CONDITIONS AFFECTING THE FREEZING TEMPERATURE OF SILVER

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ABSTRACT

A study was made of the precautions which should be observed in using the freezing point of silver as a thermometric fixed point. Observations were made on three samples of silver containing various amounts of impurities. The depression of the freezing point due to absorption of oxygen was measured under a number of conditions. It was found that graphite crucibles and covers were as effective in protecting silver from oxygen as a vacuum 0.005 to 0.03 mm of Hg.

CONTENTS

I. INTRODUCTION

The International Temperature Scale [1] is defined in the range 660° to 1,063° C. in terms of the indications of a platinum to platinum-10 percent rhodium thermocouple calibrated at three thermometric points—the freezing points of gold, silver, and antimony. In order that the scale so defined may be definite and reproducible, it is necessary not only that the metals used be of high purity so that variations due to differences in the metals themselves be eliminated as far as possible but also that the conditions under which the metals are frozen be sufficiently definite to eliminate significant differences from this cause.

Comparisons [2] of the International Temperature Scale as realized at the Bureau of Standards in this country, at the National Physical Laboratory in England, and at the Physikalisch-Technische Reichsanstalt in Germany have indicated that both of these requirements have been met in the case of the gold and antimony points. It was found, however, that the same thermocouple, when immersed successively in the crucibles of freezing silver employed as the temperature standards by the three national laboratories, yielded emfs differing by more than the amount which could be ascribed to accidental errors. The emf differences were equivalent to approximately 0.5° C. It was thought that these discrepancies were due in part to differences in experimental procedure. At the Bureau of Standards and the

[1] Proc. Seventh General Conference of Weights and Measures, 1927, p. 56. Text in annex IV, p. 94.
G. K. Burgess, B. S. Jour. Research, vol. 1, p. 635, October 1928.
[2] B.S.Jour. Research (subsequent publication).

Physikalisch-Technische Reichsanstalt the freezing silver is contained in a covered graphite crucible. The atmosphere is presumed to be principally nitrogen, carbon monoxide, and carbon dioxide. At the National Physical Laboratory the silver is frozen in vacuo.

All the work available in the literature indicates that the three gases—nitrogen, carbon monoxide and carbon dioxide—are not appreciably soluble in this metal. However, it is well known that molten silver, exposed to an atmosphere containing oxygen, will absorb oxygen and that the freezing point of the metal will thereby be changed by an amount depending upon the quantity absorbed. Calculation by van't Hoff's equation shows that it requires but 0.007 percent of dissolved oxygen by weight to lower the freezing point of silver 0.5° C. which was the magnitude of the discrepancies among the various laboratories. The work of Sieverts and Hagenacker [3] indicates that this amount of oxygen would be absorbed by molten silver in equilibrium with oxygen at a pressure of 0.4 mm of Hg. There have been no observations reported on the freezing point of silver in vacuo at pressures of 0.4 mm of Hg or less.

The present investigation was originally undertaken to determine the source of the discrepancies among the results obtained by the various laboratories at the freezing point of silver. Although early in the investigation it was found that the above-mentioned discrepancies were due primarily, if not wholly, to metallic impurities, the investigation was completed as planned in order to show (1) the difference in the freezing points of various lots of silver, including that used by Day and Sosman in the determination with the gas thermometer which led to the adoption of 960.5° C. for this point; (2) the effectiveness of graphite in protecting silver from oxygen and the effect of the other gases present when the metal is melted in graphite crucibles; (3) the amount of the depression of the freezing point when no precautions are taken to eliminate oxygen; (4) the amount of the depression when the silver is saturated with oxygen at the pressure prevailing in the atmosphere; and (5) the amount of the depression when the silver is saturated with oxygen at the pressure of 1 atmosphere.

It is recognized that the freezing point of any substance depends upon the pressure, but a calculation using Clapeyron's equation reveals that the freezing point of silver is only 0.005° C. lower in vacuo than at a pressure of 1 atmosphere. Since the instruments used in this investigation are not accurate to better than 0.02° C., differences in the freezing point due to changes in the pressure, may be neglected.

II. METHODS

Three samples of silver were available for the investigation: (1) The silver which had been in use at the Bureau of Standards for five years and which is designated "old silver"; (2) a new lot of greater purity than the above, obtained from the United States Bureau of the Mint, and known as "inquartation silver"; and (3) the sample used by Day and Sosman [4] in their work with the nitrogen gas thermometer. The cooperation extended by Dr. A. L. Day, of the Geophysical Laboratory, in lending us this sample of silver is gratefully acknowledged.

The analyses of the various samples of silver are given in table 1.

[3] Sieverts and Hagenacker, Zeits. fur Phys. Chem., vol. 68, p. 115, 1910.
[4] Day and Sosman, Car. Inst. of Wash., Pub. No. 157, 1911; Am.J.Sci., vol. 33, p. 517, 1912.

TABLE 1.—*Analyses of silver samples*

Element sought	Percent of impurities		
	Old silver [1]	Inquartation silver [1]	Day and Sosman silver [2]
Cu	0.0680	0.0020	Mere trace
Pb	.0005	.0050	0.0008
Fe	.0003	.0010	.0011
Au	Not detected	Not detected	.0005
Pt	Not detected	Not detected	.0001
Ni	Not detected	Not detected	Not detected
Zn	Not detected	Not detected	Not detected
S			.0004
C			.0003
As			Not detected
Sb			Not detected
Sn			Not detected
Bi			Not detected
Hg			Not detected
Cd			Not detected
Co			Not detected
Total	.0688	.0080	.0032
Silver by difference	99.931	99.992	99.997

[1] By J. A. Scherrer, Chemistry Division, Bureau of Standards.
[2] From An Investigation of the Metals, by E. T. Allen, in High Temperature Gas Thermometry, The Carnegie Institution of Washington, Publication No. 157.

The four platinum to platinum-10 percent rhodium thermocouples used in this investigation were taken from the same lots of wire, and consequently had practically identical characteristics. The thermoelectric power (microvolts per ° C.) for thermocouple G_2 ($dE/dt = 8.298 + 0.003235\ t$) obtained from calibration in accordance with the specifications of the International Temperature Scale, may be used for the other couples without introducing errors greater than 0.2 percent. This is sufficiently accurate, since the other couples were only used for measuring temperature differences of the order of 0.5° C.

The measurements may be divided into six groups. In the first series of measurements the difference between the freezing points of the "old silver" and the "inquartation silver" in graphite crucibles was measured, using the same equipment and following the same procedure as described in a previous publication.[5]

In the second series of measurements the differences between the freezing points of the "old silver", the "inquartation silver", and the Day and Sosman silver in graphite crucibles were measured, using an electric furnace 3.8 cm in diameter and 25 cm long. Smaller samples were used in this case, crucibles 2.2 cm inside diameter and 10 cm deep, since the mass of the sample of silver obtained from Dr. Day was only about 200 g, and in order to obtain the highest accuracy in the measurement of temperatures with thermocouples, it is necessary to use the couples at the same depth of immersion during any series of measurements.

In the third series of measurements samples of the "old silver" and "inquartation silver" in graphite crucibles 3 cm inside diameter and 15 cm deep were placed successively in a silica tube, as shown in figure 1. For obtaining observations at the freezing points in vacuo,

[5] Wm. F. Roeser, B.S.Jour. Research, vol. 3, p. 343, 1929.

the silica tube was closed at the top by a pyrex glass cap. The silver was melted and the thermocouple protection tube then lowered into the silver to a depth of 10 cm. The cap was sealed to the silica tube and the protection tube by means of De Khotinsky cement. The silica tube was then evacuated by means of a 2-stage mercury diffusion

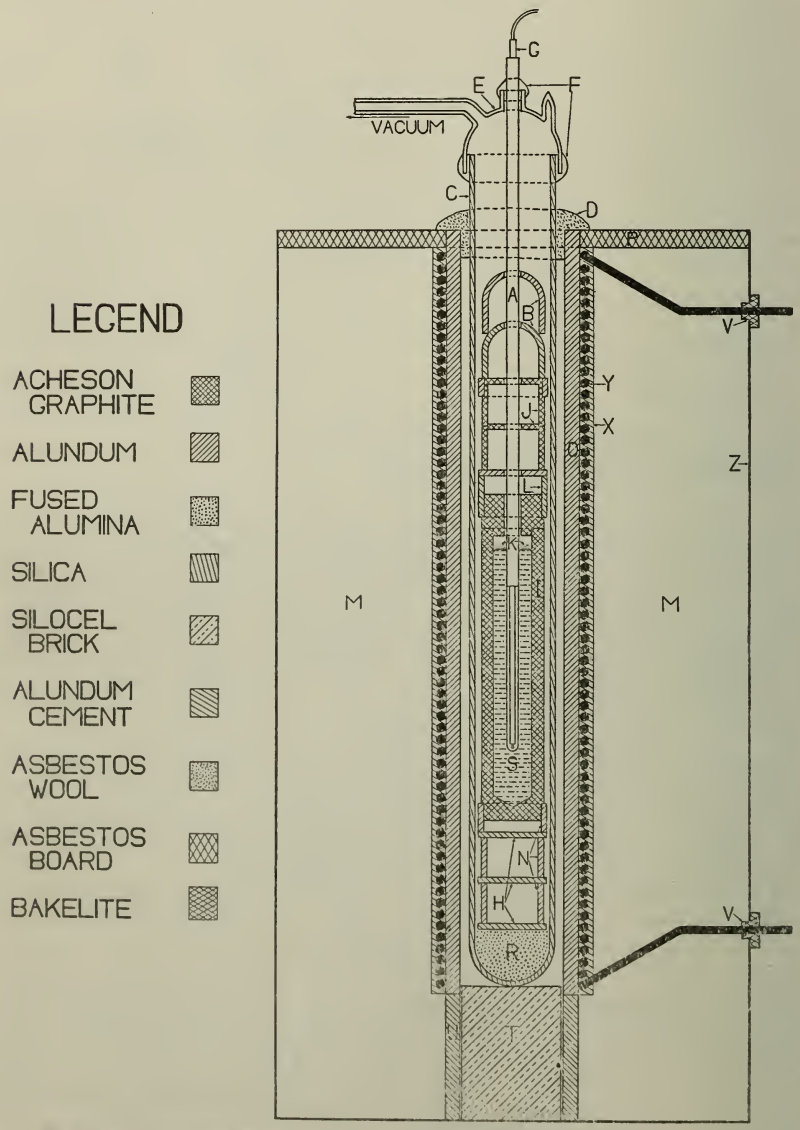

FIGURE 1.—*Arrangement for obtaining freezing point of silver in vacuo.*

pump backed by a Cenco Hyvac pump. A liquid air trap was placed between the pump and the silica tube. After completing the observations on a sample in vacuo, the cap was removed and similar measurements made with the tube open to the atmosphere. These measurements on the two samples of silver duplicated the first series

of measurements in addition to yielding the difference between the freezing point of each sample in vacuo and in a graphite crucible exposed to the atmosphere. The samples of silver used in these measurements were from the same lots of silver, though not the identical samples used in the first series.

In the fourth series of measurements the sample of "old silver" used in the third series was placed in a porcelain crucible at the same location in the furnace as before. Observations were taken at the freezing point with no provision for preventing access of oxygen, the silica tube being open to the atmosphere.

The fifth series of measurements was very similar to the fourth, with the exception that air was bubbled through the molten silver for various intervals of time preceding the freeze. The air was carried to the bottom of the silver by means of a porcelain tube which was removed a few seconds before freezing began.

The sixth series of measurements was the same as the fifth, with the exception that pure oxygen was bubbled through the molten silver. Since the pressure of the oxygen was slightly greater than that of the atmosphere and since the opening to the atmosphere was restricted by the diaphragms, the gas above the silver was practically all oxygen at a pressure of about 1 atmosphere.

In any series of measurements the thermocouples were immersed in the silver and in the furnace to the same depth. The cold junctions were maintained at 0° C. and the electromotive forces of the couples were read to 0.1 μv (approximately 0.01° C.).

III. RESULTS

The observed differences between the freezing points of the "old silver" and the "inquartation silver" are given in table 2.

TABLE 2.—*Differences in freezing points of "old silver" and "inquartation silver" in graphite crucibles*

Experiment No.	Air pressure above crucible	Freezing point "inquartation silver" minus freezing point "old silver"				
		Thermocouple				Mean
		G_1	G_2	G_{11}	G_{12}	
		°C.	°C.	°C.	°C.	°C.
1	Atmospheric	0.40	0.39	0.40	0.40	0.40
2	do		.65			.65
3	do	.53	.54	.49	.40	.49
3	0.03 to 0.005 mm of Hg	.56	.53	.51	.47	.52
Average difference.		0.5° C.				

Since different samples were used in each experiment, part of the differences in the values obtained in the various experiments are probably due to variations in the samples. The average value of 0.5° C. is probably good to ± 0.1° C.

The freezing point of the Day and Sosman silver under identical conditions was found to be 0.01° C. higher than that of the "inquartation silver." Only one thermocouple, G_2, was used in these measure-

ments but this couple was the most homogeneous of the lot and therefore best adapted to the measurement of such small differences.

The observed differences between the freezing points of silver in vacuo and in graphite crucibles exposed to the atmosphere are given in table 3.

TABLE 3.—*Difference between freezing points of silver in vacuo (0.03 to 0.005 mm of Hg) and in air with graphite protection*

Silver	Freezing point in graphite crucibles minus freezing point in vacuo				
	Thermocouple				Mean
	G_1	G_2	G_{11}	G_{12}	
	°C.	°C.	°C.	°C.	°C.
"Inquartation"	0.06	0.02	0.04	0.04	0.04
"Old"	.11	.01	.05	.10	.07
Average difference	0.05° C.				

The effect of pressure alone would account for only one-tenth of this difference. Since the temperature gradients in both the furnace and the thermocouple wires in the determination at low pressure were appreciably different from those prevailing in the measurements at atmospheric pressure, the measurements are not believed to be accurate to better than 0.05° C. However, the observations with thermocouple G_2 lead us to believe that the freezing point of silver in vacuo does not differ significantly from that in graphite crucibles.

The observed depressions of the freezing point of silver, in a porcelain crucible, when merely exposed to air and when air or oxygen is bubbled through the molten metal previous to freezing are summarized in table 4. Only the "old silver" and thermocouple G_2 were used in these measurements.

TABLE 4.—*Depression of the freezing point of silver by absorbed oxygen*

	Depression ° C.
Silver in porcelain crucible, surface exposed to air	1.5
Air bubbled through silver for 25 minutes	7.2
Air bubbled through silver for 30 minutes	8.0
Air bubbled through silver for 40 minutes	6.7
Air bubbled through silver for 70 minutes	11.2
Air bubbled through silver for 120 minutes	11.3
Oxygen bubbled through silver for 1 minute	5.4
Oxygen bubbled through silver for 50 minutes	22.6

No difficulty was encountered in reproducing the depressions of 11.2° and 22.6°, which leads to the conclusion that the silver was saturated with oxygen at the prevailing pressures (approximately 140 and 760 mm of Hg, respectively).

The freezing curves obtained under some of these various conditions are shown in figure 2. The freezing point was taken as the temperature corresponding to the initial freezing in each case.

IV. DISCUSSION OF RESULTS

As pointed out earlier, this investigation was undertaken to determine the differences in the freezing point of silver under different experimental conditions. Such questions can be settled only by experiments. Values for some of the differences measured may be computed from the chemical analyses of the silver samples, the

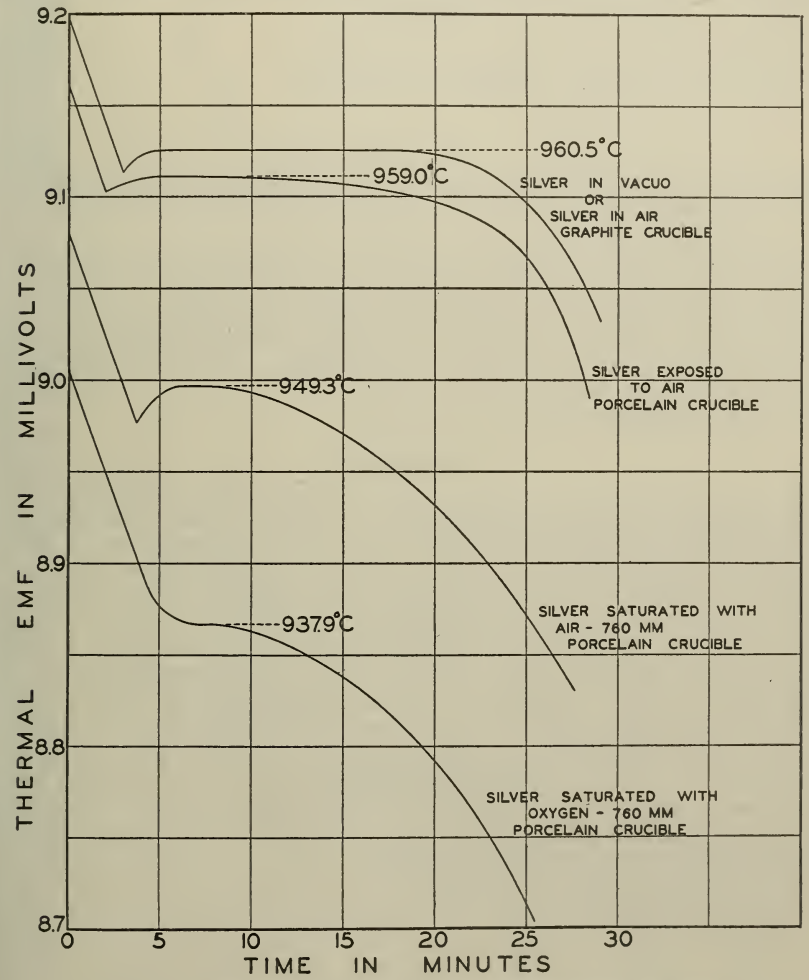

FIGURE 2.—*Freezing curves of silver under various conditions.*

absorption of oxygen by silver, other data available in the literature, and certain assumptions regarding the solution of impurities. The test of the applicability of such calculations is their agreement with experiments.

The computed and observed values are given in table 5, together with the estimated accuracy of the observed values. In the computations the latent heat of fusion of silver was taken to be 2,790 calories per gram-atom.

TABLE 5.—*Comparison of computed and observed values*

	Computed	Observed	Estimated accuracy of determination
	°C.	°C.	°C.
Freezing point of Day and Sosman minus freezing point of "inquartation silver"	0.01 or 0.05	0.01	0.05
Freezing point of "inquartation silver minus freezing point of old silver"	[1] 1.18	.5	.1
Freezing point of silver in graphite (atmospheric pressure) minus freezing point in vacuo	.005	.05	.05
Freezing point of silver in graphite minus freezing point of silver saturated with air (760 mm Hg)	10.2	11.2	.5
Freezing point of silver in graphite minus freezing point of silver saturated with oxygen (760 mm Hg)	22.3	22.6	.5

[1] This value is based upon the hypotheses that the dissolved copper is monatomic and that mixed crystals are not formed to an appreciable extent. If either of these hypotheses is not true, the actual depression will be less than that calculated. The equilibrium diagram for copper and silver indicates that mixed crystals are formed and that the initial freezing point of silver is lowered 0.5° C. by 0.068 percent of copper.

In the methods generally employed in obtaining observations at the freezing point of silver, the silver is molten for only a short time, and since the diffusion of absorbed oxygen through the silver is evidently a slow process, it appears that any of the methods now in use for protecting silver from oxygen are adequate. However, it appears necessary to limit the metallic impurities to 0.01 percent in order to obtain an accuracy of 0.1° C.

V. SUMMARY

A comparison of the freezing points of silver of three lots of silver under various conditions revealed (1) that the freezing point of silver containing 0.068 percent of copper was 0.5° C. lower than that of a sample containing only 0.008 percent impurities; (2) that the silver now in use at the Bureau of Standards is essentially the same as that used in the gas thermometer measurements of Day and Sosman, both in purity and freezing point; (3) that the freezing point of silver in a graphite crucible exposed to the atmosphere is the same within experimental error (0.05° C.) as that of the same silver in vacuo; (4) that the freezing point of silver saturated with air at 760 mm Hg pressure is 11.2° C. lower than that of the same silver protected from access of oxygen; and (5) that the freezing point of silver saturated with oxygen at 760 mm Hg pressure is 22.6° C. lower than that of the same silver protected from oxygen.

WASHINGTON, March 13, 1933.