THE GALLIUM POINT, AN ALTERNATIVE REFERENCE TEMPERATURE TO THE WATER TRIPLE POINT

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ABSTRACT/SUMMARY

The Water Triple Point with absolute Zero are the two defining points of the Kelvin Thermodynamic Temperature Scale, however water is a mixture of isotopes and therefore has more than one possible triple point temperature.

The author considers Gallium as a possible alternative to the Water Triple Point.

Eight properties of Gallium are considered;

Impurities, the possibility of peritectics, the isotopic composition, the effects of oxides. The spread of actual measurements, the interoperability of Gallium Cells, the hydrostatic head effects and the life of the Gallium Cell.

A table listing the advantages of either Water or Gallium is presented and discussed it is considered that Gallium should be considered seriously as an alternative to the Water triple Point because of its immediate availability for use compared to the fully annealed Water Triple Point Cell.

INTRODUCTION

The Kelvin Thermodynamic Temperature Scale (KTTS) is defined by only two temperatures, absolute Zero and the Triple Point of Water.

The Kelvin or Degree Celsius is 1 ÷ 273.16 of the interval between those two temperatures.

There is no particular reason why the Triple Point of Water is chosen except that water is abundant and has traditionally been the key fixed temperature in the form of pure Ice/Water mix.

There are a number of reasons why the Water Triple Point may not be the best artefact to define the Kelvin.

Apart from the fragile nature of the glass container and the sophisticated procedures required firstly to create the Water Triple Point and then to fully anneal the Ice Mantle before accurate measurements are made. [8]

There are two main areas of concern.

Firstly very pure water dissolves its glass container, slowly but inexorably. [9]

Secondly, water is an isotopic mixture of ^{2}H, ^{3}H, ^{17}O and ^{18}O and therefore does not have a single triple point temperature. [10]

An uncertainty of 100µK is usually given to the Water Triple Point unless very special analysis and procedures are used.

If the Water Triple Point is not ideal, then is there a better alternative?

Gallium stands out from the other ITS-90 Fixed Point materials for a number of reasons and may be a candidate for an alternative to the Water Triple Point.

GALLIUM

Discovery and Occurrence

Gallium was discovered in 1875 by the French chemist, Lecoq de Boisbaudran. Spectroscopic examination of concentrates from a Pyrenean zinc blende revealed emission lines whose positions corresponded to those predicted for “eka-aluminium”, a missing element between aluminium and indium in Mendeleev’s periodic scheme of the elements. Boisbaudran subsequently prepared this new element by electrolysis of caustic solutions and observed some of its properties. He named it gallium from the Latin *Gallia* in honour of his fatherland.

Table 1 - Physical Properties

Symbol	Ga
Atomic weight	69.72 (60.2% Ga-69; 39.8% Ga-71)
Crystal structure	pseudtetragonal (a=4.5167, b=4.5107, c=7.6448)
Specific gravity, 29.6° (solid)	5.904
29.8° (liquid)	6.095
Surface tension, 30°	735 dynes/cm
Viscosity, 100°	1.60 centipoises
500°	0.81
1000°	0.59
Melting point	29.7646°C
Latent heat of fusion	19.16 cal/g
Vapour pressure, 900°	0.0001mm
1000°	0.0008
1100°	0.0059
1200°	0.0309
1500°	1.41
Specific heat, 29-127°C.	0.0977 cal/g/°C
Coefficient of linear thermal expansion	1.8 x 10-5
(average)	0.08 cal/sec/cm/°C
Thermal conductivity, 30°C	17.5 microhm-cm
Electrical resistivity (solid) a axis	8.20
b axis	55.3
c axis	

PHYSICAL PROPERTIES

Some of the physical properties of gallium are given in table 1.

As a solid, gallium strongly resembles zinc, showing a bluish luster and a semibrittle fracture. The liquid metal, when free of oxidation limits the number of applications that could be envisioned for a metal that is liquid near room temperature. The adherence of this oxide to most surfaces gives the appearance of wetting. Oxide-free gallium does not wet any surface, however, until the actual onset of alloying or chemical reaction with the surface.

Gallium has a very unusual crystal structure. It is pseudotetragonal, with a very open lattice. The average nearest neighbour distance in the solid is greater than that in the liquid, and the metal expands more than 3% on freezing. Bismuth is the only other element that exhibits this property.

Gallium can be maintained liquid indefinitely at temperatures considerably below its normal freezing point. Occasionally, it can be held at liquid nitrogen temperature (77°K) for short periods without freezing. The unusual crystal structure of gallium is perhaps responsible for the inability of dust particles, oxide, container walls, etc., to nucleate crystallisation of this super-cooled liquid, since nucleation requires some conformity between the structure of the nucleus and the crystal. Speculation in the early literature that the supercooling behaviour of gallium is related to the purity of the material has not been verified.

PURIFICATION OF GALLIUM

Almost all current uses of gallium require material of extreme purity. Fractional crystallisation is universally employed to upgrade the purity of gallium after acid cleaning. Practices by different gallium producers differ in the manner in which crystallisation is nucleated, the size of the crystals that are produced, fraction of metal frozen per crystallisation, number of crystallisations, recycling schedule of the liquid, etc. no peritectic impurities have been observed in gallium; hence, there is no benefit from rejecting the first fraction to freeze. Silver, lead, copper, gold and zinc concentrate strongly in the last portion to freeze.

Probably, elements that do not show a pronounced tendency to segregate during freezing, such as iron, aluminium, magnesium, silicon, and calcium, have migrated to exposed surfaces where they were oxidized and became incorporated in the oxide skin, or they were not truly dissolved in the gallium.

Since gallium is perhaps the purest metal that can be obtained commercially there has been considerable interest in determining some of its fundamental properties.

USES OF GALLIUM

When gallium first became available, it appeared that its chemistry was uninteresting and that there were few applications of its compounds where cheaper materials would not serve as well. In the metallic form, on the other hand, gallium seemed to offer properties not found in any other material. It is relatively inert, nontoxic, and with a melting point only slightly above room temperature and a boiling point of 2403°C it has one of the widest liquid range of any metal.

The above general description is only part of the story, since we propose a specific application for gallium i.e. the replacement of the Water Triple Point.

It is possible to refine gallium to 99.99999% purity and this is done economically because of its wide use in the semi-conductor industry.

During the 1970's it was developed by Henry Sostmann, NBS and others as a new Fixed Point on the temperature scale and because of its proximity to body temperature it is probably the most important new point on the ITS-90 scale.

At 7N+ purity it is capable of as good reproducibility as the Water Triple Point.

The Gallium Melt Point appeared for the first time on the ITS-90 and has a designated temperature of 29.7646°C. gallium expands, 3% on freezing and so cells are made of Teflon. Because it is rugged and very easy to melt, (a thermos of warm water is all that is required) it has been suggested that it be used instead of the Water Triple Point as the Reference Standard.

This paper lists some of the factors that need to be considered if uncertainties smaller than ±100µK are to be associated with the Gallium Point.

1. Impurities[1]; Gallium is available with impurities close to 10^{-8} or 0.01ppm. Impurities of 1ppm would cause a melt slope of 1 to 2mK and one would expect a slope of 10 to 20µK for an 8N pure cell. Measurements confirm this.

2. There are no known peritectics of gallium[2], all impurities lower the melt temperature, thus selecting a gallium cell of the highest temperature implies the highest purity.

3. There are only 2 stable isotopes of Gallium[3];

   ${}_{31}Ga^{68}$ has atomic weight 68.92558.
   ${}_{31}Ga^{71}$ has atomic weight 70.9247.

   What we call gallium is a mixture of the two isotopes. Gallium contains 60.2% of the lighter isotope and with 39.9% of the heavier.

   This gives gallium an atomic weight of 69.72123.

   The actual isotopic composition is very stable and uniform because of the very high boiling temperature. (Gallium has the largest temperature span between melt and boil temperature 29.7646°C and 2400°C respectively) – *private correspondence with Dr. P. Dennis.*

4. The oxide is insoluble in the metal[4] and therefore the Gallium Melt does not change its temperature if oxygen is present.

5. Practical Measurement[5]; NIST have made 12 cells of 3 designs with gallium from 4 sources of $7N^+$ purity.

   All had the same triple Point the True Triple Point would require a vacuum of 10^{-14} Bar and so to be accurate we should say that we approximate to the Triple Point within ±20µK.

6. Interoperability[6]; The highest temperature NIST cell was compared to a $7N^+$ cell made at Isotech in England and housed in a locally made apparatus they agreed within 4µK after all corrections were made.

7. Hydrostatic head change during melt[7]; A typical cell has 230mm immersion from surface to well bottom and gallium contracts approximately 3% on melting thus the H.H. would reduce approximately 0.75cm during the complete melt or 9µK in terms of temperature change.

8. Life over a 25 year period no change in performance was noted [11].

DISCUSSION

All the above factors need consideration both for the Water Triple Point and for the Gallium Triple Point. Table 2 below summarises the relevant aspects of both cells.

Table 2 – Intercomparison of Water & Gallium Triple Points

	Water	**Gallium**
Impurities	Small	Small
Peritectics	None	None
Variation with Isotopes	Large	None Found
Interoperability	Good	Good
Practical Variation	40µK	40µK
H.H. Uncertainty	Small	10µK
Ruggedness	Poor	Good
Ease of Use	Difficult	Easy
Apparatus	Ice Bath & CO_2	Warm Water
Price	Low	High
Drift with Time	4µK/year	None Detected
Time before Best Accuracy	10 days	1 to 2 Hours

It is perhaps useful to consider various levels of operation and uncertainties.

At the very highest level of use it would take a great deal of convincing for BIPM to change from the Water Triple Point.

Provided the best Water Triple Point Cells are accompanied by a Certificate of Isotopic Composition, are relatively new and regularly compared with other cells of known Isotopic Composition. Provided the cells are meticulously made, maintained and measured, then the Water Triple Point is capable of very small uncertainties.
However, the melt plateau of $7N^+$ gallium is as accurate, as reproducible, requires no annealing time, is rugged and needs only warm water as its apparatus and so is recommended for all day-to-day measurements.

Considering costs, one has to take the complete cost over a 5 year period. A typical Water Triple Point Cell costs say $1,200 and a full sized gallium cell $5,000, apparatus costs are similar if an automated system is used around £5,000.

For accuracies of 100µK the Water Cell needs to be left a minimum of 24 hours and ideally 10 days, whereas for 100µK a 7N pure Gallium Cell will give this within 1 hour. Since the Gallium Point can be completely automated the Gallium Cell is available 365 days a year 16 hours a day the Water Triple Point cannot give this performance.

The cost of ownership in terms of time spent in making up the Water Triple Point Cell means that over a 5 year period the total cost of a Gallium System is less than the Water Triple Point.

CONCLUSION

The Gallium Melt, or Triple Point Cell has a lot to recommend it and should perhaps have a special place on the next temperature scale.

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