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NOTE ON THE TEMPERATURE SCALE BETWEEN 100° AND 500° C

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At the present time the standard scale of temperatures in the interval 0° to 100° C is that defined in a resolution of the International Committee on Weights and Measures, namely, that of the constant-volume hydrogen thermometer.[1] Above 100° temperature measurements have been made with air, hydrogen, and nitrogen thermometers, and in recent years there seems to be a preference to work with the constant-volume nitrogen thermometer.

In a previous paper[2] the authors determined the melting and freezing points of a number of metals on the temperature scale defined by the platinum resistance thermometer calibrated in ice, steam, and sulphur vapor (444°.70 on the constant-volume nitrogen thermometer). In order to throw further light on the probable accuracy of the temperature scale so defined, in the interval 100° to 500° C, the authors have made some further measurements by the same method on the boiling points of naphthaline and benzophenone, which temperatures have been determined by a number of observers using both platinum and gas thermometers.

Four thermometers were used, made of different sizes of pure platinum wire from Heraeus and from Johnson, Matthey & Co., and having fundamental intervals ranging from 1.1 to 10.6 ohms. Three of these thermometers were used both as Siemens three-lead compensated and as four-lead potential terminal thermometers. The apparatus and methods are fully described in the previous paper.

The boiling points were determined with the sulphur-boiling apparatus, using glass tubes about 4.5 cm diameter and 45 cm

[1] References will be found at the end of the paper.

long, furnished with a side condenser tube with inlet near the top, and the thermometer was shielded by an aluminium cone in exactly the same way as in sulphur. With this shield omitted, the thermometer readings were about 0°.08 low in naphthaline and 0°.35 low in benzophenone. Raising the thermometer 6 cm produced a lowering in temperature of less than 0°.02.

Besides the boiling-point determinations, a few measurements were also taken of the freezing points of tin, cadmium, and zinc to compare with the previous work. The results are given in Tables I and II. It will be seen that the freezing points newly determined are practically identical with those previously found by the authors, showing that the temperature scale of the present work is in agreement with that of the previous investigation.

TABLE I

Determinations of Boiling Points of Naphthaline and Benzophenone, Wheatstone Bridge and Potentiometer Methods

On Ice, Steam, Sulphur (=444.70) Scale of Platinum Resistance Thermometer

1. BOILING POINT OF NAPHTHALINE

Date 1910	Therm. No.	Method	Observed Resistance	R_0	F. I.	δ	Obs. Pt. Temp. $=Pt_n$.	Obs. Temp. of Boiling	Reduced Barometer	Boiling Point	Substance
3.29	1787 B	W. B.	20.8987	11.5263	4.3787	1.513	214.04	217.93	758.34	218.03	K
3.30	"	"	20.8953	"	"	"	213.97	217.85	756.74	218.04	K
4.19	"	"	20.8572	11.5262	4.3784	"	213.11	216.95	742.11	217.99	K 1 recrys
3.29	1787 C	W. B.	6.33964	3.47222	1.33965	1.505	214.04	217.91	757.99	218.03	K
3.30	"	"	6.33815	"	"	"	213.93	217.79	756.54	217.99	K
4.19	"	"	6.32746	3.47219	1.33975	"	213.12	216.94	742.03	217.98	K 1 recrys
3.29	1787 D	W. B.	51.6262	28.7925	10.6674	1.500	214.05	217.90	757.98	218.02	K
4.15	"	"	51.5562	28.7923	"	"	213.40	217.22	747.06	217.97	K 1 recrys
4.19	"	"	51.5307	28.7921	10.6675	"	213.16	216.97	742.49	217.99	K 1 recrys
4.28	"	P. T.	51.5706	28.7801	10.6623	"	213.75	217.59	753.15	217.99	K 1 recrys
4.15	1787 F	W. B.	5.27421	2.89055	1.11702	1.502	213.39	217.21	746.89	217.97	K 1 recrys
4.19	"	"	5.27122	"	"	"	213.13	216.94	742.33	217.97	K 1 recrys
4.28	"	P. T.	5.32087	2.93016	1.11854	1.500	213.73	217.57	752.85	217.98	K 1 recrys
"	"	"	5.32080	"	"	"	"	"	752.94	217.98	K 1 recrys
				Boiling Point of Naphthaline, Kahlbaum ..... 218.02±0.01$_4$							
				" " " " " 1 recrys ..... 217.98±0.01$_1$							

Some measurements made in 1907 by one of the authors also gave for Kahlbaum naphthaline boiling point 218°.02.

TABLE I—Continued.

Determinations of Boiling Points of Naphthaline and Benzophenone, Wheatstone Bridge and Potentiometer Methods—Continued.

2. BOILING POINT OF BENZOPHENONE

Date 1910	Therm. No.	Method	Observed Resistance	R_o	F. I.	δ	Obs. Pt.* Temp. $= Pt_b$	Obs. Temp. of Boiling	Reduced Barometer	Boiling Point	Substance
4.6	1787 B	W. B.	24.4616	11.5263	4.3787	1.513	295.41	304.85	741.14	306.04	K
4.8	"	"	24.4884	"	"	"	296.03	305.53	751.20	306.08	K
4.14	"	"	24.4989	"	"	"	296.27	305.79	752.31	306.27	M 2 recrys
5.3	"	P. T.	24.4585	11.50955	4.3739	1.511	295.05	305.54	751.86	306.05	K recrys
4.6	1787 C	W. B.	7.42996	3.47222	1.33965	1.505	295.43	304.83	742.01	306.02	K
4.8	"	"	7.43603	"	"	"	295.89	305.32	751.99	305.83	K
4.8	1787 D	W. B.	60.3668	28.7925	10.6674	1.500	295.99	305.40	750.83	305.98	K
"	"	"	60.3716	"	"	"	296.03	305.43	750.81	306.02	K
4.14	"	"	60.3943	"	"	"	296.25	305.68	752.58	306.15	M 2 recrys
4.8	1787 F	W. B.	6.19652	2.89056	1.11703	1.502	295.96	305.38	750.92	305.95	K
4.14	"	"	6.19967	"	"	"	296.24	305.68	752.15	306.17	M 2 recrys
5.3	"	P. T.	6.24232	2.93016	1.11854	1.500	296.11	305.53	752.11	306.03	K recrys
				Boiling Point of Benzophenone (Kahlbaum)..... 306.00 ±0.053							
				" " " " (Merck, 2 recrys) 306.2							

K=Kahlbaum best grade, M=Merck, W. B.=Wheatstone Bridge with Siemens three lead thermometer, P. T.=potential terminal thermometer, R_o=resistance in ice, F. I.=fundamental interval, δ=constant in the formula $t-pt=\delta(t/100-1)t/100$.

TABLE II

Freezing Points of Tin, Cadmium, and Zinc

(To Connect With Temperature Scale of Previous Investigations)

1. FREEZING POINT OF TIN

Date 1910	Therm. No.	Method	Observed Resistance	R_o	F. I.	δ	Pt.	Freezing Point	Remarks
4.2	1787 F	W. B.	5.42965	2.89056	1.11703	1.502	227.31	231.91	K in Acheson graphite
4.27	"	P. T.	5.47290	2.93016	1.11854	1.500	227.32	231.91	" " " "
4.27	1787 D	P. T.	53.0111	28.7801	10.6623	1.500	227.25	231.84	" " "
			Range of previous observations (5 samples)..					231.94 231.83	K gave 231.92

TABLE II—Continued.

Freezing Points of Tin, Cadmium, and Zinc—Continued.

2. FREEZING POINT OF CADMIUM

Date 1910	Therm. No.	Method	Observed Resistance	R_0	F. I.	δ	Pt.	Freezing Point	Remarks
4.1	1787 C	W. B.	7.63076	3.47222	1.33965	1.505	310.42	321.10	K in Acheson graphite
"	1787 D	"	61.9000	28.7925	10.6674	1.500	310.36	321.00	" " " "
"	1787 F	"	6.35755	2.89056	1.11703	1.502	310.38	321.03	" " " "
			Range of previous observations (3 samples)					321.05 320.39	K gave 321.01

3. FREEZING POINT OF ZINC

4.28	1787 D	P. T.	71.3483	28.7801	10.6623	1.500	399.24	419.32	K in Dixon graphite, 1907 crucible
			Range of previous observations (5 samples)					419.46 419.25	K (3 samples) gave 419.37

For nomenclature, see Table I.

The reduction of the boiling points to normal pressure was made by means of formulæ satisfying the data both of Crafts and of Jaquerod and Wassmer.

For Naphthaline: $T_{760} = T_{obs} - 0.058\ (H - 760)$.

For Benzophenone: $T_{760} = T_{obs} - 0.063\ (H - 760)$.

The freezing points of 250 gram samples of the naphthaline and benzophenone used were found to be as follows:

Description	Freezing point of	
	Benzophenone	Naphthaline
From Kahlbaum	47.2	79.9
From Kahlbaum, recrystallized	47.2	80.4
From Merck, recrystallized	46.9	.....

In Table III are collected the determinations of the boiling points of naphthaline and benzophenone as made by the various observers, and where possible the values have been reduced to the

same basis, namely, to a scale on which the sulphur boiling point is 444°.70.

TABLE III

Boiling Points of Naphthaline and Benzophenone

Date	Observers	Method and Remarks	Naphthaline		Benzophenone	
			Observed	Reduced to S.B.P.= 444.70	Observed	Reduced to S.B.P.= 444.70
1883	Crafts[3]	Hydrogen thermometer	218.06	218.03	306.08	306.01
1891	Callendar and Griffiths.[4]	Pt. Therm. compared with c. p. air therm. (S. B. P.=444.53),	217.94	217.97	305.82	305.89
1891	Griffiths[5]	" " "	218.04	218.07	.....	.....
1904	Jaquerod and Wassmer.[6]	Hydrogen thermometer	217.68	(217.65)	305.44	(305.37)
1905	Travers and Gwyer[7]	Platinum thermometer (S. B. P.= 444.53).	218.04	218.07	305.8	305.87
1908	Holborn and Henning[8]	Pt. therm. compared with c. v. nitrogen therm. (S.B.P.=445.00).	218.04	217.99	306.08	305.95
1910	Waidner and Burgess	Platinum thermometer (S. B. P.= 444.70).	.....	217.98	.....	306.02
	Reduced Mean including all observations		217.97±0.08		305.85±0.16	
	" " excluding Jaquerod and Wassmer		218.02±0.04		305.95±0.05	

It will be seen that, with the exception of the determinations of Jaquerod and Wassmer, there is a close agreement. Their results may be low, owing to the fact that the condenser of their boiling apparatus was immediately above the gas thermometer bulb, which was not screened in any way against the cooling effects of condensation and radiation. It should also be noted that the volume of their gas thermometer bulb was only 66 cc, which is small for work of precision. Their results may be indirectly tested by assuming either of their boiling points as the third standardization temperature of a platinum thermometer and using the thermometer so calibrated to determine the sulphur boiling point. This procedure would give S. B. P. = 443°.0, a value 1°.5 lower than any determination, and for the constant δ of the platinum thermometer 1.40 instead of the usual 1.50 as found when S. B. P. = 444°.7 is used as the third standardization temperature.

In view of the very general use of the S. B. P. for the standardization of platinum thermometers, we have summarized in Table IV the results of the more important determinations of this temperature, and reduced them to the same basis, namely, that of the nitrogen constant-volume thermometer under a pressure of 1 meter of Hg at 0° C. The temperatures thus observed are obtained only under very definite experimental conditions which are described at length in the previous paper and elsewhere.

TABLE IV

Boiling Point of Sulphur by Gas Thermometer

Date	Observers	Method and Remarks	Observed S. B. P.	Reduced to const. vol. p_0= 1 m Hg	Weight
1862	Regnault [9]	Constant volume; by interpolation	447.5	.....	.....
1891	Callendar and Griffiths.[4]	Constant pressure	444.53	444.74	2
1894	P. T. Reichsanstalt [10]	Constant volume, Wiebe and Bötcher scale.	444.5	444.5	1
1900	Chappuis and Harker [11]	Constant volume, corrected from 445.2	444.7	444.7	2
1901	Holborn [12]	Constant volume, extrapolated by Pt. resistance.	444.55	444.55	1
1903	Rothe [13]	Constant volume P. T. R. scale, Hg thermometers. (Thermocouples gave 445.0)	444.7	444.7	1
1909	Eumorfopoulos [14]	Constant pressure (Extrapolated for Hg expansion=443.7)	444.55	444.76	2
		Mean S. B. P.	.....	444.68±0.08	

Messrs. Day and Sosman in a recent elaborate investigation [15] with a nitrogen constant-volume thermometer at high temperatures (400 to 1,550° C) have determined the freezing points of a number of metals, among them zinc and cadmium, by transferring from the gas scale with thermocouples. They find for the freezing point of zinc 418°.2, and for cadmium 320°.0, whereas the platinum resistance thermometer calibrated in ice, steam, and sulphur vapor (444°.70) gives 419°.4 and 321°.0 for zinc and cadmium, respectively, with a precision of 0°.05 C. The explanation of this difference is of great importance in accurately fixing the gas scale in the interval 100 to 500° C. If the freezing point of pure zinc is 418°.2, instead

of 419°.4, then it would follow that the boiling point of sulphur must be 443°.5 instead of 444°.7, as found by a number of observers as above shown. (See Table IV.)

It should also be noted that the gas thermometer as used by Day and Sosman was adapted primarily to give the highest attainable accuracy for the higher range of temperatures; that is, above 1000° C, and that no measurements with the gas thermometer itself were made below 400°, nor did they consider their thermometer of sufficient sensitiveness in the lower temperature ranges to warrant a determination of its fundamental interval, 0–100° C.

Some further evidence on the accuracy of the gas scale that is defined by a platinum resistance thermometer calibrated in ice, steam, and sulphur (444°.70) is afforded by the comparison by Holborn and Henning of two platinum thermometers with a nitrogen thermometer in the interval 150° to 200° C. This work shows that the two scales so defined are in agreement to within a few hundredths of a degree. If the value usually assigned to the S. B. P. (444°.70) were over 1° high, then the scale defined by the platinum thermometer at 200° might be expected to be about 0°.2 high, whereas these observers find an extraordinarily close agreement between these two scales. It is also of interest to note that these observers give evidence that their gas thermometer agrees with Regnault's gas scale to within 0°.02 up to 230° C.

In view of the doubt, however, which is thrown on the present generally accepted value of the S. B. P. by the work of Day and Sosman, new determinations of this point made with the best modern facilities with apparatus designed for work in this range are much to be desired. Ordinarily one would conclude that the highly satisfactory agreement of the determinations by so many different observers, using different methods, as summarized in Table IV, would settle this point. A careful study of the gas thermometers and methods used, however, shows that they are open to many criticisms, and many refinements are now possible that were not available or whose importance was not so clearly recognized at the time these determinations were carried out. Thus, in some of these determinations air was used as the gas instead of nitrogen.

Glass or porcelain bulbs, so subject to changes in volume or to the emission or absorption of gases, were employed instead of metal bulbs. The coefficient of expansion of the bulb was not always determined with sufficient accuracy over the whole of the temperature range, and in some cases the coefficient used was found by an unwarranted extrapolation.

The use of a uniform scale by different experimenters is always most desirable. In view of the very general use of the value 444°.7 as the boiling point of sulphur on the scale of the constant volume gas thermometer, and in the light of the evidence that is now available, no change in this point is possible at this time. It is well to bear in mind, however, that the standard gas scale is not yet definitely and certainly fixed to an accuracy of 1° at 450° C.

The following fixed points represent the temperature scale which appears to best satisfy the available observations to 0°.1 for the reproduction of temperatures in the interval 100° to 500° C:

Freezing Points		Boiling Points	
Tin	231°.9 C	Naphthaline	218°.0 C
Cadmium	321 .0	Benzophenone	306 .0
Zinc	419 .4	Sulphur	444 .7

As these temperatures are on the constant volume scale, the reduction to the thermodynamic scale may be effected approximately if desired by adding 0°.2 at the sulphur point and a proportional amount at the lower temperatures, remembering that this correction is zero at 100° C. All of these substances may readily be obtained of sufficient purity to give a reproducibility of 0°.05 C from one sample to another.

WASHINGTON, May 13, 1910.

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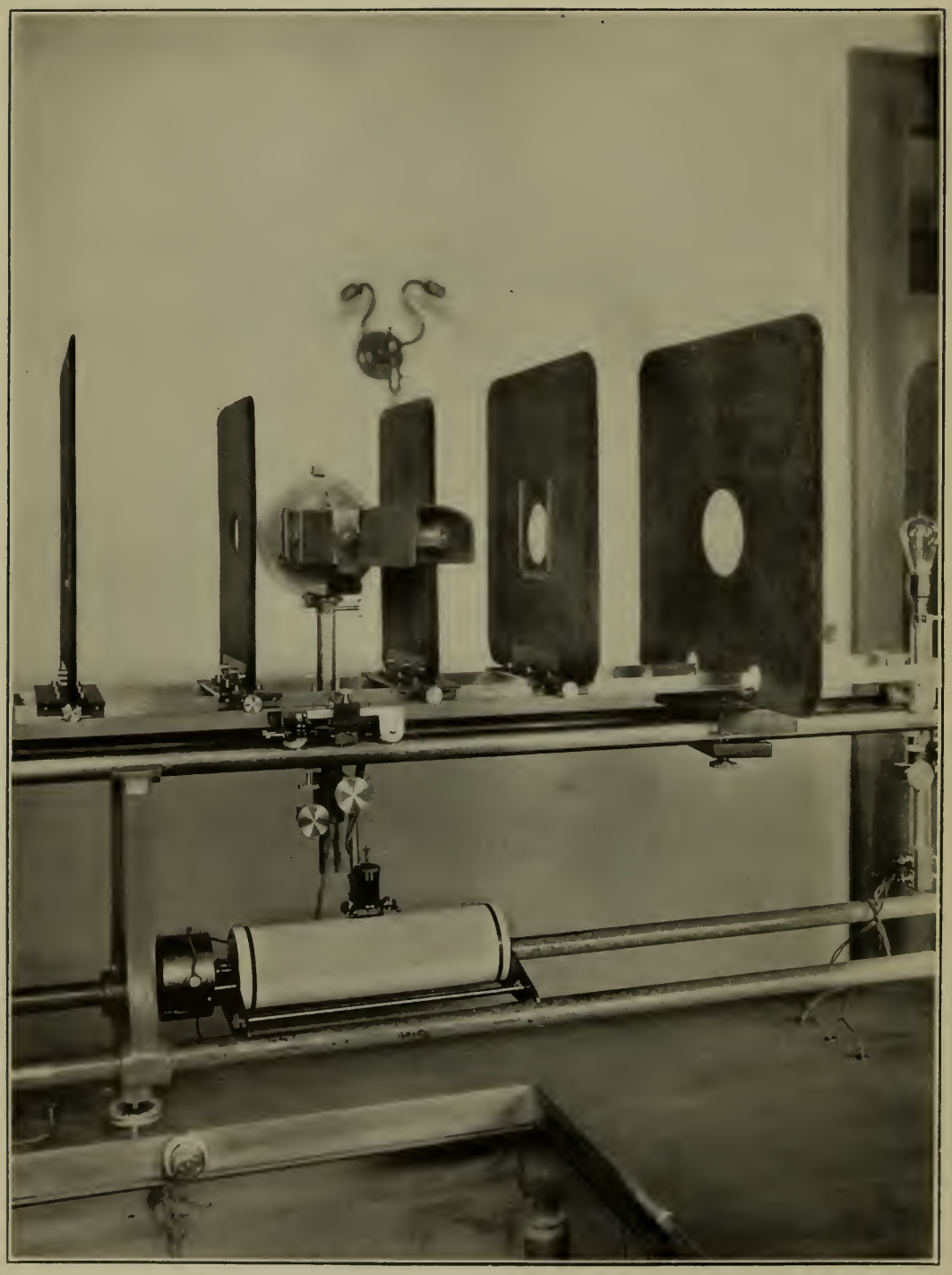

Fig. 1.—*Recording Apparatus Mounted on Photometer Frame.*