1.55 mm. The excess of the static over the dynamic may perhaps be held roughly to represent the minimum value of the error of the older static methods *per se*. Now this difference is 1.22 mm., or about fifteen times the total divergence of our results due to all causes.

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: IV. A REDETERMINATION OF THE VAPOR PRESSURES OF MERCURY FROM 250° TO 435°.

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Both for practical and theoretical purposes, an exact knowledge of the physical constants, and particularly of the vapor pressures of mercury, is of the greatest importance. Mercury is used in innumerable ways in research and in many instances the accuracy of the results depends on a knowledge of the vapor pressures of this substance. Since mercury shows no evidence of a tendency to association, and since its vapor is monatomic, presenting in the former respect a great contrast to water, and in the latter respect even to the liquids of more normal behavior, like benzene, an exact knowledge of its vapor pressures should be of the utmost value in the study of the laws pertaining to vaporization. The relations, for example, between temperature and pressure and between these two and heat of vaporization, on account of the absence of complicating factors, should be of special simplicity in the case of mercury. Moreover, it is more easily obtained in a state of extreme purity than almost any other substance. Yet, in spite of all this, as Laby says, "the greatest—and it should be added, unnecessary—disagreement is to be found in the current values of this vapor pressure." For these reasons, and because accurate data were required for a study of calomel vapor which will shortly be published, a redetermination of the vapor pressures from 250° to 435° was undertaken. The range chosen was limited to the region required for this special purpose, but we intend later, with a longer gage, to extend the series. The theoretical study of our results is postponed until the longer series shall be available.

Previous Determinations.—The work of previous observers has been subjected to a critical study and their data have been combined by Laby.[1] We are not concerned with the values at low temperatures, of which those of Pfaundler,[2] Morley,[3] and Hertz[4] (the latter's extend to 207°) are in excellent agreement, and are irreconcilable with the erratic values of

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[1] *Phil. Mag.*, [6] 16, 789 (1908).

[2] *Ann. Physik*, [3] 63, 36 (1897).

[3] *Phil. Mag.*, [6] 7, 662 (1904).

[4] *Ann. Physik*, [3] 17, 193 (1882)

Van der Plaats,[1] Hagen,[2] and McLeod.[3] As regards Regnault's[4] three low-temperature series, including observations up to 205°, he himself states that they give data that are only approximate. The series of determinations discussed below are those which touch the region covered by our experiments. The data themselves will be found in a comparative table (Table VI) given towards the end of the paper.

Regnault's values at the highest temperatures are based, (1) on four old determinations of the boiling point of mercury (about 357°) made with an air thermometer, two of which differ by about 2° at the same pressure, and (2) a new series from 251° to 511.7°. In the latter, the mercury boiled under varying air pressures. The temperatures were determined with a constant-volume air thermometer. The boiling metal began to bump occasionally at 345° and violently at 428°. The values near the ordinary boiling point are obviously discordant, as the three following observations show: 354.60°, 758.20 mm.; 354.83°, 761.87 mm.; 356.69°, 754.43 mm. Later workers have made much of Regnault's statement that his results were inaccurate, but he makes no such admission in regard to these two sets of values, leaving them to speak for themselves. All he says is that the experiments were not done in the same way as those which he made with other substances, because, when the bulb of the thermometer was surrounded by vapor, constant temperatures could not be obtained, and in this case, therefore, the bulb was completely below the surface of the liquid. Owing to the great depth of the mass of mercury (50 kilos), the lowest layers must have been seriously superheated.

Ramsay and Young's[5] well-known series of vapor pressures of mercury was based upon four groups of observations. Young, in a paper which appeared five years after and seems to have escaped notice,[6] utilized later values for a part of the fundamental data, and gives a corrected and very considerably altered table (see Table VI). The four original groups of observations were:

1. Four static measurements with mercury in a U-tube[7] heated by the vapor of methyl salicylate boiling at a known pressure. The temperature of the vapor was ascertained indirectly from a previously determined p.-t. curve. This p.-t. curve not having given satisfactory

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[1] *Rec. trav. chim.*, 5, 149 (1886).

[2] *Ann. Physik*, [3] 16, 610 (1882).

[3] *Brit. Assoc. Rep.*, 1883, 443.

[4] *Mem. Acad. Sci.*, 21, 30, 502 (1847); 26, 506 (1862).

[5] *J. Chem. Soc.*, 49, 37 (1886).

[6] *J. Chem. Soc.*, 59, 629 (1891). Not referred to in Landolt and Börnstein, [3] (1905), nor in Abegg's *Handb.*, II, ii (1905), which give the old set of values.

[7] For proof of the difficulty in excluding foreign gases from such a tube see preceding paper, Sec. 2.

results in other cases, Young, in the second paper, discards these observations and substitutes for them two new readings with aniline vapor as the heating agent at 183.7° and one with quinoline vapor at 236.9°. These temperatures (const.-vol., air-therm. scale) are therefore ascertained indirectly as before.

2. Two static measurements with mercury in a U-tube heated by the vapor of bromonaphthalene boiling at known pressures. It is a little difficult to make out the exact status of this part of the data. These were old observations, originally made as part of a study of the vapor pressures of bromonaphthalene.[1] On that occasion, the temperature corresponding to the observed bromonaphthalene pressure was ascertained by taking from Regnault's formula the temperature at which mercury exercised the vapor pressure observed in the U-tube. These, along with three other series of measurements made in a different way, were employed in making the bromonaphthalene p.-t. curve. They entered directly into the making of the curve, and were used also for ascertaining the correction of an English thermometer employed in one of the other (the fourth) series.

On the present occasion they play the reversed roles of measurements of the vapor pressure of mercury. One of these agrees with the final p.-t. curve of bromonaphthalene and the other is adjusted by altering the temperature 0.4° to bring it onto this curve. As these results are retained and used by Young in the second paper, it is necessary to consider their probable accuracy.

The values, as adjusted, were considered to be correct for two reasons. One was because they gave normal results when used in the study of certain vapor pressure relations of water and bromonaphthalene, expressed by the formula $R' = R + c\ (t'-t)$.[2] But water is an abnormal substance and is admitted to be unsuitable for the study of this relation,[3] so that the agreement of the results with the theory in this instance affords no guarantee of the accuracy of the data. The vapor pressures of mercury adopted on the basis of this observation, when compared with those of water in the light of the same relation, again showed good, but, for the same reason as before, unavailing agreement with the theory. The value of the results must be judged, therefore, solely by the other reason for considering them correct, namely, the accuracy of the p.-t. curve of bromonaphthalene on which they are based.

This curve[4] is founded on several series of observations. Two series were made by Ramsay and Young's dynamic method,[5] in which the

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[1] *J. Chem. Soc.*, 47, 65 (1885).

[2] *Phil. Mag.* [5], 20, 515 (1885); 21, 33 (1886).

[3] Young, *Stoichiometry* (1908), 144.

[4] *J. Chem. Soc.*, 47, 646 (1885).

[5] For detailed criticism see preceding paper, Sec. 2.

thermometer bulb is surrounded by cotton and immersed in the vapor. No correction for dilatation of the bulb[1] is mentioned, but its absence would not affect the results at 280°, with which we are concerned, as the pressure is there atmospheric. The objections on account of the introduction of dissolved gases along with the liquid, and of the gradual concentration of impurities, however, still remain. The results of the second series are below those of the first by 0.8° at 278°. In the fourth series, the bromonaphthalene boiled in a tube under known pressures and its temperature was ascertained by means of a thermometer immersed in the vapor. This was the thermometer standardized by assuming Regnault's vapor pressure curve of mercury to be correct. The results are above those of the second series at 280° by 1.9°. The temperatures in these series were all reduced to the constant-volume, air-thermometer scale. The third series consisted of the pair of observations first referred to.

It appears, therefore, that these two observations are not independent of the p.-t. curve of bromonaphthalene, and that the latter is made from data diverging as much as 1.9° at 280°.

In a later paper, Young[2] refers to certain discrepancies in results obtained by the use of the p.-t. curve of bromonaphthalene vapor, which he believes to be due to a slight underestimation of the temperatures at 280°. Table IV, however, will show that these two sets of observations from 183.7 to 280° are probably much more accurate than those of Hertz in the same region.

3. The third group of data pertaining to the vapor pressures of mercury used by Ramsay and Young consisted of the four boiling points of mercury originally employed by Regnault, two of which differed by 2° at the same pressure. Young, in the later paper, rejects these and substitutes Callendar and Griffiths'[3] determination of the boiling point of mercury at 760 mm., reduced to the sea level at latitude 45°, the value of which is generally quoted as 356.76° (const.-press. air-therm. scale). In this work, the details of which cannot be discussed here, the authors used values obtained with four improved platinum resistance thermometers, each compared in the vapor of boiling sulphur and at 0° and 100° with a constant-pressure air-thermometer. The mean result, reduced to the basis of the S b. p. = 444.53°, which the same observers had determined, was 356.76°. The mean of the results with five earlier, trial platinum thermometers, similarly reduced, was 356.74°. A final set of three "very careful" observations with a new platinum thermometer gave the mean value 356.73°. The final mean value with the five best ther-

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[1] THIS JOURNAL, 32, 905.

[2] *J. Chem. Soc.*, 77, 1147 (1900).

[3] *Phil. Trans.*, *A*, 182, 150–2 (1891).

mometers is 356.74°, in exact agreement with that of the five earlier instruments.

4. The fourth, and last, of the groups of observations used by Ramsay and Young consisted in two static measurements of the vapor pressure of mercury when heated by boiling sulphur. For the temperature, Regnault's boiling point of sulphur, 448.34°, the only one then available, was used. Young retains the pressure data and substitutes Callendar and Griffiths'[1] value for this boiling point (444.53°). According to Ramsay and Young's table, a difference of 4°, such as this, corresponds to a change in pressure at 445° of 139 mm. Hence this substitution greatly altered the value at 445°, as well as all the values between 760 and 2850 mm., which, in the absence of intermediate determinations, were all obtained by interpolation.

The vapor pressures were determind by heating the mercury in an apparatus shaped like a round-bulbed thermometer, with the stem bent into a horizontal position. The mercury, when cold, filled the bulb and a part of the stem, and was driven along the latter, compressing the air in the end, when mercury vapor was formed in the bulb. The bulb and a portion of the non-horizontal part of the stem of this thermometer-shaped apparatus were surrounded by the vapor of sulphur boiling in a vessel which in one experiment was a flask and in the other a wide test tube. Dr. Young, whom we desire to thank for most courteously giving us additional information on a number of points, states that the air column, before compression, was approximately 400 mm. in length. At four atmospheres pressure its length was thus reduced to 100 mm. Since the reading was probably accurate to ±0.1 mm., the pressure error should be only ± 1 in 1000, or about 3 mm. The accuracy of the pressure reading was therefore satisfactory.

It is unquestionable, however, that in assuming that the bulb was really heated to 444.53° by the arrangement used, a serious error is introduced. The flask and test tube containing the boiling sulphur were not covered or protected in any way. Now, Callendar and Griffiths devote much space in their paper to a detailed description of their observations on this point. They used a Victor Meyer vapor density tube 4 cm. in diameter. Even when such a tube was padded externally with asbestos to retain the heat, the temperature reached by the thermometer was only 442.38°. They showed that the temperature of their thermometer (corresponding in Ramsay and Young's experiment to the bulb) was reduced by the trickling down of condensed, cooled sulphur and by radiation to the layer of condensed sulphur on the walls. By introducing a little hood to divert the sulphur running from the stem, and two cylindrical screens (one of metal and one of glass) to stop radia-

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[1] *Phil. Trans., A*, 182, 119 (1891). See also preceding paper, Sec. 3.

tion, they finally brought the observed temperature up to 444.53°. In Ramsay and Young's experiment, therefore, the temperature actually reached was probably not far from 442.38°, or about 2° short of the value assigned to it by Young.

Gebhardt[1] boiled mercury in a glass globe. The temperatures of the vapor were taken with "a thermometer," presumably a mercury thermometer. No attempts to standardize the instrument, or to correct the readings for exposed thread or dilatation are described. Corrections of the gage are likewise lacking. But the pressures are given to tenths of a millimeter (see Table II).

Cailletet, Colardeau, and Rivière[2] determined, by a static method, the vapor pressures in atmospheres from 400° to 880°. The results are of interest as showing the order of the pressures at very high temperatures. The authors state that their results are sensibly the same as Regnault's, so far as the latter extend. Laby used these results although he rejected Regnault's, and this accounts for the fact (see Table VI) that above 360° his figures are higher than those of Young. No information as to the values assumed for the fundamental points, or as to the scale of temperature employed, is given.

Summarizing the history of this subject, we find that our knowledge of the higher vapor pressures of mercury rests on no very secure foundation. The boiling point at 760 mm. is the only point ascertained with precision. Not one observer makes any statement in regard to the purity of his mercury. Aside from Callendar and Griffiths, Regnault is the only investigator who states what he did in every experiment with perfect lucidity and completeness. Unfortunately, his results at closely adjacent points are inconsistent, his temperatures are those of the liquid and not of the vapor, and his air thermometer was inexact in its readings.

The Vapor Pressures of Mercury.—The apparatus used was identical with that described in the preceding paper.[3] The U-tube of the static isoteniscope contained mercury. The mixture of potassium and sodium nitrates was used as the bath liquid. The vibration communicated from the stirrer prevented bumping, which otherwise might have occurred when the metal in the bulb was allowed to boil.

The mercury, already distilled *in vacuo*, was redistilled in the same way at the rate of 30 cc. per hour. It was then washed ten times with dilute nitric acid in a tube 1.3 meters long, by the method recommended by Hildebrand.[4] This method is like Ostwald's excepting that the metal

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[1] *Ber. physik. Ges.*, 7, 184 (1905).

[2] *Compt. rend.*, 130, 1585 (1900).

[3] THIS JOURNAL, 32, 1419.

[4] *Ibid.*, 31, 933 (1909).

is strained through muslin, which divides it into extremely small streams, instead of being allowed to enter the acid in a single stream. It was then dried and tested by the method of Hulett and Minchin,[1] which is incomparably the most sensitive. A portion of the metal was distilled twice in air, which oxidizes the more active metals, if present. Samples of each lot were then placed in a cell containing *N* KCl solution saturated with calomel. The potential difference of the two samples was less than 0.000002 volt, the limit of sensitiveness of the galvanometer employed. The method is capable of detecting one part of zinc in 10^{10} parts of mercury, and corresponding amounts of other active metals. The mercury in the gage was also tested and found to be of a like degree of purity.

The corrections and the precautions, such as frequent redeterminations of the fixed points, were identical with those used in the observations with water which are recorded in the preceding paper.

Two series of readings, hereafter named the first and second series, were completed. In the first attempt to make the second seiies, the isoteniscope broke after the fourth reading. Since the next, and successful second series overlapped the first series for a considerable distance, rendering the four observations in the same region unnecessary, and since the instrument may have been defective before the breakage occurred, the four readings of the abortive series were not used. Aside from those four, every observation that was completed is recorded in Table I. The results, 43 in all, are given in the order of ascending temperatures, in which they were obtained. The members of the second series are distinguished by an asterisk.

It may be noted that an alteration in the zero of the thermometer, requiring a change of about 0.1°, occurred between the first and second series. On account of the overlapping, however, the individual observations are affected only to the extent of 0.05°. The aim was to secure observations with a temperature error of less than ±0.1°. The temperatures are worked to hundredths of a degree as, although not accurate to one unit in this place, the second decimal has nevertheless some significance.

The temperatures are on the thermodynamic scale, and assume the boiling point of sulphur to be 445° on that scale. If, later, a slightly different value for this point should be finally accepted, the preceding paper supplies the data required for any recalculation. If the S b. p. is taken 0.1° lower (*i. e.*, 444.9°), which is the present most probable value, then at 357°, for example, a correction of —0.06° is required.

The error of the individual gage readings, considered by themselves, is less than ±0.2 mm. The pressures are given to hundredths, although the second place has very little significance.

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[1] *Physic. Rev.*, 21, 388 (1905).

Critical Study of the Results.—The observations were first plotted on a large scale, equivalent to a piece of cross-section paper 118 x 220 cm., and a smooth curve was drawn through them. This made easy the selection of three points, from which a Kirchoff-Rankine-Dupré formula was calculated. From this formula the pressures at every 2° in the region studied were reckoned. By linear interpolation, which is sufficiently accurate for intervals of 2°, the calculated temperatures corresponding to the observed pressures were then obtained. A study of the divergencies of the calculated and observed temperatures now showed that an alteration in two of the fundamental points would cause the formula better to fit the observations as a whole. With the very slightly altered points the whole process was repeated, and a further slight change in all three points was made. Thus, after two approximations, a final set of three points and a corresponding formula of a very satisfactory nature were secured. The fundamental points on which the final formula is based are:

264.16°, 106.52 mm.; 356.95°, 760 mm.; 433.96°, 2598.67 mm. The formula is $\log p = A + B/\theta + C \log \theta$, or, with the constants inserted:

$$\log p = 9.9073436 - 3276.628/\theta - 0.6519904 \log \theta, \qquad \text{(R)}$$

where $\log B = 3.5154272$; $\log C = \bar{1}.8142412$.

The following table contains: the reference numbers of the experiments (Col. 1), arranged in the order of ascending temperatures, with those of the second series distinguished by an asterisk; the observed pressures (Col. 2); the observed temperatures (Col. 3); the temperatures calculated with the use of the formula by the process indicated above (Col. 4); and the differences (Δ) between the observed and the calculated temperatures.

If the formula fitted the observations exactly, the algebraic sum of the divergencies should be zero. It is actually +0.07°. A change of 0.003° in the middle point might improve the correspondence, but it did not seem desirable at present to attempt any such refinement.

Since the calculated temperatures lie on a smooth curve, the divergencies from them of the observed temperatures represent essentially the irregularities in the individual observations. A study of column 5 will, therefore, show the degree of consistency of the results. Of the forty-three observations, thirty show very small deviations, ranging from 0.00° to 0.05°. In eight cases the divergence is from 0.06° to 0.10°, in only five cases does it exceed 0.10°. Observation No. 37 is undoubtedly defective, on account of a misreading of the resistance or of the gage. The mean deviation from the smooth curve of a single observation (including No. 37) is 0.050°. This is well within the limit proposed for the accuracy of the absolute temperature measurements.

TABLE I.—THE OBSERVATIONS.

No.	Press. obsd.	Temp. obsd.	Temp. calc.	Δ.	No.	Press. obsd.	Temp. obsd.	Temp. calc.	Δ.
1	82.08	253.97	253.91	—0.06	23	747.81	355.98	356.05	+0.07
2	96.84	260.35	260.36	+0.01	24	765.44	357.32	357.34	+0.02
3	106.52	264.16	264.16	0.00	25*	769.26	357.72	357.62	—0.10
4	117.04	267.99	267.96	—0.03	26	817.00	361.04	360.99	—0.05
5	128.57	271.82	271.81	—0.01	27*	836.43	362.43	362.32	—0.11
6	141.05	275.68	275.66	—0.02	28*	885.76	365.62	365.58	—0.04
7	169.82	283.61	283.55	—0.06	29*	932.66	368.54	368.55	+0.01
8	210.79	293.07	293.04	—0.03	30*	1002.55	372.74	372.74	0.00
9	236.96	298.34	298.31	—0.03	31*	1008.68	378.66	378.69	+0.03
10	273.24	304.75	304.86	+0.11	32*	1210.58	383.95	383.99	+0.04
11	309.73	310.75	310.77	+0.02	33*	1265.60	386.66	386.69	+0.03
12	334.92	314.33	314.51	+0.18	34*	1326.12	389.56	389.56	0.00
13	428.93	326.65	326.69	+0.04	35*	1425.97	394.04	394.07	+0.03
14	457.10	329.87	329.91	+0.04	36*	1675.34	404.28	404.32	+0.04
15	498.01	334.16	334.30	+0.14	37*	1744.34	407.17	406.94	—0.23
16	537.55	338.21	338.27	+0.06	38*	1847.35	410.66	410.69	+0.03
17	586.76	342.82	342.88	+0.06	39*	2037.15	417.17	417.19	+0.02
18*	635.00	347.13	347.11	—0.02	40*	2125.78	420.10	420.07	—0.03
19	642.22	347.74	347.72	—0.02	41*	2334.34	426.52	426.47	—0.05
20	697.73	352.13	352.23	+0.10	42*	2599.17	434.02	433.95	—0.07
21*	697.72	352.24	352.23	—0.01	43*	2624.35	434.71	434.65	—0.06
22	732.13	354.85	354.87	+0.02					

Comparison with Other Methods.—The qualities of the method used are best seen by applying the same mode of study to the observations of other observers. Cailletet, Colardeau, and Rivière do not publish their observations, but only the rounded results. Ramsay and Young's observations are not numerous enough for the purpose. Only in the cases of Regnault and Gebhardt[1] can the data be investigated as regards their consistency. In the following table (Table II) the observations of Gebhardt (taken from Laby's paper, as the dissertation is not accessible) are given. It contains the observed pressures (Col. 1), the observed temperatures (Col. 2), the temperatures calculated by the use of formula R (Col. 3), and the differences (Δ_1) between the temperatures as observed and as thus calculated (Col. 4). The algebraic sum of these deviations divided by the number of observations is +0.81°, showing that the observed temperatures are on the whole 0.81° below those calculated.

A curve was drawn fairly to represent his results, and the divergencies of the individual observations from this curve are given under Δ_2 (Col. 5). The sum of these divergencies is +0.2°, that is, approximately zero, as it should be. It will be noted that the individual temperatures, besides being, as we have seen, on the whole 0.81° too low, are exceedingly irregular. The mean deviation of a single observation from the smooth curve is 1.2°, or about twenty-four times as great as in the case of the present observations. The method is, in part, responsible for this.

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[1] *Loc. cit.*

TABLE II.—GEBHARDT'S OBSERVATIONS.

Press. obsd.	Temp. obsd.	Temp. calc.	Δ_1.	Δ_2.	Press. obsd.	Temp. obsd.	Temp. calc.	Δ_1.	Δ_2.
1.00	129.0	126.0	—3.0	—3.8	94.40	256.0	259.3	+3.3	+2.5
3.93	157.5	158.4	+0.9	+0.1	105.69	264.0	263.8	—0.2	—1.0
8.22	176.5	178.2	+1.7	+0.9	122.90	268.0	270.0	+2.0	+1.2
12.51	188.0	190.3	+2.3	+1.5	126.11	271.5	271.0	—0.5	—1.3
21.07	207.0	206.3	—0.7	—1.4	150.80	277.5	278.4	+0.9	+0.1
38.82	224.5	226.6	+2.1	+1.3	147.50	278.5	277.5	—1.0	—1.8
46.49	230.5	232.9	+2.4	+1.6	185.00	286.5	287.3	+0.8	0.0
51.58	236.0	236.6	+0.6	—0.2	224.90	295.5	295.9	+0.4	—0.4
68.42	245.0	247.0	+2.0	+1.2	263.90	302.5	303.3	—0.8	—1.6
71.39	248.0	248.6	+0.6	—0.2	308.10	309.5	310.2	—0.7	—1.5
87.87	255.0	256.5	+1.5	+0.7	360.20	315.0	318.1	+3.1	+2.3

Regnault's main series (251° to 512°) is exhibited in Table III. Col. 3 contains the temperatures calculated by our formula, and Col. 4 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation is 2.84°. Col. 5 shows the temperatures as calculated by Regnault's own formula (shorter form) and Col. 6 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation from the smooth curve represented by Regnault's formula is 3.29°. Our formula thus fits his results better than does his own. The character of his work on this subject hardly justifies the extent to which his results have been quoted and used. It must be remembered, however, that he does not discuss their exactness, much less claim for them any special accuracy.

TABLE III.—REGNAULT'S OBSERVATIONS.

Press. obsd.	Temp. obsd.	Temp. calc. (S & M).	Δ_1.	Temp. calc. (Reg.).	Δ_2.
74.10	251.08	250.00	— 1.08	249.15	— 1.93
78.10	252.60	252.00	— 0.60	251.26	— 1.34
85.10	255.45	255.30	— 0.15	254.71	— 0.74
238.38	297.21	298.14	+ 0.93	299.28	+ 2.07
345.80	314.06	316.02	+ 1.96	316.88	+ 2.82
486.31	331.60	333.07	+ 1.47	333.83	+ 2.23
624.90	344.89	346.25	+ 1.36	346.84	+ 1.95
761.87	354.83	357.09	+ 2.26	357.48	+ 2.65
758.20	354.60	356.82	+ 2.22	357.22	+ 2.62
1529.60	412.96	398.50	—14.46	397.70	—15.26
2686.2	428.35	436.31	+ 7.96	433.96	+ 5.61
3180.6	444.06	448.51	+ 4.45	445.62	+ 1.56
4613.8	475.73	476.01	+ 0.28	472.74	— 2.99
7316.7	511.67	515.75	+ 4.08	509.58	— 2.09
6990.1	508.53	511.72	+ 3.19	505.75	— 2.78
5966.2	499.88	498.13	— 1.75	492.79	— 7.09
754.43	356.69	356.54	— 0.15	356.95	+ 0.26

Comparison of all Observations.—Since it thus appears that the present observations are probably of a relatively high order of accuracy, it is instructive to compare the results of other observers. In the following tables are given all the published observations, omitting those of Regnault and most of Gebhardt's. The initials are those of the observers: Young (Y), Ramsay and Young (R Y), Hertz (H), Callendar and Griffiths (C G), Cailletet, Colardeau, and Rivière (C C R), Pfaundler (P), Morley (M).

In the first table (Table IV) appear the observations above 200°, with two others, and also the rounded values of C C R (no observed data having been published by them). Since in this region the chief experimental error lies in the measurement of temperature, rather than of pressure, the comparison is made in the same way as before.

TABLE IV.—OTHER OBSERVATIONS, CHIEFLY ABOVE 200°.

Obsr.	Press. obsd.	Temp. obsd.	Temp. calc.	Δ.
Y	9.94	183.8	183.62	−0.18
Y	9.85	183.7	183.35	−0.35
H	20.35	203.0	205.29	+2.29
H	22.58	206.9	208.56	+1.66
Y	51.85	236.9	236.78	−0.12
RY	124.35	270.35	270.43	+0.08
R Y	157.15	280.2	283.23	+0.03
C G	760	357.08	356.95	−0.12
C C R	1596	400	401.00	+1.00
R Y–Y	2896.90	443.15	441.71	−1.44
R Y–Y	2904.50	444.15	441.92	−2.23
C C R	3230	450	449.65	−0.35
C C R	6080	500	499.7	−0.3
C C R	10488	550	549.0	−1.0
C C R	16948	600	599.4	−0.6
C C R	25840	650	647.1	−2.9
C C R	38000	700	696.3	−3.7
C C R	77320	800	804.6	+4.6
C C R	123120	880	889.6	+9.6

Callendar and Griffiths' value is the mean of all their boiling-point observations reduced to thermodynamic temperature (S b. p. = 445°). None of the other temperatures have been reduced. At the high temperatures (C C R), where the reduction would make the most difference, no data are furnished by the authors. The values of the temperatures near 443–444° (Young) are about 2° too high, for the reason already given.

Table V contains all the observations below 200°. Since in this region the pressures are very low, the chief errors affect the pressures rather than the temperatures. In this table, therefore, the observed pressures (Col. 3) are compared with those calculated by formula R (Col. 4). The differences are given in column 5, and in column 6 is stated the percentage of the calculated value which was observed (*i. e.*, calculated value = 100).

TABLE V.—OBSERVATIONS BELOW 200°.

Obsr.	Temp. obsd.	Press. obsd.	Press. calc.	Δ.	Percentage.
P........	15	0.00081	0.000844	+0.000034	96.0
M........	16	0.0010	0.000922	—0.000078	108.5
M........	30	0.0027	0.00298	+0.00028	90.3
M........	40	0.0052	0.00648	+0.00128	80.2
M........	50	0.0113	0.01339	+0.00209	84.4
P........	56.3	0.01807	0.02068	+0.00267	87.1
M........	60	0.0214	0.02648	+0.0050	80.8
M........	70	0.0404	0.0529	+0.0125	76.4
H........	89.4	0.16	0.1575	—0.0025	101.6
P........	98.8	0.26305	0.26220	—0.0008	100.3
H........	117	0.71	0.6552	—0.0548	108.4
G........	129	1.000	1.144	+0.144	87.4
H........	154.2	3.49	3.3280	—0.162	104.9
G........	157.5	3.93	3.718	—0.212	105.7
H........	165.8	5.52	5.216	—0.304	104.3
G........	176.5	8.22	7.732	—0.488	106.4
H........	177.4	8.20	7.985	—0.215	102.7
R Y.....	183.4	9.87	9.8670	—0.003	100.0
H........	184.7	11.04	10.322	—0.718	107.0
G........	188	12.51	11.560	—0.95	108.2
H........	190.4	12.89	12.540	—0.35	103.0

Morley's results were obtained by saturating carbon dioxide with mercury vapor. The calculated values seem to represent the results as a whole fairly well.

TABLE VI.—COMPARATIVE TABLE OF ROUNDED RESULTS.

Temp.	Reg.	R & Y.	Y.	G.	Laby.	S & M.
255°	85.9	85.0	....	.....	86.2	84.45
260	96.7	96.7	96.5	100.0	97.8	95.94
270	123.0	123.9	124.0	120.0	124.8	123.02
280	155.2	157.4	157.8	158.8	158.4	156.29
290	194.5	198.0	198.9	199.5	199.3	196.81
300	242.2	246.8	248.6	249.0	248.6	245.85
310	299.7	304.9	308.0	309.0	307.7	304.69
320	368.7	373.7	378.5	.....	378.1	374.82
330	450.9	454.4	461.7	.....	461.3	457.85
340	548.4	548.6	559.1	.....	559.1	555.54
350	663.2	658.0	672.5	.....	673.3	669.77
360	797.7	784.3	803.7	.....	805.9	802.62
370	954.7	930.3	954.7	.....	959.2	956.25
380	1140	1096	1228	C C R	1135	1133.0
390	1347	1284	1325	.....	1337	1335.4
400	1588	1496	1549	1596	1566	1566.1
410	1864	1734	1801	....	1826	1827.6
420	2178	2000	2085	....	2119	2123.4
430	2533	2299	2403	....	2446	2456.0
435	2728	2459	2572	....	2628	2637.5
440	2934	2629	2757	....	2817	*2828.8*
445	3153	2808	2939	....	3018	*3031.5*
450	3384	2996	3150	3230	3229	*3245.0*

The preceding comparative table (Table VI) gives the smoothed results of various observers, for the most part for every ten degrees. It comprises only the region of the present experiments, with an extension of 450°, to include the boiling point of sulphur and two values by C C R. The values under S & M are calculated from formula R, and those which are extrapolated are in italics. Laby's recalculation took into account all the preceding data, excepting those of Regnault. But it will be seen that, above 340° at least, the errors in the latter are not as great as was at first suspected.

The Boiling Point of Mercury.—As considerable interest attaches to the knowledge of the exact boiling point of mercury at 760 mm., the values found for that point by different observers may be compared.

Regnault made seven measurements close to this point. The mean, when the results are reduced to 760 mm. and to thermodynamic temperature[1] (S b. p. = 445°), and when all are given equal weight, is 357.7°. The average deviation of a single observation from this mean is 1.34°.

Callendar and Griffiths' result with the five best thermometers, giving equal weight to each determination, is 356.74°. The correction to the thermodynamic scale (S b. p. = 445°) is about +0.34°, making the value 357.08°, with an average deviation of the individual observations from this mean of 0.02°. They believe that their absolute temperature measurement is correct ±0.1°. In judging of the probable accuracy of this value it is to be noted that they heated their mercury at the bottom with a small flame. The layer from which the vapor proceeded was therefore under a head of mercury indicated by the scale of their drawing to have been about 53 mm. The vapor was therefore probably superheated, and no mention is made of experiments to ascertain whether lowering or raising the thermometer altered the value of the observed temperature. We should expect, therefore, that their temperature would be, if anything, too high.

The present value, from the formula, is 356.95°, with the absolute temperature measurement believed to be accurate to ±0.1°. The possibility of superheating is here eliminated.

Table of Smoothed Results.—Finally, a table (VII) of the vapor pressures of mercury for every two degrees from 0° to 458°, calculated by formula R, is given. The extrapolated values, below 255° and above 435°, are in italics. The values below 255° probably represent, as we have seen, the somewhat divergent observations as well as would smoothed values made from these observations themselves. Intermediate values may be obtained by linear interpolation:

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[1] As reduced by Dr. Edgar Buckingham, whom we have to thank for a private communication on the subject. His value, 357.1°, was on the scale S b. p. = 444.9°, and we have adjusted it to our scale.

TABLE VII.—VAPOR PRESSURES OF MERCURY FOR EVERY TWO DEGREES.

Temp. thermodynamic, press. mm. Hg at 0° and normal g. Extrapolated values in italics.

Temp.	0°.	2°.	4°.	6°.	8°.
0°	*0.000207*	*0.000252*	*0.000306*	*0.000370*	*0.000447*
10	*0.000537*	*0.000645*	*0.000773*	*0.000922*	*0.00110*
20	*0.00131*	*0.00155*	*0.00183*	*0.00216*	*0.00254*
30	*0.00299*	*0.00350*	*0.00410*	*0.00478*	*0.00558*
40	*0.00648*	*0.00752*	*0.00872*	*0.01008*	*0.01163*
50	*0.01340*	*0.01541*	*0.01768*	*0.02027*	*0.02319*
60	*0.02648*	*0.03020*	*0.03439*	*0.03909*	*0.04437*
70	*0.05029*	*0.05692*	*0.06432*	*0.07258*	*0.08179*
80	*0.09204*	*0.1034*	*0.1161*	*0.1301*	*0.1457*
90	*0.1628*	*0.1818*	*0.2028*	*0.2259*	*0.2513*
100	*0.2793*	*0.3100*	*0.3438*	*0.3807*	*0.4212*
110	*0.4655*	*0.5140*	*0.5668*	*0.6245*	*0.6873*
120	*0.7557*	*0.8301*	*0.9109*	*0.9987*	*1.094*
130	*1.197*	*1.309*	*1.430*	*1.560*	*1.701*
140	*1.854*	*2.018*	*2.195*	*2.385*	*2.590*
150	*2.811*	*3.047*	*3.302*	*3.574*	*3.866*
160	*4.179*	*4.514*	*4.873*	*5.256*	*5.665*
170	*6.102*	*6.568*	*7.065*	*7.594*	*8.158*
180	*8.758*	*9.396*	*10.07*	*10.79*	*11.56*
190	*12.37*	*13.23*	*14.15*	*15.11*	*16.14*
200	*17.22*	*18.36*	*19.58*	*20.86*	*22.21*
210	*23.63*	*25.14*	*26.72*	*28.40*	*30.16*
220	*32.01*	*33.96*	*36.02*	*38.18*	*40.45*
230	*42.83*	*45.34*	*47.96*	*50.72*	*53.62*
240	*56.64*	*59.82*	*63.15*	*66.64*	*70.29*
250	*74.10*	*78.09*	82.27	86.63	91.19
260	95.94	100.91	106.09	111.50	117.14
270	123.02	129.14	135.52	142.17	149.09
280	156.29	163.78	171.57	179.66	188.08
290	196.81	205.92	215.31	225.14	235.31
300	245.85	256.79	268.13	279.89	292.07
310	304.69	317.77	331.30	345.32	359.82
320	374.82	390.34	406.39	422.97	440.13
330	457.85	476.20	495.06	514.59	534.74
340	555.54	576.99	599.13	621.97	645.57
350	669.77	694.78	720.56	747.11	774.45
360	802.62	831.60	861.44	892.15	923.75
370	956.25	989.68	1024.0	1059.4	1095.7
380	1133.0	1171.4	1210.7	1251.2	1292.8
390	1335.4	1379.2	1424.1	1470.2	1517.6
400	1566.1	1615.8	1666.9	1719.2	1772.9
410	1827.5	1884.1	1941.8	2000.9	2061.4
420	2123.4	2186.9	2251.9	2318.3	2386.4
430	2456.0	2527.3	2600.1	2674.7	2753.6
440	2828.8	2908.5	2990.0	3073.1	3158.2
450	3245.0	*3333.8*	*3424.5*	*3517.1*	*3611.7*