XLV.—*On the Vapour-pressures of Bromine and Iodine, and on Iodine Monochloride.*

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So far as we know, the vapour-pressures of bromine and iodine have not been measured. The action of these elements on mercury precludes the ordinary method of experiment; but it is possible to use the method described by us in the Transactions, **47**, 42, substituting for the cotton-wool on the thermometer bulb a similar covering of asbestos, and interposing, between the still-apparatus and the manometer, a tube filled with solid sodium amalgam.

Although the vapour-pressures of these elements have not been determined, there are numerous isolated determinations of melting and boiling points; these, however, differ so widely from each other that a revision would seem desirable.

(1.) *Melting Point of Bromine.*—The following determinations have previously been made:—

Regnault	− 7·32°	Balard	− 18·0°	(freezing point).
Pierre	− 7·5	Serullas	− 18° to 20°	,,
Philipp	− 7·2 to − 7·3	Liebig	− 25·0°	,,
		Quincke	− 20·0	,,
		Baumhauer	− 24·5°	,,

Besides the statements of these authors, those of text-books are very contradictory: for example, Roscoe and Schorlemmer, −21°; Miller, −12·5°; Frankland, "Lecture Notes," − 20°; Wurtz's Dictionary, freezing point −22°, melting point above −12°.

(2.) *Boiling Point of Bromine.*—

Pierre, 63·0° at 760·32. Thorpe, 59·27° at 760.
Andrews, 58·0° at 760·0. Bolas and Groves, 59·6° at 751·0.
Landolt, 58·6° at ?

Besides these, Balard gives 47° and Löwig 45°, and one of these numbers is quoted in Williamson (47°).

(3.) *Melting Point of Iodine.*—

Regnault, 107°. During solidification, 113·6°.
Stas, 113—115°.

(4.) *Boiling Point of Iodine.*—

Regnault, 175° (about). Stas, above 200°.

Two sets of experiments were carried out with samples of bromine obtained from different sources. The first portion, after drying over sulphuric acid and boiling with potassium bromide to remove chlorine, distilled with absolute constancy from beginning to end at 57·65°* at 749·8 mm. The second sample was boiled with potassium bromide, dehydrated with phosphoric anhydride, and boiled, after a small quantity had come over, constantly at 58·85°, at a pressure of 755·8 mm. Both of these samples were tested for iodine with negative results; and on adding 0·25 per cent. of iodine to a portion of one of the samples, the boiling point was no longer constant. We are unable to account for this difference in boiling point in the two samples, which was found to be persistent throughout the whole range of pressures.

The results with the first sample are as follows:—(b. p. 57·65° at 749·8 mm.).

* All the temperatures were determined with a mercurial thermometer, but are corrected to express air-thermometer temperatures, for the mercurial thermometers had previously been carefully compared.

Series I.

Temperature.		Pressure.	Temperature.	Pressure.
Solid.	Liquid.		Liquid.	
− 18·44°	—	18·05 mm.	15·98°	147·4 mm.
− 11·65	—	32·0 ,,	19·30	174·35 ,,
− 11·59	—	32·85 ,,	19·92	175·45 ,,
− 7·25	—	45·55 ,,	28·23	255·2 ,,
—	− 5·1°	51·6 ,,	30·25	275·6 ,,
—	− 3·71	55·1 ,,	32·96	305·1 ,,
—	+ 0·19	67·8 ,,	35·68	340·9 ,,
—	3·95	82·5 ,,	38·57	379·8 ,,
—	5·28	88·05 ,,	41·47	421·4 ,,
—	10·44	112·95 ,,	44·24	465·0 ,,
—	10·52	113·35 ,,	46·86	511·3 ,,
—	15·59	143·7 ,,	49·22	558·3 ,,

Series II.

Temperature.		Pressure.	Temperature.	Pressure.
Solid.	Liquid.		Liquid.	
− 12·65°	—	28·2 mm.	12·63°	125·5 mm.
− 12·27	—	29·9 ,,	21·11	188·6 ,,
− 11·02	—	33·05 ,,	27·69	243·2 ,,
− 9·9	—	36·65 ,,	38·49	379·0 ,,
—	− 9·4°	39·70 ,,	44·60	474·3 ,,
—	+ 4·75	85·6 ,,	44·65	475·3 ,,

Repeated with sample 2 (b. p. 55·85 at 755·8 mm.).

	Temperature.	Pressure.	Temperature.	Pressure.
Liquid ..	− 9·88°	38·55 mm.	− 2·63°	57·9 mm.
Solid ..	− 9·68	35·55 ,,	− 0·31	65·25 ,,
,, ..	− 8·65	40·05 ,,	+ 10·4	111·8 ,,
Liquid ..	− 6·90	46·35 ,,	28·55	251·0 ,,
,, ..	− 5·04	50·9 ,,	47·65	518·2 ,,

With sample 1, series I, after the bromine had been frozen, on admitting air to raise the pressure, the temperature remained stationary at −7·05°; in series II, on solidification, the temperature rose from −9·45° to −7·45° and then fell again to −9·9°; and when the pressure was made to rise, the temperature again became stationary at −7·0°. With sample 2, the temperature rose to −7·25° and then fell again. From direct observation, therefore, the melting point is seen to be between −7·0° and −7·45°.

As a comparison of these samples did not give concordant results, the second sample was first treated with caustic soda, evaporated, and the resulting bromate decomposed by heat. The bromine was recovered by distillation with potassium dichromate and dilute sulphuric acid. By this treatment all organic impurity must have been destroyed. The bromine was then digested with potassium bromide, and finally dried with sulphuric acid. It boiled constantly at 58·65° under a pressure of 757 mm.

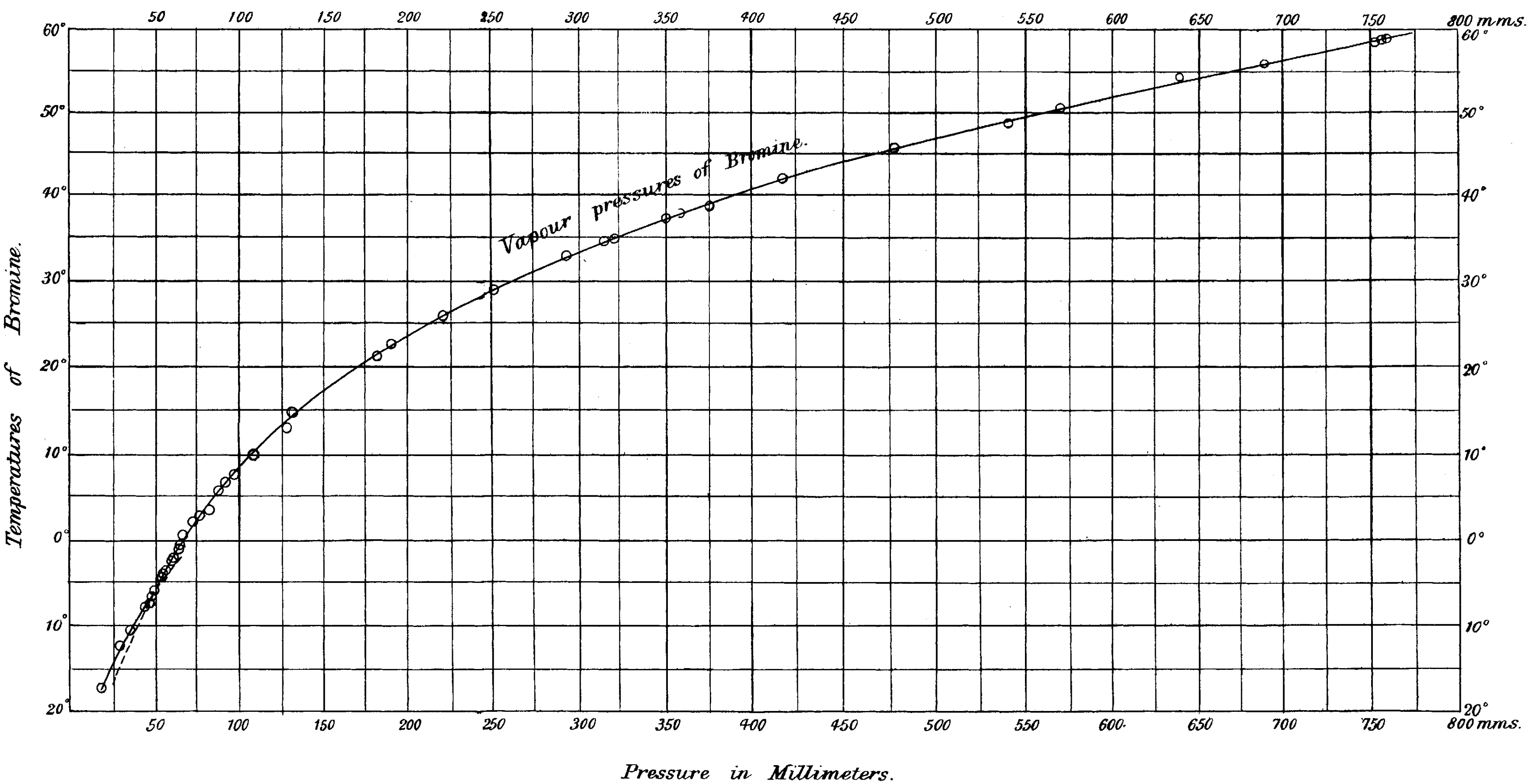
A third sample, from a different source, was distilled alone, and boiled at 56·8—58·5° at 757 mm. It was then digested at the boiling point with potassium bromide, and allowed to stand over night; the boiling point was then 57·8° to 58·45° at 750·9 mm. It was then shaken with strong sulphuric acid and distilled at once, when it boiled from 58·35° to 58·5° at 750·9 mm.; and on standing for two days with strong sulphuric acid with occasional shaking, it boiled at 58·5° to 58·6° at 754·4 mm. This determination agrees with the result given by the purified sample, hence the last sample was used for experiment, and its vapour-pressures were measured. The rate of change of temperature at the boiling point of bromine is very nearly 1° for 25 mm.; corrected to 760 mm., the various determinations are as follows:—

First sample	58·05°
Second sample.....................	59·0
,, ,, after purification	58·75
Third ,, ...	58·75

The vapour-pressures of sample 3 were then determined.

Series I.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
−7·87°	42·65 mm.	−3·87°	53·8 mm.	+3·43°	80·35 mm.
−7·0	45·7 ,,	−2·40	57·8 ,,	5·45	87·8 ,,
−5·74	49·1 ,,	−1·06	62·2 ,,	7·55	97·65 ,,
−4·69	51·5 ,,	+0·31	65·0 ,,	9·88	108·8 ,,
−4·35	52·9 ,,	+2·03	73·95 ,,	12·31	127·25 ,,



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Series II.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
− 17·12°	18·9 mm.	− 0·85°	63·2 mm.	28·80°	250·55 mm.
− 12·74	28·1 "	+ 2·78	75·75 "	32·70	293·4 "
− 12·70	27·65 "	6·38	91·7 "	34·68	321·0 "
− 10·36	34·85 "	14·30	133·65 "	36·98	350·25 "
− 6·39	47·05 "	20·96	181·25 "	38·61	375·75 "
− 4·79	51·0 "	22·20	189·75 "	—	—
− 2·02	59·0 "	25·72	220·25 "	—	—

Series III (with a Different Thermometer).

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
34·4°	315·05 mm.	45·50°	478·2 mm.	54·1°	636·1 mm.
37·44	357·0 "	48·7	540·5 "	56·0	689·0 "
41·85	418·6 "	50·2	567·3 "	—	—

The boiling point was again determined, and was found to be 58·7° at a pressure of 759·1 mm. The melting point was also directly observed twice, it was −7·1°.

On considering these results, we think that the evidence goes against the first sample, inasmuch as the second sample, after purification, had a boiling point identical with that of the third.

The results of the vapour-pressures of the third sample are represented as a curve (No. 1), and it will be seen that the curve representing the vapour-pressures of the solid is not continuous with that of the liquid, and that the two curves intersect at a point corresponding to a temperature of −7·1°, and a pressure of 44·5 mm.

The ratios of the absolute temperatures of bromine and water at equal vapour-pressures were calculated, and are given in the following table. The value of c in the formula $R' = R + c\,(t' - t)$ is for liquid bromine −0·000586, and for solid bromine + 0·00114. (See *Phil. Mag.*, 1886, p. 33.)

Ratios of Absolute Temperatures of $\frac{\textit{Water}}{\textit{Bromine}}$.

	Pressure.	Temp. of water.	Temp. of bromine.	Ratio.
Solid	20 mm.	273 + 22·3°	273 − 16·65°	1·1519
,, ...	25 ,,	,, 26·0	,, 14·0	1·1544
,, ...	30 ,,	,, 29·1	,, 12·0	1·1575
,, ...	35 ,,	,, 31·8	,, 10·05	1·1592
,, ...	40 ,,	,, 34·2	,, 8·4	1·1610
,, ...	45 ,,	,, 36·3	,, 7·0	1·1628
Liquid ..	50 ,,	,, 38·3	,, 5·05	1·1618
,, ...	100 ,,	,, 51·7	,, + 8·20	1·1547
,, ...	150 ,,	,, 60·1	,, 16·95	1·1488
,, ...	200 ,,	,, 66·6	,, 23·45	1·1456
,, ...	300 ,,	,, 75·9	,, 33·05	1·1400
,, ...	400 ,,	,, 83·0	,, 40·45	1·1357
,, ...	500 ,,	,, 88·7	,, 46·8	1·1310
,, ...	600 ,,	,, 93·5	,, 51·95	1·1278
,, ...	700 ,,	,, 97·7	,, 56·3	1·1257
,, ...	760 ,,	,, 100·0	,, 58·75	1·1243

It will be seen that these ratios, mapped against temperatures of bromine (*see* Curve 2) give points in a straight line; in other words c is constant.

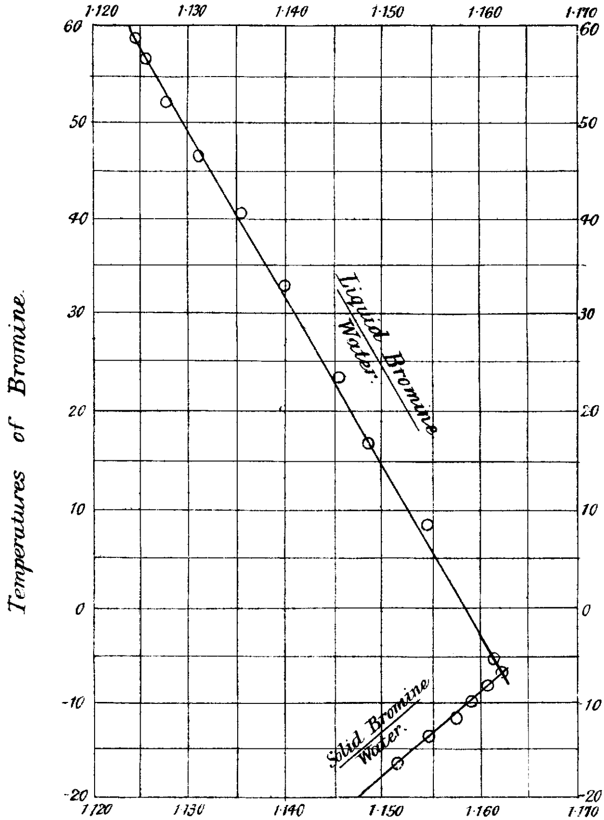
Vapour-pressures of Iodine.

Series I.

Solid.		Liquid.	
Temperature.	Pressure.	Temperature.	Pressure.
58·1°	4·9 mm.	114·1°	89·8 mm.
64·5	6·05 ,,	114·9	93·55 ,,
66·3	6·25 ,,	117·8	103·0 ,,
75·2	11·5 ,,	120·4	113·4 ,,
80·4	15·15 ,,	123·15	124·5 ,,
86·0	21·25 ,,	125·5	135·8 ,,
91·8	28·95 ,,	127·1	142·9 ,,
91·9	29·6 ,,	166·6	475·0 ,,
96·8	37·8 ,,	169·4	505·5 ,,
102·7	50·65 ,,	171·7	535·6 ,,
105·7	59·85 ,,	174·5	575·3 ,,
113·8	87·0 ,,	177·6	630·3 ,,
—	—	177·7	633·9 ,,
—	—	180·75	680·5 ,,
—	—	{186·4	764·2 ,,
—	—	{185·2	—
—	—	{185·45	—
—	—	{185·45	—
—	—	{185·55	—

Ratio of Absolute Temperatures.

$\frac{\text{Water}}{\text{Bromine}}$.



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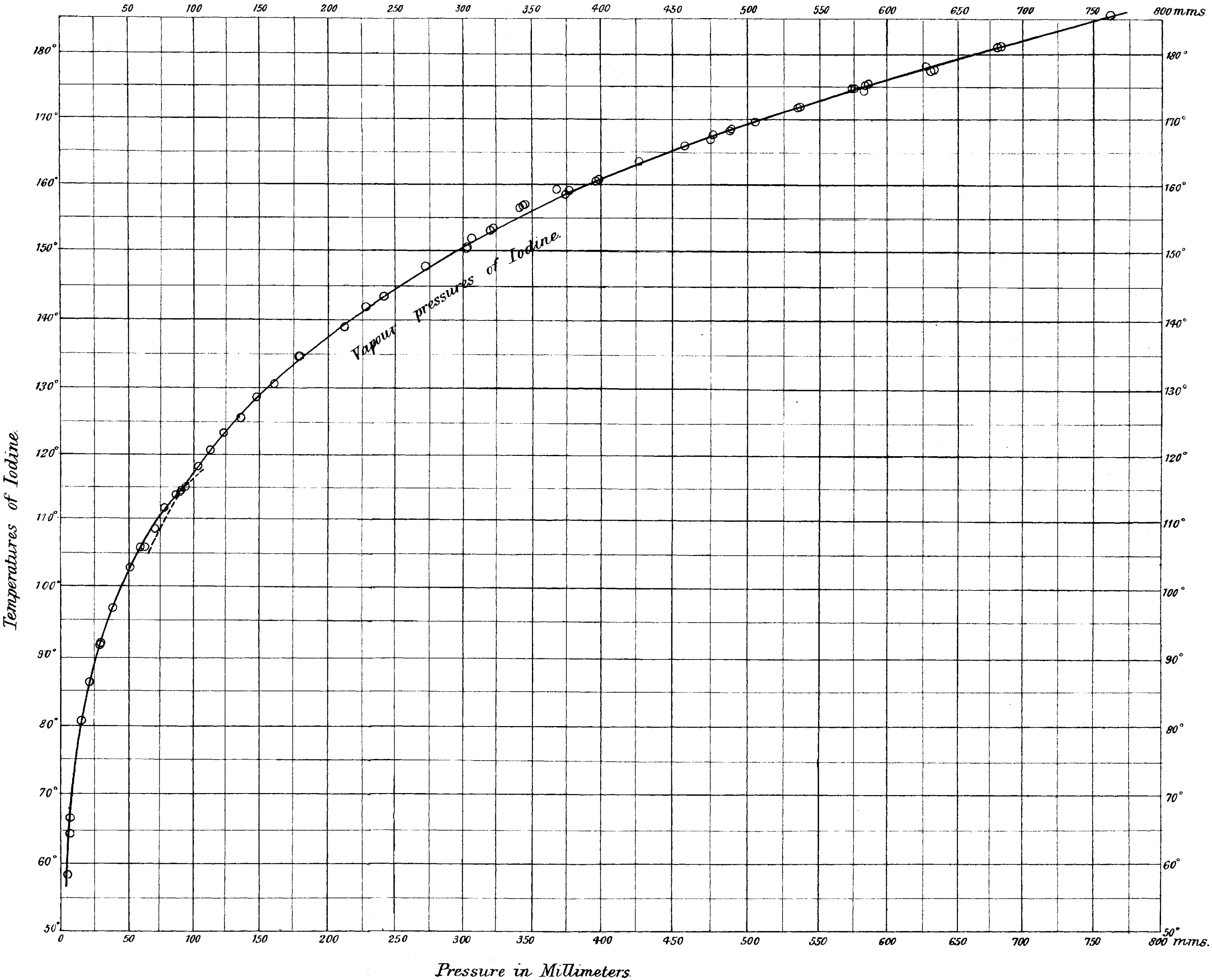

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Series II.

Solid.		Liquid.	
Temperature.	Pressure.	Temperature.	Pressure.
105·6°	61·8 mm.	127·4°	143·1 mm.
108·4	70·6 ,,	130·1	157·3 ,,
111·6	78·8 ,,	134·4	180·5 ,,
114·2	90·5 ,,	147·8	273·2 ,,
—	—	158·4	374·6 ,,
—	—	158·9	376·0 ,,
—	—	167·2	475·6 ,,
—	—	174·4	574·3 ,,
—	—	177·9	625·8 ,,
—	—	180·8	679·1 ,,

Liquid.					
Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
134·5°	179·9 mm.	153·6°	323·0 mm.	163·2°	425·9 mm.
138·6	211·7 ,,	156·2	340·8 ,,	165·8	456·9 ,,
141·1	227·1 ,,	156·5	344·2 ,,	168·0	486·6 ,,
143·0	241·0 ,,	156·6	346·1 ,,	168·2	488·6 ,,
147·7	273·0 ,,	158·9	369·1 ,,	171·9	536·3 ,,
150·2	300·4 ,,	159·6	385·2 ,,	174·2	581·6 ,,
150·7	302·4 ,,	160·4	395·8 ,,	175·0	583·8 ,,
151·6	305·3 ,,	160·7	399·0 ,,	175·3	586·8 ,,
153·2	321·2 ,,	—	—	—	—

These numbers are not so accordant as usual. The reason for this is that the stem of the thermometer being invisible through the iodine vapour, the vapour was always kept below the level of the mercury in the thermometer, and hence a correction, not always certain, had to be introduced for the expansion of the mercury in the stem. It should be stated that the temperatures of both bromine and iodine are those of an air thermometer, for the thermometer used was calibrated by a measurement of the vapour-pressure of water, and of the substances described in the Transactions, **47**, 640.

It may be noticed in this case also, that the curve expressing the relation of pressure to temperature for solid iodine is not a continuation of that for liquid iodine, but that they intersect at 114·3° and a pressure of 91 mm. This has been already experimentally proved by us for a number of substances (*Phil. Trans.*, 1884, Part II, 461).

The melting point was directly observed to be between 113·8° and 114·1°; and another observation gave 114·2°.

Ratios of Absolute Temperatures of $\frac{\textit{Iodine}}{\textit{Water}}$.

	Pressure.	Temp. of water.	Temp. of iodine.	Ratio.
Solid	20 mm.	273 + 22·0°	273 + 85·0°	1·2123
,,	30 ,,	,, 29·1	,, 92·2	1·2089
,,	50 ,,	,, 38·3	,, 102·15	1·2051
,,	70 ,,	,, 44·6	,, 109·05	1·2029
,,	90 ,,	,, 49·55	,, 114·15	1·2003
Liquid	100 ,,	,, 51·7	,, 117·0	1·2011
,,	150 ,,	,, 60·1	,, 128·9	1·2066
,,	200 ,,	,, 66·6	,, 137·05	1·2075
,,	300 ,,	,, 75·9	,, 150·7	1·2144
,,	400 ,,	,, 83·0	,, 160·9	1·2188
,,	500 ,,	,, 88·7	,, 169·05	1·2222
,,	600 ,,	,, 93·5	,, 176·0	1·2251
,,	700 ,,	,, 97·7	,, 182·0	1·2274
,,	760 ,,	,, 100·0	,, 185·3	1·2287

These points were mapped in the ordinary way. The value of c for liquid iodine is + 0·0003986, and for the solid −0·000407. The two lines intersect one another at 114·3°, the melting point of iodine.

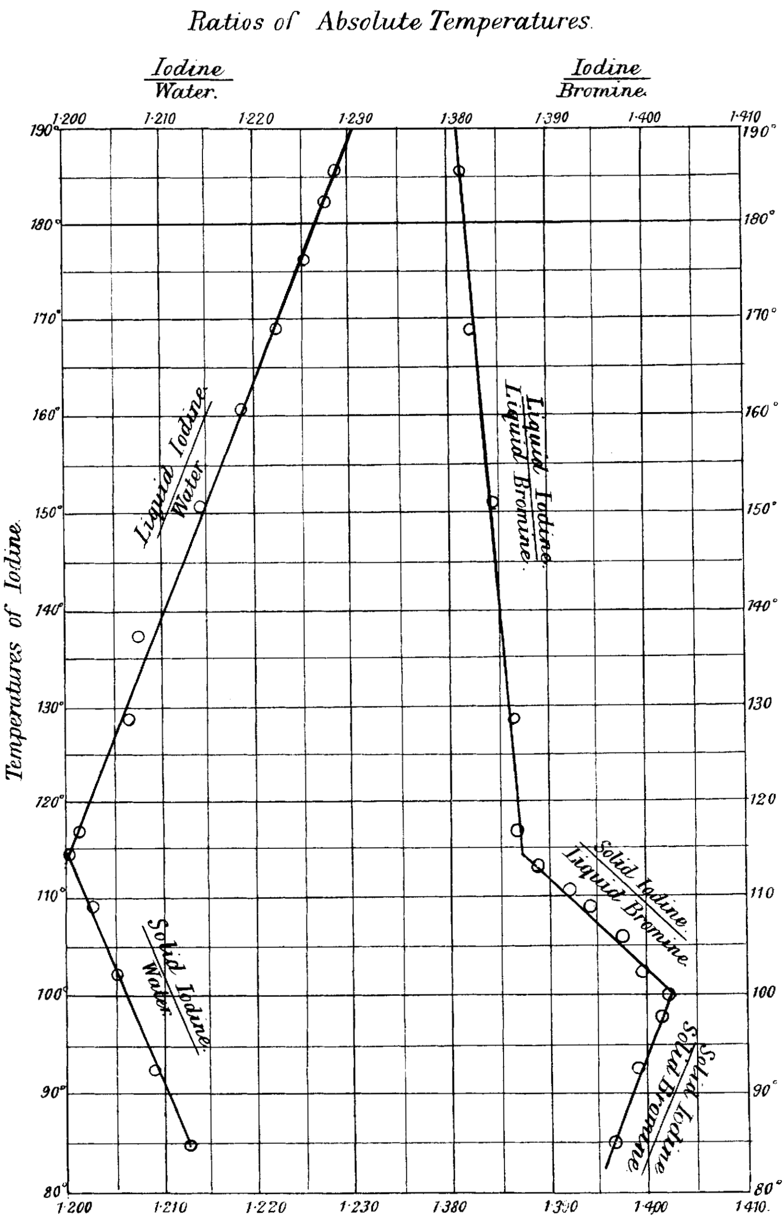
We have also constructed a diagram to show the ratios between the absolute temperatures at constant pressures of—

1. Liquid iodine ÷ liquid bromine, where c = −0·000080.
2. Solid ,, ÷ ,, ,, where c = −0·001125.
3. ,, ,, ÷ solid ,, where c = +0·000413.

In these cases the ordinates are the temperatures of iodine. The first two lines intersect at the melting point of iodine, and the second at a temperature of iodine, where iodine vapour exerts a pressure equal to that of bromine at its melting point. The points do not fall well in a straight line, owing probably to the difficulty we experienced in measuring the vapour-pressures of iodine.

From our results, the following data for the melting point of bromine are obtained:—

1. Highest temperature attained on solidification −7·45°.
2. Constant temperature during fusion, −7·0° and −7·05°, and with the third sample, −7·1°.
3. Intersection of vapour-pressure curves of solid and liquid, −7·05°.
4. Intersection of lines representing ratios for bromine and water, −7·0°.



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The first result, −7·45°, is of little value, inasmuch as the highest possible temperature is not necessarily attained on solidification. We believe that −7·05° expresses the true melting point very closely.

As regards the boiling point of bromine at normal pressure, the corrected number found by us is 58·0° for the first sample; that of the second and third samples is 58·7°; these numbers approximate to those given by Andrews and by Landolt, 58·0° and 58·6° respectively; but that which we place most confidence in, 58·7°, differs from that found by Thorpe by 0·55°, and yet Thorpe's method of purification appears unexceptionable. Thorpe's remark in his paper (*Chem. Soc. J.*, **37**, 172) on the thermal expansion of various bodies, that the high solidifying point of the sample of bromine, viz., −7·5° to −8°, used by Pierre, points to its contamination with water is, however, quite unfounded on fact. The temperature to which a liquid can be cooled without freezing depends on various circumstances, and is not a fixed point; whereas the melting point, or the point of intersection of the vapour-pressure curves, is constant.

The following data are available for the melting point of iodine:—

1. Direct observation, 114·1—114·3°.
2. ,, ,, 113·8—114·1°.
3. Intersection of vapour-pressure curves of solid and liquid, 114·3°.
4. Intersection of lines representing ratios for iodine and water, 114·3°.
5. Intersection of lines representing ratios for bromine and iodine, 114·05°.

The true melting point may be expressed by the number 114·15°, which agrees well with that given by Stas, 113—115°, and with Regnault, who found the temperature during solidification to be 113·6°.

The boiling point of iodine at 760 mm. pressure was found to be as a mean of five direct observations, 184·61° at 764·2 mm.; corrected to 760 mm. the temperature is 184·35°.

It was hoped by a study of the vapour-pressures of iodine monochloride to obtain results interesting on account of their comparison with the constants of bromine. Iodine monochloride is, however, not a stable substance. On distilling it at normal pressure, it dissociates, giving a sublimate containing trichloride, and while most of it boils at a temperature of 102°, the last portions boil as high as 106°, owing to the presence of free iodine. The vapour-pressure curve, therefore, obtained by our usual method presents great irregularity; the iodine monochloride fractionates during measurement, and it is a matter of chance if two observations coincide. We spent a great deal of time over this compound, and from the results obtained a curve was constructed fitting the observed points as accurately as we were able to draw it. On comparing the ratios between the absolute temperatures of iodine monochloride and water, it was evident that the lines representing the ratios of vapour-pressure of the solid should intersect that representing the ratios of the liquid; but the results were so irregular that the point of intersection could not be observed. All that we can say is that the value of c for the solid body is positive, whilst it is negative for the liquid.

Note.—Since writing this paper, a few measurements of the vapour-pressures of solid iodine have been given by v. Richter (*Ber.*, 1886, 1060). His results corroborate ours in a remarkable manner. At 20 mm. pressure he found a temperature of 85°; at 30 mm., 90°; and 90 mm. at its melting point. Our numbers at these pressures are 85° and 92·2°, and at the melting point we observed 89·8 mm. pressure. V. Richter, however, appears to be unaware of the fact that we long ago made careful measurements of results which he gives for the most part only qualitatively.

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