definition has provided an acceptable basis for thermometry but it leaves temperature (and other thermal quantities) apart from the rest of the SI. Temperature and the other fundamental quantities are only linked through the Boltzmann constant k , whose value is subject to experimental determination.

It is now suggested that this situation should be reversed: the value for k should be assigned in the SI and the unit of temperature thereby fixed.

As part of a wider move to define the units of the SI in terms of fundamental constants, the CIPM now proposes that the kelvin should be defined not by reference to a particular state of matter, but by specifying the value for the Boltzmann constant.

The advantages of making this change are:

- The unit would be simply related to a fundamental physical constant, much as has been done for other units
- The unit becomes independent of any particular substance, or temperature, or measurement method
- By linking the unit directly to energy, it is more fully integrated with mechanical, electrical, optical and other units in the SI
- The determinations of thermodynamic temperature can be made directly, without the need to refer to the triple point of water.

The Boltzmann constant k is the conversion factor between thermal and mechanical energies for a particle. The value of k can thus only be obtained by carrying out an appropriate experiment linking thermal to mechanical quantities at a given temperature.

The relative uncertainty with which the given temperature can be known provides the lowest relative uncertainty with which the value of k can be determined by such an experiment. The lowest relative uncertainty for a temperature can be obtained at the water triple point: the uncertainty in the realization of the water triple point is in fact about 50 μ K (0.18 ppm). That is the reason why all the experiments performed until now to determine k were carried out at the triple point of water.

The smallest uncertainty in k obtained so far in any of these experiments was 1.8 ppm. (10 times worse than the uncertainty of realization of the water triple point).

When the redefinition of the kelvin will take place, the Boltzmann constant will become a defined quantity (with no uncertainty) and the numerical value of thermodynamic temperature of the water triple point (still 273.16 K) will not be anymore exact by definition but it will have an uncertainty that would be initially the uncertainty of the measurements of k at the moment of redefinition. If such a redefinition took place today, the uncertainty of the thermodynamic temperature of the triple point of water would be 0.46 mK (1.8 ppm).

If, in due course, more precise measurements of k were made that indicated a value different from 273.16 K for the temperature of the triple point of water (hopefully within the present uncertainty of 0.46 mK) then we will have to decide whether or not to change the value of 273.16 K. The sort of experiment that would lead to such a new value would simply be, for example, an acoustic thermometer at the triple point of water that using the new value for R obtained from k and N_A , would give a value for the triple point temperature different from 273.16 K.

Acknowledgments

The last chapter is extracted from two different specialist papers:

1. T. Quinn, "*Temperature scales and units and implications for practical thermometry of a possible redefinition of the Kelvin in terms of the Boltzmann constant*", CCT document CCT/05-26, BIPM, Paris (restricted).
2. R. Rusby et al., "*Review of methods for a redetermination of the Boltzmann constant*", National Physical Laboratory (NPL) report DEPC TH 006, not restricted.