[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Ice-point as a Standard of Reference[1]

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In the course of setting up a temperature scale it was found that an ice-bath prepared with ordinary precautions could not be relied upon to reproduce temperatures, from day to day, much closer than about 0.004°. White[2] recently has demonstrated that by a special procedure the melting point of ice can be reproduced to within 0.0001°. However, a reproducibility of 0.001° is generally the extreme requirement for a temperature scale (in the range 0 to 100°)[3] and this accuracy also suffices for the most precise measurement of many physical properties such as vapor pressure, conductivity, gas density. Two exceptions are calorimetry and the freezing points of dilute solutions; here the value of the absolute temperature is not as important as the small temperature changes. The procedure of White provides a reference temperature for these exceptions and in this paper no such precise requirements will be considered.

The inner container used in White's procedure offers some difficulties if apparatus more bulky than an electrical thermometer is to be immersed in the ice-bath. For example, a glass globe of 500-cc. capacity would require a Dewar tube of some 25 cm. internal diameter. Also if the globe was attached to a glass vacuum line through a glass capillary tube (as in gas thermometry), the inner container would be very impractical. The valuable contribution of White is somewhat restricted in its application and leaves uninvestigated the range 0.004 to 0.0001° reproducibility. The work reported in this paper was undertaken to ascertain whether a constancy of 0.001° could not be achieved by a simpler[4] means than the cold-cell of White. It has been found that a reproducibility of this order may be accomplished by adopting a part of White's technique, namely, the washing of the ice-bath, prepared in a simple Dewar tube, with chilled distilled water, providing certain other precautions are observed.

Experimental

Apparatus.—A four lead, 25-ohm helium-filled, coiled filament, platinum resistance thermometer[5] with a Mueller type 5-dial resistance bridge immersed in a controlled (25.0 ± 0.1°) oil-bath was used to measure the temperatures. A commutator, interchanging the thermometer leads and at the same time reversing the battery polarity, served to cancel effectively all lead resistance and stray electromotive force. The commutator and the external circuit from bridge to commutator was of massive copper bar, nickel-plated, with all connections made through the medium of mercury cups and heavy links. The various electrical circuits were shielded wherever possible.[6] The galvanometer[7] was of all-copper-electrical-circuit construction and gave a scale deflection of about 1 mm. per 0.0001 ohm with 2.6 m. a. in the thermometer circuit. The fundamental interval ($R_{100} - R_0$) was found to be 10.01 ohms, so that by estimating the galvanometer deflection to 0.5 mm., 0.0005° could be detected. The constants obtained from the standardization (sulfur, steam, ice, carbon dioxide and oxygen points) of this thermometer over the range −183 to +445° indicated that the platinum constituting the coil was of the requisite purity.[8] Excellent constancy of the ice-point resistance of the thermometer was observed; as an example, the value of R_0 changed by only 0.0001 ohm as a result of heating the thermometer to the boiling point of sulfur (445°). In order to ensure a strain-free condition, the thermometer was kept in an ice-bath at all times throughout these reported measurements (six days).

Procedure.—Clear, crushed (*ca.* 8-mm. particle size) or shaved ice is placed in a Dewar tube, inserting the thermometer so that the sensitive portion is well below the surface of the ice and 4 to 10 cm. above the bottom of the container. A glass-tube siphon is then placed permanently in the Dewar, its inner limb reaching to the bottom. The ice is now washed *in situ* with thoroughly chilled distilled water, which is then completely drained from the ice; it cannot be emphasized too strongly that chilled wash water (at *ca.* 0 ± 0.1°) be used, for if water at the temperature of the room is used, the major purpose of the washing is partly defeated, namely, to rid the ice of surface impurities without bringing more electrolytes into solution

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(1) Original manuscript received March 21, 1936.

(2) White, THIS JOURNAL, **56**, 20 (1934).

(3) Henning and Heuse, *Z. Physik*, **6**, 215 (1921).

(4) Dr. White, in a personal communication, has pointed out that from the viewpoint of obtaining 0.0001° reproducibility (which would be meaningless on the thermometer and bridge used in this work) it would be very undesirable to discard the inner cell.

I would like to take this opportunity to thank Dr. White for his valuable comments and suggestions concerning this paper.

Very recently a paper has appeared by Beattie, Tzu-Ching Huang and Benedict, *Proc. Am. Acad. Arts Sci.*, **72**, 137 (1938), concerning the reproducibility of the ice point and of the triple point of water. A high reproducibility (5×10^{-5} °C.) was calculated for the ice-point cell (White's cold cell) from a consideration of the experimentally measured conductance of the water obtained from the ice, the effect of pressure on the melting point and the depth of immersion of the thermometer. This work does not invalidate the statement made above that the range 0.004 to 0.0001° remains uninvestigated.

(5) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

(6) For such a bridge and accessories, see (a) *Bull. Bur. Standards*, **13**, 547 (1917); (b) *ibid.*, **11**, 295, 571 (1915).

(7) Constructed by the Leeds and Northrup Co., as was the thermometer and the bridge proper.

(8) Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

from melting of the ice. With a Dewar tube of about 1.5 liters capacity, 3 liters of chilled wash water added in six separate, equal increments, each increment being drained before the next is added, has always served to cleanse properly our crushed ice from electrolytes, and, as White has shown, the ice-bath will then take a temperature as determined solely by the purity of the wash water present.[9]

The ice-baths needed an additional charge of ice every four to six hours and if the measurements in one series were extended over a longer period than this, more of the same type of ice was added to the existent bath, which necessitated another washing process. Such a replenished ice-bath constituted the basis of one series which, in one case, was studied intermittently for five days. During the intervals in which measurements were not being taken, the thermometer was kept covered with ice.

TABLE I

ILLUSTRATING THE REPRODUCIBILITY OF THE MEASURING INSTRUMENTS

Time, P. M.	Temp.,[a] °C. ±0.0005°
Series JJ.	Ice Sample C
7:13	0.0000
7:15	− .0005
7:30	− .0005
7:31	.0000
Series KK.	Ice Sample D
2:35	0.0000
2:36	.0000
2:37	.0000
2:38	.0000

[a] Individual determinations, consisting of two resistance measurements, one for each position of the commutator.

TABLE II

PARTIAL RESULTS SHOWING THE REPRODUCIBILITY OVER PERIODS OF TIME AND FOR WASHED ICE-BATHS PREPARED FROM THE SAME TYPE OF ICE

Date	Number of ice charge	Θ, time interval from adding ice charge, hours	Temp.,[a] °C. ±0.0005°
	Series JJ.	Ice Sample C (Crushed)	
Dec. 14	I	3.0	0.0000
14	I	6.7	− .0005
15	II	0.3	− .0010
16	III	.3	− .0010
16	III	.5	− .0005
17	IV	.2	− .0010
17	IV	1.0	− .0005
18	V	0.5	.0000
18	V	1.5	− .0005
18	V	2.0	− .0005
	Series LL.	Ice Sample C (Shaved)	
18	I	0.5	0.0000
18	I	.8	− .0005
18	I	1.0	− .0005

[a] Mean of all single determinations (generally three) performed at time Θ.

Ice from three sources was used: Sample D was frozen distilled water, in contact only with tin during the freezing process. Sample C was clear commercial ice, rinsed with tap water prior to crushing; Sample L was frozen tap water obtained from the Laboratory refrigeration machine, rinsed as for C.

Readings of the thermometer resistance taken over an interval of a few minutes will show the variations in the thermometer and the electrical measuring circuit, while readings taken over an interval of longer periods will have the ice-bath fluctuations superimposed upon the instrument error. A few selected values are given for illustrative purposes in Tables I and II. The data seem to indicate that the ice-bath fluctuations are of the same order as the instrument error, namely, ±0.0005°.

Establishment of 0.000$_0$° on the Thermometer.—The temperature given by ice sample D in contact with air-saturated distilled water was taken as 0.0000 ± 0.0005° by definition, corresponding to a thermometer resistance of 25.5329$_1$ ohms. The readings were taken over a period of four hours, varying the conditions in the ice-bath to make certain that it was really composed of pure ice in contact with pure, air-saturated water. These tests consisted of re-washing several times with air-saturated distilled water, re-washing with air-saturated conductivity water and withdrawal of all the liquid phase. In all the determinations performed on this ice-bath, of which there were 26, no change greater than the experimental error was observed.

The Effect of Variable Conditions.—A number of variable factors were studied: (a) ice quality; (b) purity of the washing water; distilled water and freshly prepared conductivity water were intercompared in the same bath; (c) time interval; (d) state of subdivision of the ice (samples of ice C were intercompared when crushed and when shaved); (e) degree of air-saturation of the washing water; (f) presence or absence of bulk liquid phase.

For the six variables studied, the temperature attained in the ice-baths, in all cases, was within 0.001° of the value as established as 0.0000° on the thermometer, providing, of course, that the proper washing procedure was applied when necessary.

Results

A summary of the results obtained is presented in Tables III and IV; in Table III the effect of the washing process is very evident and in Table IV the values for washed ice have been grouped according to the temperature established irrespective of the different conditions existing in the ice-bath. These data, plotted as a distribution curve in Fig. 1, graphically represent the variations observed. An inspection of the graph shows that it is of the general type of a probability curve but is not symmetrical about the 0.0000° ordinate. Rough measurement indicates that the area under the curve below 0.0000° is three

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(9) With some conditions, more or less washing water will be required; under any circumstances if a precise temperature measuring device is available (a Beckmann thermometer is not included in this classification), the temperature rise may be determined after each washing operation and when it has attained a constant value, this may be taken to be 0.000 ± 0.001°.

TABLE III

THE EFFECT OF THE WASHING PROCEDURE WITH DIFFERENT TYPES OF ICE

Ice designation	Before washing, temp. in °C., ±0.0005°	After washing to a constant temp.,[a] temp. in °C., ±0.0005°
D	0.0000	0.0000
C	− .0035	− .0005
L	− .0055	.0000

[a] Mean of all values obtained.

TABLE IV

SUMMARY OF ALL OBSERVATIONS ON WASHED ICE SAMPLES SHOWING THE TYPE OF DEVIATIONS ENCOUNTERED

Galvanometer deflection,[a] mm. ±0.5 mm.	Thermometer resistance, ohms, ±0.00005	Corresponding temp., t, °C., ±0.0005°	Number of observations, n, with value of t
−1.5	25.53276	−0.0015(and less)	0
−1.0	25.53281	− .0010	14
−0.5	25.53286	− .0005	31
.0	25.53291	.0000	51
+ .5	25.53296	+ .0005	6
+1.0	25.53301	+ .0010	2
+1.5	25.53306	+ .0015(and greater)	0

[a] Arbitrary scale.

times the area above. This non-symmetrical nature of the curve might be expected, since most of the difficulties will be experienced from electrolytes which will tend to give irregularities below the melting point. The implications are that irrespective of the variable conditions in the ice-bath which we have studied, the temperature established was within ±0.001 of 0.000° for washed baths. It would seem to be a fairly secure deduction that any ice of reasonable purity could be brought to ±0.001° by properly washing as described under *Procedure.*

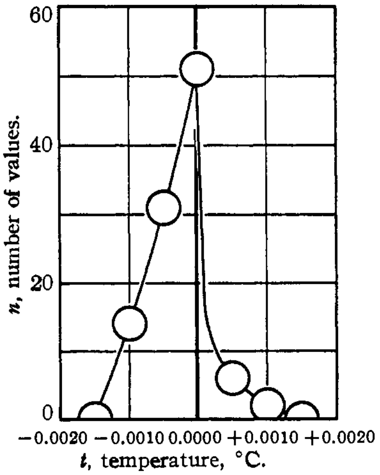

Fig. 1.—Distribution curve.

Air Saturation of the Liquid Phase.—It is possible for this effect to cause changes of several times the experimental error involved; for this reason it is entitled to special discussion. By definition,[8] the ice-point is taken as the temperature of equilibrium between pure ice and pure, air-saturated water at normal atmospheric pressure. Foote and Leopold[10] have given a discussion of the effect of dissolved air upon freezing points; they state that the freezing point of air-free water is +0.0023°, that is, −0.0023° is the colligative effect of the dissolved oxygen and nitrogen at a saturation pressure of 76 cm. No work appears to have been done on the rate of saturation, although Foote and Leopold are of the opinion that it is rapid. White[2] mentions that his water was chilled for three days and that occasionally sucking through pure air served to saturate completely the cold water. White also gives a method of testing for air saturation in the ice-bath: upon withdrawal of the liquid phase, the remaining water spread in a thin film on the surface and among the interstices of the ice particles almost instantaneously becomes saturated with air. The temperature drop after this withdrawal is then a measure of the extent of air saturation in the bath when the bulk liquid phase was present.

In this research, some samples of washing water were purposely saturated with air and others were not. Washing water denoted as "bubbled" had clean, carbon dioxide-free, air bubbled through the chilling water for various periods of time (one to thirty-six hours for various portions), and water denoted as "non-bubbled" did not receive this treatment but was chilled in loosely stoppered liter flasks, by direct immersion in Dewar jugs of crushed ice. Since the temperature attained by the ice in equilibrium with this non-bubbled water did not vary (±0.001°) either from that given by the bubbled water or from that obtained when all of the liquid phase was withdrawn from the ice, it can be concluded that the non-bubbled water must have been at least 65% saturated with air when it was added to the ice-bath. This saturation probably took place during the time required for chilling.

Applications

This washing procedure has been utilized by the author to prepare ice-baths which were used for: (1) temperature scale establishment, (2) vapor pressure investigations, (3) adsorption measurements, and (4) gas density determina-

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(10) Foote and Leopold, *Am. J. Sci.*, 11, 42 (1926).

tions. In the last-named application, a 500-cc. globe was immersed in an ice-bath made in a gallon Dewar jug (3.8-liter) and three liters of chilled, distilled washing water was used. In the first three applications, the ice was washed until no further change was noticed in the property being measured; such a method could be applied to conductivity of solutions, electromotive force of cells, surface tension by capillary rise, to mention but a few types of physico-chemical measurements in which the experimental data are obtained directly from a reading performed on the apparatus while it is immersed in the ice-bath. Indirectly measured properties such as surface tension by the drop weight method, density of liquids, are not suited to this type of verification of constant temperature in the bath. In such cases it is best to wash with a large excess of chilled water in order to be assured of 0.000°. No thermometer was used in these applications, since the work reported in this paper seems to indicate that an ice-bath prepared as directed is as constant as our delicate resistance thermometer. By this method of verification, considerable time was saved in collecting data, and it offers to workers not having access to a precise thermometer a method of obtaining 0.000°, to a greater accuracy than will be given by the best Beckmann thermometers.

Conclusions

(1) All three samples of ice could be brought to the same temperature[11] by the washing process described, although they differed initially by 0.006°. (2) Our distilled water when chilled to 0.0° in open flasks is then so saturated with air that the remaining effect of incomplete saturation is less than 0.001°. (3) The temperature attained after properly washing is the same over periods of time up to *ca.* six hours. (4) Duplicate ice-baths prepared by properly washing produce the same temperature. (5) The temperature established is identical whether the bulk liquid phase is present or absent; an ice-bath with no apparent liquid phase present seems to be as constant over a period of a few hours as one in which the ice is covered with water. This interval, from three to six hours, is about the maximum time during which the ice-bath should be left unattended.[12] (6) The state of subdivision of the ice was without effect upon the final temperature attained after washing. It was found, as would be expected, to be more difficult to free from electrolytes the shaved than the crushed ice. (7) If contaminating gases are present[13] this washing procedure offers a simple solution to the problem of maintaining a pure ice-bath. (8) Large ice-baths, containing bulky apparatus immersed therein, may be washed to constant temperature by employing relatively larger quantities of chilled wash water.

I wish to thank Professor Arthur B. Lamb for his advice in this work and for laboratory facilities placed at my disposal.

Summary

It has been demonstrated that by an adoption of White's washing technique crushed ice in a simple Dewar tube can be made to establish and maintain with certainty, a temperature of 0.000° with an accuracy of ±0.001°, and that this can be reproduced in other ice-baths prepared by the same method.

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[11] In this section, the same temperature is to be taken as to mean ±0.001°.

[12] See White, *Rev. Sci. Instruments*, **4**, 143 (1933), on this point. The heat leak into the Dewar influences the frequency with which the ice must be washed (assuming that electrolytes are present in the ice) to maintain a given tolerance of temperature, for the more rapid the melting process, the greater the amount of electrolytes that go into solution in a given time. The heat leak will be influenced by three factors: (a) the size of the apparatus extending from the room into the ice; (b) the heat leak of the Dewar tube proper, which in turn will be influenced by the form, the reflectivity of the silvered surface if present and the degree of exhaustion of the interspace; (c) the temperature of the room.

[13] See Thomas, *Bur. Standards J. Research*, **12**, 317, 323 (1934).