FREEZING POINT OF MERCURY

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The temperature at which mercury freezes is of importance in thermometry. It marks the lower limit in the use of mercurial thermometers, and its location at about –39° makes it an important fixed point of the temperature scale below 0° C.

Among the investigators who made precise determinations of this constant may be mentioned Regnault,[1] who in 1862 obtained –38°.50, B. Stewart,[2] 1863, whose value –38°.85 was the result of a very excellent experiment in which a constant volume gas thermometer was used, Vicentini and Omodei[3] in 1888, Chappuis[4] in 1896, and C. Chree[5] in 1898, who obtained the values –38°.80 ±0°.02, –38°.85, and –38°.86, respectively, using mercurial thermometers which had been previously compared with a gas thermometer. The latest determination of this point was made by Henning[6] in 1914. He obtained the value –38°.89, using platinum resistance thermometers which had been compared with a gas thermometer. The above values are fairly consistent and would indicate the freezing point of mercury to be in the neighborhood of –38°.8. However, two determinations of this point, –39°.44 and –39°.38, attributed to Hutchins[7] and Cavendish,[8] who investigated the subject in the period 1776 to 1783, have been published along with the later values and apparently have, in many cases,

[1] Mem. d. l'Acad., **26**, p. 525; 1862.
[2] Phil. Trans., **153**, p. 425; 1863.
[3] Atti della R. Acc. di Torino, **23**; 1887.
[4] Compt. rend. de la Conférence Générale, p. 291; 1896.
[5] Phil. Mag., **45**, p. 224; 1898.
[6] Annalen der Physik (4), **43**, p. 291; 1914.
[7] Phil. Trans.; 1776.
[8] Phil. Trans.; 1783.

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been given equal weight with them, although these early determinations are obviously entitled to little weight.

All the evidence at present available indicates that the scale defined by the platinum resistance thermometer, when calibrated at 0°, 100°, and 444.°6 (the boiling point of sulphur [9]), defines temperatures in agreement with those given by the hydrogen thermometer down to −40° C. A redetermination of the freezing point of mercury on the scale defined by the resistance thermometer seemed, therefore, of value.

SAMPLES OF MERCURY

The freezing points of three different samples of mercury were observed. These three samples were furnished by Mr. McKelvy, of this Bureau, and were designated as "U. S. P.," "Anode," and "Hulett Still." The modes of purification were as follows: U. S. P.: Purified to meet the test requirements of the U. S. Pharmacopœia. Anode: Electrolyzed in a mercurous nitrate solution with the mercury as anode. About 5 per cent was deposited on the cathode to eliminate metals more electropositive than mercury. The product remaining on the anode was then once distilled in vacuum. Hulett Still: An anode sample was distilled in a Hulett still under reduced pressure with a stream of air bubbling through the mercury. The last named of the three samples would thus be considered to be the purest. However, the three samples showed no difference in electromotive properties when used in a normal cadmium cell, nor do the results of the freezing-point determinations indicate the existence of any difference between the three samples.

THERMOMETERS AND MEASURING INSTRUMENTS

The three-resistance thermometers used were selected from a number made by H. K. Griffin, of this Bureau, about a year ago. These thermometers were made with potential terminals and the coils were wound to give a flexible mounting for the wire in the manner described by Waidner and Burgess.[10]

The highest purity Heraeus wire was used for the coils, and short (2 cm) lengths of the same wire were used for the connections between the ends of the coil and the gold lead wires. The glass tubes in which the thermometer coils were inclosed were closed at the top with plugs, sealed in with Khotinski cement, through

[9] Henning used 444.°51, but this introduces a difference of only 0.°004 between the two scales at the freezing point of mercury.

[10] Waidner and Burgess, this Bulletin, 6, p. 155; 1910.

which the lead wires passed. In this way access of moisture to the coils was prevented. The dimensions and constants of these thermometers are given in the Table 1.

TABLE 1

[R_0=mean observed resistance at 0°; F. I.=resistance at 100° minus resistance at 0°; δ=constant in Callendar formula]

Thermometer	R_0	F. I.	$\frac{F. I.}{R_0}$	δ	Diameter of wire	Length of coil	Internal diameter of tube
					mm	cm	cm
C 28	2.5373	0.99360	0.39160	1.496	0.15	4	0.5
C 24	10.0143	3.9143	.39088	1.496	.1	5	.8
C 22	25.5474	9.9875	.39094	1.495	.1	8	.8

The thermometers were calibrated in the ordinary way at 0°, 100°, and the sulphur boiling point (444°.6 at normal pressure). For the calibration use was made of a new sulphur boiling point apparatus to be described by Mueller and Burgess in a paper to appear later in this Bulletin.

The heating effect on the thermometers of the measuring current used was investigated. This effect is proportional to the square of the current and was found to be the same at 0°, 100, and −39°; thus no significant error could have been introduced from this source.

Table 2 shows the magnitude of this effect for the thermometers used.

TABLE 2

Thermometer	Usual measuring current in milliamperes	Heating effect— Per milliampere [2]	
		Per milliampere [2]	For usual current
		°C	°C
C 22	2	0.0004	0.0016
C 24	3	0.0003	0.0027
C 28	4	0.0002	0.0032

Three different Wheatstone bridges and also a potentiometer and standard resistance were used in making the resistance measurements. These bridges were designed at this Bureau. The bridges used are described [11] in Scientific Papers 241 and 288. By using a commutator as described by Mueller [12] the resistance between the potential terminals of the thermometers could be measured.

[11] This Bulletin, 11, p. 571; 1914. Ibid, 13, p. 547; 1916. [12] Ibid, 13, p. 556; 1916.

The bridges were calibrated in terms of international ohms, so that they could be used interchangeably. The potentiometer was of the Diesselhorst type made by Otto Wolff. The potentiometer was used to secure a check method but it did not give as high precision, at least with the low resistance thermometer, as the Wheatstone bridge method.

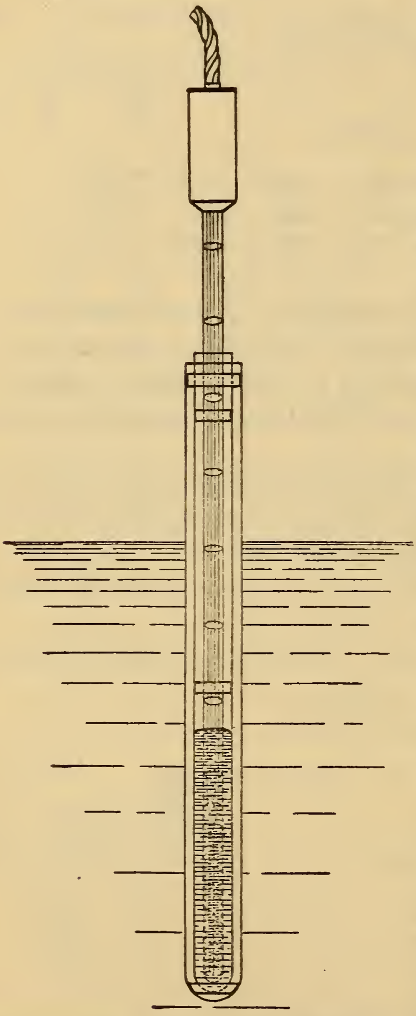

FIG. 1.—*Freezing point tubes with thermometer in position*

METHOD

The mercury was frozen in a glass tube 2 cm inside diameter and about 34 cm long. This tube was inserted in another glass tube 3 cm inside diameter. The thermometer and tubes were held in position by corks. Fig. 1 is a sketch of this apparatus showing one of the thermometers in position. About 38 cc of mercury was used which filled the inner tube to a depth of about 12 cm, which was increased to from 13 to 16 cm when the thermometer was introduced.

In freezing the mercury the tubes containing it were immersed to a depth of about 20 cm in a stirred bath which could be cooled to −50° by expanding carbon dioxide through a coil immersed in a liquid consisting of a mixture of gasoline and carbon tetrachloride. Under these conditions the temperature of the freezing mercury remained constant sometimes for as long as 30 minutes. In some cases where a complete freezing and melting point curve was desired the bath was held at a temperature lower than the freezing temperature until the entire mass of the mercury had frozen and its temperature had begun to fall. If the bath were then allowed to heat up to a temperature higher than the freezing temperature, the melting point could be observed.

PRECAUTIONS

Care was taken to insure that the thermometer coil was sufficiently immersed in the mercury. Conduction down the leads might cause a higher or lower reading, depending on whether the surrounding bath, and thus the air above the mercury, was at a higher or lower temperature than the mercury. Errors from this source would be more likely to occur in the use of thermometer C 22, the coil of which was longer than those of the other two. The effect of raising and lowering the thermometer while the mercury was freezing was observed for C 22. It was found that

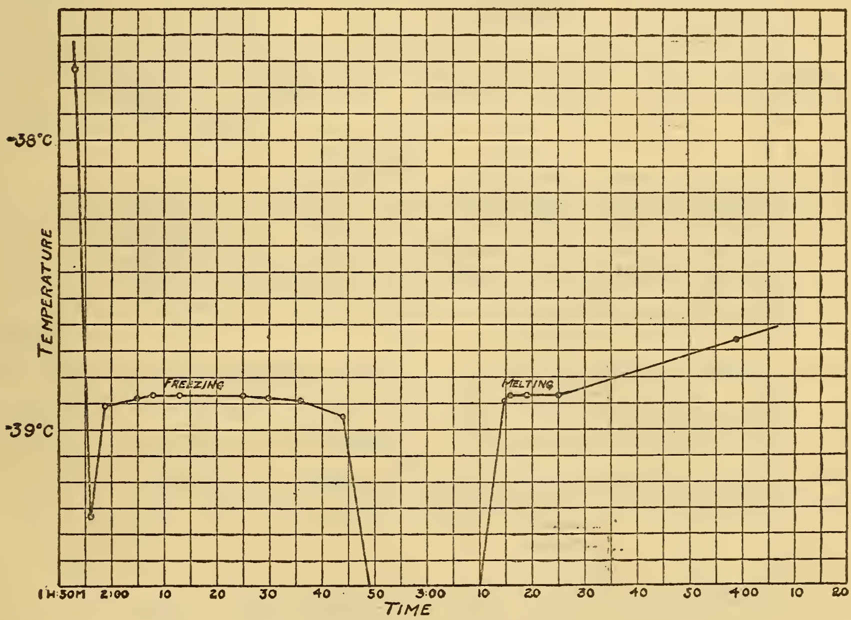

FIG. 2.—*Freezing and melting point curve*

an immersion of 13 cm (measured from end of tubing) was sufficient to eliminate this source of error. The absence of any disturbing effects due to conduction is also attested by the fact that the results obtained were independent of the outer bath temperature, which varied from below $-50°$ up to $-30°$.

FREEZING AND MELTING POINT CURVES

Fig. 2 shows a typical freezing and melting point curve. A supercooling of several tenths of a degree precedes the constant temperature assumed later when freezing is taking place. No significant difference was noted between the temperatures of the freezing and melting points.

RESULTS

The results are given in Table 3. The mean of the freezing points obtained by the bridge method of resistance measurement with all of the thermometers was $-38^\circ.871$ for the U. S. P. mercury, $-38^\circ.872$ for the anode mercury, and $-38^\circ.872$ for the Hulett still mercury. The mean of all results obtained using the bridge method of resistance measurement is $-38^\circ.872$, while the mean result by the less precise potentiometer measurements is $-38^\circ.875$. The mean of all the freezing point determinations is $-38^\circ.873$ and the mean of the melting point determinations is the same.

TABLE 3

Date	Thermometer	R_0	Rt	t	Sample of mercury	Measuring instruments	Freezing or melting point
1916							
Feb. 7....	C 22.....	25.5473	21.5843	−38.872	Anode.........	Bridge 11672...........	Freezing.
Feb. 8....	...do.....	25.5472	21.5843	−38.872	.....do.........	.....do................	Do.
Do......	...do.....	25.5472	21.5845	−38.874	.....do.........	.....do................	Melting.
Mar. 11...	...do.....	25.5475	21.5844	−38.874	Hulett still....	Bridge 1648............	Freezing.
Apr. 3.....	...do.....	25.5475	21.5842	−38.875	.....do.........	.....do................	Do.
Mean..	....	....	....	−38.873			
Mar. 13...	C 22.....	25.5479	21.5848	−38.874	.....do.........	Potentiometer 11576...	Do.
1915							
Aug. 14...	C 24.....	10.01438	8.46127	−38.871	.....do.........	Bridge 1648............	Do.
1916							
Jan. 22....	...do.....	10.01438	8.46127	−38.871	U. S. P........	Bridge 7481............	Do.
Mar. 11...	...do.....	10.01402	8.46104	−38.868	Hulett still....	Bridge 1648............	Do.
Mean..	....	....	....	−38.870			
Mar. 13...	C 24.....	10.01416	8.46109	−38.870	.....do.........	Potentiometer 11576...	Do.
Mar. 20...	...do.....	10.01432	8.46087	−38.877	.....do.........	.....do................	Do.
Mean..	....	....	....	−38.874			
Jan. 19....	C 28.....	2.53740	2.14310	−38.875	U. S. P........	Bridge 7481............	Melting.
Jan. 27....	...do.....	2.53734	2.14311	−38.868	.....do.........	.....do................	Do.
Jan. 28....	...do.....	2.53731	2.14305	−38.871	.....do.........	Bridge 1648............	Freezing.
Do......	...do.....	2.53731	2.14303	−38.873	.....do.........	.....do................	Melting.
Do......	...do.....	2.53731	2.14304	−38.872	Anode.........	Bridge 7481............	Freezing.
Mar. 11...	...do.....	2.53726	2.14301	−38.870	Hulett still....	Bridge 1648............	Do.
Mean..	....	....	....	−38.872			
Mar. 11...	C 28.....	2.53703	2.14273	−38.875	.....do.........	Potentiometer 11576...	Do.
Mar. 21...	...do.....	2.53729	2.14296	−38.877	.....do.........	.....do................	Do.
Mean..	....	....	....	−38.876			

These results show that the precision attainable in the determination of the freezing point of mercury is better than 0°.01. It seems probable that the experimental conditions were varied sufficiently in the present work to preclude the possibility of a systematic error of as much as 0°.01 in the result, expressed on the scale defined by the platinum resistance thermometer. The difference between this result (−38°.87) and that found by Henning (−38°.89), also in terms of the scale defined by the platinum resistance thermometer, is greater than would be expected from the accidental errors of either determination. It seems improbable that the discrepancy is due to impurities in the mercury, although it is known that the method of purification used by Henning (distillation in vacuum) [13] is not effective in removing traces of certain metals.

SUMMARY

The freezing point of mercury was determined, using platinum resistance thermometers.

A short historical sketch gives the names of previous investigators, their methods of temperature measurement, and values obtained.

Nineteen determinations were made on three samples of mercury purified by different methods. Three resistance thermometers having resistances in melting ice of approximately 2.5, 10, and 25 ohms, respectively, were used. Resistance measurements were made both by the Wheatstone bridge method and the potentiometer method.

The result of all the measurements gives −38°.873 for the freezing temperature. The maximum deviation of any determination from the mean is 0°.005.

WASHINGTON, August 1, 1916.

[13] Geo. A. Hulett and Howard D. Minchin, Phys. Review, 21, p. 388; 1905.