PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On Evaporation and Dissociation. Part III. A Study of the Thermal Properties of Ethyl Oxide

William Ramsay and Sydney Young

Phil. Trans. R. Soc. Lond. A 1887 **178**, 57-93
doi: 10.1098/rsta.1887.0003

III. *On Evaporation and Dissociation.*—Part III. *A Study of the Thermal Properties of Ethyl Oxide.*

By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*

Communicated by Professor G. G. STOKES, *D.C.L., P.R.S.*

Received April 23,—Read May 20, 1886.

[PLATES 6–10.]

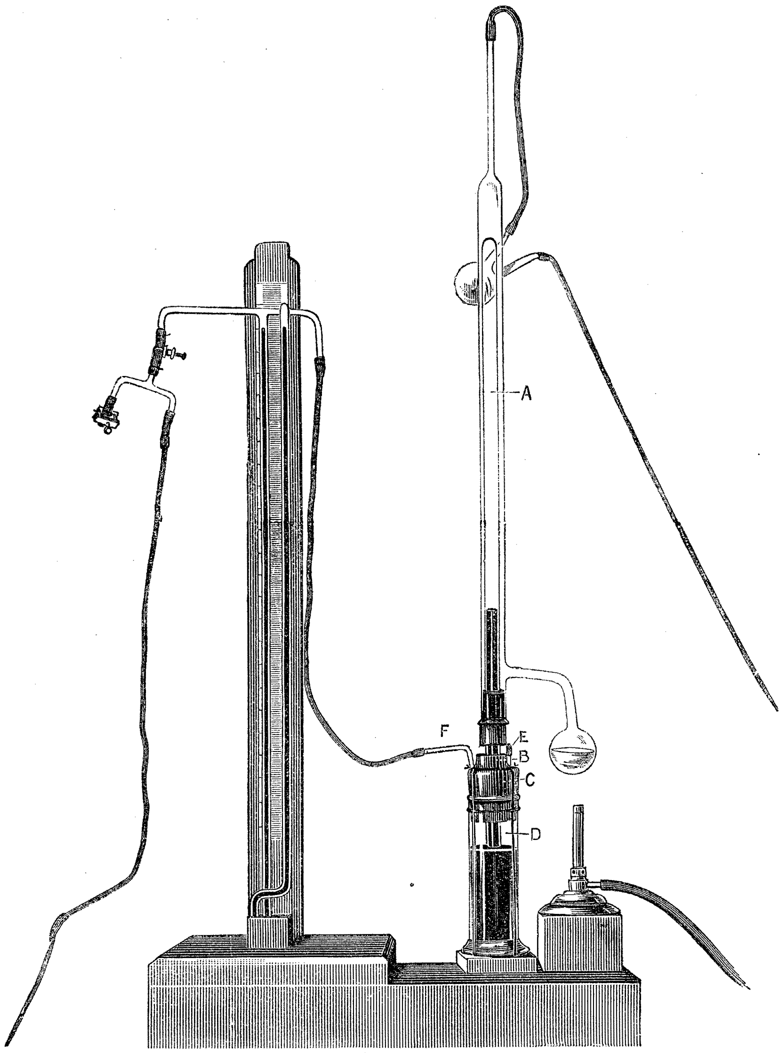
IN a memoir published in the Royal Society's 'Philosophical Transactions,' 1886 (Part I.), p. 123, "On the Thermal Properties of Ethyl Alcohol," we gave the results of a research on the vapour-pressures of alcohol, the densities of its vapour—both unsaturated and saturated—and the expansion and compressibility of liquid alcohol at various temperatures; and from these data were deduced the amounts of heat required to vaporize alcohol at those temperatures. Our object in these researches has been to compare carefully the behaviour of stable with that of unstable bodies, and, if possible, to acquire some clear ideas of the nature of chemical combination. But, as the properties of stable bodies are still to a great extent unknown, we have deemed it advisable to extend our research with the view of investigating this relationship; and for that purpose we have made a similar series of measurements of the thermal constants of ethyl oxide $(C_2H_5)_2O$. The data, and the deductions from the data, are the subject of the following memoir.

Experiments on the vapour-pressure, vapour-density, expansion, and other properties of ether have been made by REGNAULT, KOPP, PIERRE, MENDELEJEFF, AVENARIUS, and others, and their results shall be quoted when necessary.

Preparation of Pure Ether.

A quantity of absolute alcohol was converted into ether by means of sulphuric acid in the usual way. The distillate was first shaken up with caustic soda, to remove sulphurous anhydride, and was then redistilled. In order to remove a great part of the alcohol in the distillate, it was allowed to stand over calcium chloride, and again distilled. It was then repeatedly shaken with water to remove the last traces of alcohol, and it was then again dried with calcium chloride and distilled. The distillate was cohobated with metallic sodium until gas ceased to be evolved; it was then distilled from the sodium, and left in contact with clean, fresh sodium for many months. It was again distilled, and was found to boil with absolute constancy at 34·72° at a pressure of 763·1 millims. The thermometer used was graduated in tenths of a degree, and had been frequently tested and indirectly compared with an air thermometer. In order to exclude water, the ether was preserved in a stoppered tube with a mercury joint above the stopper.

Fig. 1.



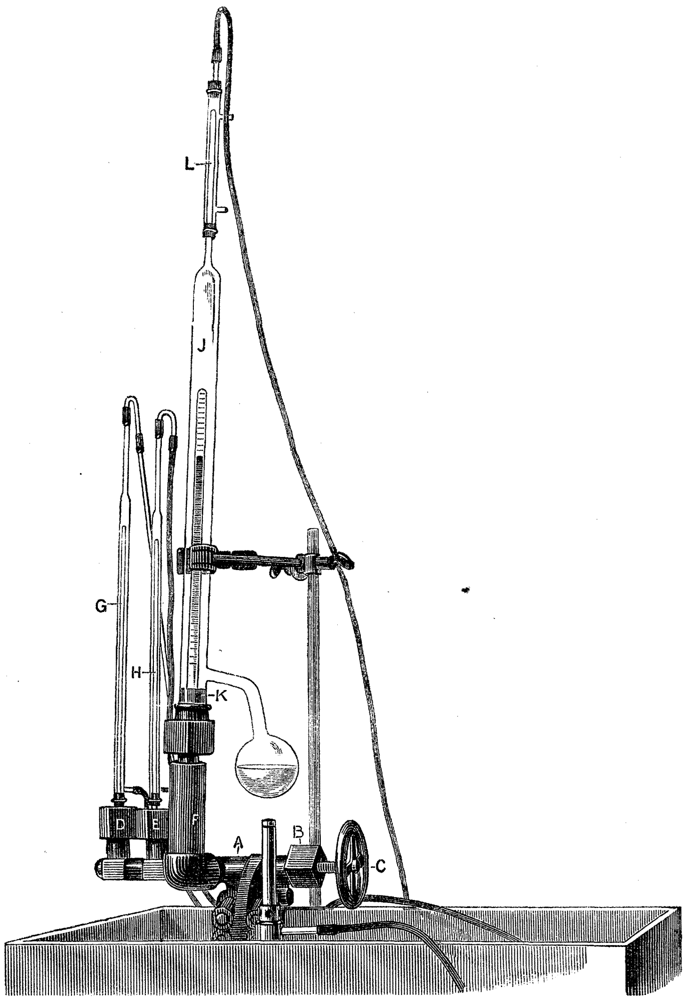
Apparatus employed.

Three different pieces of apparatus were employed in this research.

One for the determination of vapour-pressures at low temperatures. The apparatus has already been described in the 'Philosophical Transactions' for 1884, p. 37, and an improved form in the 'Journal of the Chemical Society' for 1885, p. 42. As it was impossible to use an india-rubber joint in presence of ether, a tight glass stopcock, smeared with slightly deliquesced phosphoric anhydride, was substituted.

The densities of the saturated and unsaturated vapour at low temperatures were determined by an apparatus modified from that devised by Professor HOFMANN. The form adopted was simpler than that employed in the research on alcohol. The graduated tube A (fig. 1) was completely filled with warm dry distilled mercury ; the ether, contained in a small light bulb, was introduced ; the tube was then inverted into a temporary mercury-trough B, on the top of a large india-rubber cork C, which closed the top of a large glass jar D, full of mercury, and communicating with the reservoir

Fig. 2.



by means of a hole through the cork. Through this hole the tube was inserted, and pushed down, until its extremity was distant from the bottom of the jar about 2 centims. A quantity of mercury was then forced out of the jar through the tube E, which did not dip so deeply into the mercury as the graduated tube. The tube E was then permanently closed. The tube F, which just passed through the cork, was connected with a pump and gauge, by means of which the pressure on the surface of the mercury could be altered and read.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

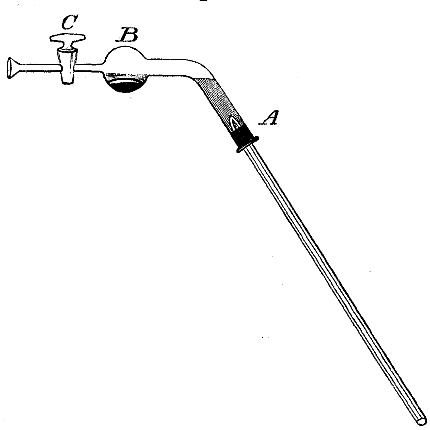
To find the weight of ether employed, the graduated tube was jacketed with the vapour of alcohol, boiling under atmospheric pressure. For lower temperatures the tube was surrounded with flowing water.

The constants at high temperatures were ascertained by help of the apparatus employed in our research on alcohol, which will now be described.

The body of the apparatus consists of a wrought-iron tube A (fig. 2), firmly fixed in a horizontal position by being clamped in a vice. As in ANDREWS's apparatus, one end is closed by a cap B, through which an iron screw passes, the joint being made tight by a packing of greased leather in which the screw C works, passing through the interior of an india-rubber cork, which closely fits the cap. On screwing on the cap, the india-rubber is compressed, so that a very high pressure can be withstood without leakage. The iron tube has no opening at the other end, but is provided with three vertical branches, D, E, and F, closed in a similar manner by iron caps, through which the gauges and the experimental tube pass. The gauge G is intended for registering high pressures, and H for low pressures. To the open end of G is sealed a glass reservoir, of known capacity, while H is a plain tube, constricted at one end. These, and also the experimental tube, which is also constricted at its open end, dip into clean, distilled mercury, filling the iron tube completely. The gauges are jacketed by narrow glass tubes, through which water flows; the temperature of the water was registered by a small thermometer, placed in the stream, immediately after passage through the gauges. It was found by experiment that, with a rapid current, the temperature did not rise sensibly during its passage. The experimental tube is fitted with a jacket J, in the bulb of which a liquid boiled under known pressure ('Chem. Soc. Journ.,' vol. 47, p. 640). The experimental tube passes through a perforated india-rubber cork, closing the jacket, and protected from the action of the condensed hot liquid by a layer of mercury K. The top of the jacket is furnished with a small condenser L, to prevent escape of vapour. The pressure under which the pure liquid was boiling was read by means of a gauge and barometer.

The experimental tube was filled with ether by fitting it, with help of a ring cut from india-rubber tube, into the end of the tube A (fig. 3). This tube is bent to an obtuse angle, and widened into a bulb at B. On the further side of B there is a tight stopcock C. Into the bulb is introduced some pure mercury and a quantity of the pure ether, much more than sufficient to fill the experimental tube. By warming the experimental tube some air is expelled; the ether in the bulb is then boiled on the surface of the mercury, the stopcock being open. When vapour freely escapes the stopcock is closed, and the tube is held in such a manner that ether covers the open end of the experimental tube. The latter is again warmed, and the ether, which enters on cooling, is boiled. The experimental tube, being at a higher temperature than the boiling-point of ether under the reduced pressure, liquid ether, trickling down into it, is at once gasified and carries with it all air, and a series of bubbles rapidly rises through the ether in the bulb. When it is judged that all air is expelled the experimental tube is cooled, and ether rushes in to fill it. It is easy to make sure, by the absence of a bubble, of complete expulsion of air. The tube is then tilted, so that mercury covers the end of the experimental tube, and a portion of the latter is warmed. The ether boils off through the mercury, and, on cooling, its place is occupied by mercury. By tapping, the column of mercury may be made to descend to any desired point. When quite cold, the experimental tube is disconnected, placed in the iron cap, and gently warmed, so as to cause a globule of mercury to hang to its constricted open end. It is then plunged under the surface of the mercury in the branch of the iron tube, and the cap is screwed tight. From this description it will be noticed that all possibility of the presence of air in the liquid to be experimented on is completely excluded; and our results prove that this was the case, for the readings of vapour-pressure at different volumes of gas and liquid give, for the same temperature, absolutely identical results.

Fig. 3.



It was thus possible to alter volume by means of the screw; to read pressures accurately by the use of the high and low pressure gauges, the readings of which were compared when possible; and to secure constant known temperatures by means of the vapour-jacket.

Experimental Results.

1. *Vapour-pressures at Low Temperatures.*

Calibration of Thermometer.—The thermometer employed was a new one by Negretti and Zambra, divided into tenths of a degree, and registering from $-20°$ to $+50°$. The zero-point at the atmospheric pressure was $+0·19°$. The bulb was immersed in mercury, contained in a vessel from which air could be exhausted by means of a Carré's pump. Unless the bulb is dipped in mercury, the temperature it registers is altered by the cooling of the air by exhaustion, or heating by compression; the mercury serves to keep the temperature constant. It was found that the temperature was apparently lowered 0·25° for a fall of pressure of 700 millims. The thermometer was next tested by a few determinations of the vapour-pressure of water. The water on the cotton-wool encasing the bulb having been frozen, pressure was raised to 6 millims., and the melting-point of ice was observed. The mercury stood constant for a long time at −0·11. An apparent fall of temperature, due to reduction of pressure, of +0·19−(−0·11)=0·3°, had thus occurred for a fall of pressure of 754 millims., which agrees with sufficient accuracy with the former observation, 0·25°, for 700 millims. This change of zero-point was considered to be proportional to the pressure, and corrections introduced accordingly. A comparison of the vapour-pressures of water by our method gave results coincident with those of REGNAULT up to 33°, and it was assumed that the graduation of the thermometer was equally regular below 0°.

Vapour-pressures at Low Temperatures.

SERIES I.

Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°
73·65	−17·73	141·0	−5·46
74·15	−17·68	152·7	−3·90
84·50	−15·30	153·85	−3·73
96·55	−12·85	168·9	−1·81
110·65	−10·33	184·05	−0·11
124·80	− 7·94	184·10	−0·07
139·85	− 5·65	186·05	+0·13
140·65	− 5·55	197·35	+1·42

SERIES II.

Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°
79·95	−16·24	216·25	+ 3·37
105·45	−11·23	258·25	7·33
133·05	− 6·74	316·40	11·96
162·60	− 2·71	392·90	17·19
181·80	− 0·33	593·05	27·64

These results were plotted and a curve drawn through them. The pressures for each 5° between −15° and +5°, read from the curve, are as follows :—

Temperature.	Pressure.
°	millims.
−15	86·0
−10	112·3
− 5	144·8
0	184·9
+ 5	233·0

The pressure at 0° agrees very well with that given by REGNAULT, 184·39 millims. ('Mémoires de l'Académie,' vol. 26, 1862, p. 393); but at the other temperatures the agreement is not nearly so close. These results will be considered subsequently.

2. *Vapour-densities at Low Temperatures.*

Weight of Ether taken.—The quantity of ether taken was not determined directly by weighing, but was calculated from vapour-density determinations at the boiling-point of alcohol under atmospheric pressure.

Series I.—Barometer, 763·1 millims. (reduced to 0°).
Boiling-point of alcohol, 78·4°.

In each set of observations the volume was altered very slightly; in the first, for instance, it varied from 154·3 to 155·3 cub. centims., while the pressure varied from 75·45 to 74·75 millims. The number of readings and the mean values are given in every case.

Number of readings.	Pressure reduced to 0°, Mean.	Volume, Mean.	Pressure × Volume.	Vapour-density.
	mms.	c.cs.		
9	75·06	154·77	11617	Taken as normal, =37
6	85·55	135·15	11562	
5	105·56	110·01	11613	
2	160·85	71·85	11557	37·13
3	438·82	25·87	11352	37·80

The mean value of *p.v.* calculated from the first three sets of readings is 11599·5. Taking the normal vapour-density of ethyl oxide as 37·0, the weight is 0·0393 gram. The pressure of the saturated vapour at this temperature is nearly 3,000 mms.; and it will be noticed that the value of *p.v.* is constant, although the volume has been reduced from 3 to 2.

Vapour-density at 12·9°.—The densities of the unsaturated and saturated vapour were then determined at 12·9°, the temperature being maintained constant by means of running water. The data follow in order.

Number of readings.	Pressure reduced to 0°, Mean.	Volume, Mean.	Pressure × Volume.	Vapour density.
	mms.	c.cs.		
2	54·07	175·25	9476	36·84
1	72·90	129·95	9473	36·85
2	118·20	79·92	9447	36·95
1	138·25	67·80	9374	37·24
2	138·70	67·40	9348	37·34
2	170·30	55·00	9355	37·30
2	207·18	44·90	9302	37·53
2	263·45	35·02	9227	37·83
2	309·68	29·60	9166	38·08
2	325·00	28·05	9116	38·30
Condensed	330·00	25·10	—	—

Vapour-pressure calculated, 330·48 mms.

3. *Constants at High Temperatures.*

For these experiments four different amounts of ether were employed. In the first case a large amount, A, was taken, and its weight calculated from its volume at known temperatures. During the early experiments a leakage took place, and, some ether being lost, the gauges had to be refilled. Measurements were again made to ascertain the weight of the remaining ether; this portion is alluded to as A′. The third amount, B, was too small to be accurately determined in this way, and was estimated by comparison of the volumes occupied by the two quantities under similar conditions of temperature and pressure. The fourth quantity, C, was still smaller, and its weight was deduced from comparison of its volumes with those of B at the same temperatures and pressures.

A. *Results of experiments on large quantity of ether. Determination of weight.*

The mean of the determinations of the specific gravity of ether at 0° by Kopp, Pierre, Mendelejeff, and Perkin was taken. Their numbers were as follows:—

Kopp ('Liebig's Annalen der Chemie und Pharmacie,' vol. 64, p. 214)	0·73658
Pierre ('Annales de Chimie et de Physique,' vol. 15, p. 325) . .	0·73581
Mendelejeff ('Liebig's Annalen der Chemie und Pharmacie,' vol. 119, p. 9)	0·73644
Perkin ('Chem. Soc. Journ.,' vol. 45, p. 474)	0·7371
,, ,, ,, ...	0·7352
Mean	0·7362

Dr. Perkin's results were from comparisons of ether and water at 15° and at 25°; the former is 0·72088, and the latter 0·70991. They were reduced to 0° by means of Kopp's formula, with the above results.

The portion of ether A gave the following measurements :—

Temperature.	Volume.	Specific gravity.	Weight.
17°·95	0·19589	0·71627	0·14031
15·50	0·19554	0·71902	0·14060
16·20	0·19571	0·71805	0·14053
		Mean weight	0·14048

The volume tube was a new one, and was carefully calibrated by weighing with ıercury. A low pressure and a high pressure gauge were employed. Where ossible, readings on both were taken. The manometers were calibrated by 'eighing with mercury, and contained air dried over phosphorus pentoxide. he following corrections for volume, pressure, and temperature were applied :—

For volume.—Meniscus of mercury and of liquid.

Expansion of glass by heat.

The expansion of the tube owing to internal pressure was not allowed for, as it would have been much within the errors of reading.

For pressure.—Meniscus of mercury.

Levels of mercury in volume tube and in pressure gauges.

Difference of temperature in water-jacket at time of filling and time of reading.

Deviation of air from BOYLE'S Law, as determined by AMAGAT ('Compt. Rend.,' vol. 99, 1884, p. 1153).

For temperature.—Reduction of the pressure under which the liquid boiled, as read on the gauge, to 0° (see 'Chem. Soc. Journ.,' vol. 47, 1885, p. 640).

The temperatures are those of an air-thermometer.

	Pressure of alcohol.	Temperature of alcohol.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.*	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
A′ (1)	133·7	40	0·20220	1·4505	0·68943	921, 920, 922, 922	921
(2)	172·2	45	0·20398	1·4632	0·68342	1085, 1085, 1086, 1086	1085·5
(3)	220·0	50	0·20611	1·4785	0·67636	1276, 1276, 1278, 1278	1277

* In this, and in all other cases, the vapour-pressures were determined at widely different volumes.

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·20576	1·4760	2,635
0·20472	1·4685	5,878
0·20401	1·4635	16,539
0·20365	1·4609	24,986
0·20296	1·4559	33,929

	Pressure of alcohol.	Temperature of alcohol.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.		Mean.
						L. P. G.*	H. P. G.*	
	mms.	° C.	c.cs.	c.cs.		mms.	mms.	mms.
(4)	278·6	55	0·20753	1·4887	0·67172	1490 1488 1491 1494	..	1491
(5)	350·3	60	0·20999	1·5063	0·66387	1732 1738 1732 1736	..	1734
(6)	437·0	65	0·21141	1·5165	0·65940	2002 2003 2004 2007	..	2004
(7)	541·2	70	0·21355	1·5319	0·65280	2299 2306 2305 2307	..	2304
(8)	665·55	75	0·21556	1·5463	0·64671	2637 2640 2639 2639	..	2639
	(Chlorobenzene.)							
(9)	144·8	80	0·21848	1·5673	0·63806	2976 2976 2978	..	2977
(10)	174·25	85	0·21984	1·5770	0·63412	3393 3388 3392 3385	..	3389
(11)	208·35	90	0·22378	1·6053	0·62293	3829 3835 3829 3832	..	3831
(12)	247·7	95	0·22590	1·6205	0·61709	4326	4322 4325 4327 4330	4326
(13)	292·75	100	0·22840	1·6384	0·61034	4849 4855 4871 4852	4855 4853 4860 4852	4857

* Low-pressure gauge and high-pressure gauge.

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·22770	1·6334	7,208
0·22700	1·6284	12,955
0·22595	1·6208	19,515
0·22420	1·6083	27,072
0·22246	1·5958	44,154

	Pressure of chlorobenzene.	Temperature of chloro-benzene.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.* L. P. G.	Vapour-pressure.* H. P. G.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.	mms.
(14)	344·15	105	0·23121	1·6586	0·60292	5441		5441
						5445	5443	
						5438	5440	
						5430	5439	
						5458	5439	
						5441	5437	
(15)	402·55	110	0·23456	1·6826	0·59431	6100		6082
						6078	6083	
						6088	6088	
						6063	6063	
						6086	6086	
(16)	468·5	115	0·23825	1·7091	0·58511	..	6773	6775
							6778	
							6772	
							6779	
(17)	542·8	120	0·24215	1·7370	0·57569	..	7496	7513
							7501	
							7520	
							7535	
(18)	626·15	125	0·24566	1·7623	0·56745	..	8274	8313
							8307	
							8327	
							8344	
(19)	718·95	130	0·24987	1·7925	0·55792	..	9156	9188
							9176	
							9216	
							9203	
A (20)	144·8	80	0·22022	1·5676	0·63790	2965	..	2971
						2976	..	
						2973	..	
	(Bromobenzene.)							
(21)	372·65	130	0·25213	1·7948	0·55715	..	9162	
							9135	9131
							9131	
							9134	
							9125	

* Under this heading are occasionally given the pressures under which the liquid was measured. It will be seen that in no case does this pressure differ so much from the vapour-pressure as to sensibly reduce the volume of the liquid.

	Pressure of bromobenzene.	Temperature of bromo-benzene.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.		Mean.
						L. P. G.	H. P. G.	
	mms.	° C.	c.cs.	c.cs.		mms.	mms.	mms.
(22)	430·75	135	0·25585	1·8213	0·54906	..	10,222	
							10,056	
							10,085	10,077
							10,086	
							10,081	
(23)	495·8	140	0·26077	1·8563	0·53870	..	11,087	
							11,048	
							11,058	11,051
							11,039	
							11,060	
(24)	568·35	145	0·26651	1·8971	0·52712	..	12,260	
							12,113	
							12,128	12,122
							12,115	
							12,133	
(25)	649·05	150	0·27133	1·9314	0·51774	..	13,348	
							13,260	
							13,228	13,241
							13,234	
							13,242	

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·26993	1·9215	13,818
0·26818	1·9091	18,258
0·26644	1·8967	20,228
0·26574	1·8917	22,705

The density of the saturated vapour was determined at this temperature.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme vapour.	Vapour-density.
0·37322	0·23042	0·11930	0·02118	0·05675			
0·51918	0·21594	0·11180	0·02868	0·05224	0·05541	18·047	56·22
0·75893	0·19121	0·09900	0·04148	0·05466			
0·91823	0·17377	0·08997	0·05051	0·05501			

	Pressure of aniline.	Temperature of aniline.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
(26)	283·7	150	0·27133	1·9315	0·51774	13,491	
						13,347	
						13,291	
						13,290	13,292
						13,259	
						13,272	
(27)	331·7	155	0·27766	1·9766	0·50593	14,818	
						14,515	
						14,532	14,514
						14,521	
						14,488	
(28)	386·0	160	0·28433	2·0240	0·49406	16,038	
						15,776	
						15,768	15,778
						15,769	
						15,799	
(29)	447·1	165	0·29170	2·0765	0·48158	17,335	
						17,265	
						17,209	17,201
						17,204	
						17,124	
(30)	515·6	170	0·30186	2·1488	0·46538	18,860	
						18,743	
						18,666	18,671
						18,668	
						18,597	
(31)	592·05	175	0·31443	2·2383	0·44677	20,238	
						20,178	
						20,181	20,199
						20,210	
						20,228	

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·31199	2·2209	21,802
0·30850	2·1961	22,556
0·30501	2·1712	23,767
0·30152	2·1464	25,496
0·29454	2·0967	30,420
0·29105	2·0719	32,780
0·28756	2·0470	36,362
0·28407	2·0222	40,177

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The density of the vapour was here determined.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme vapour.	Vapour-density.
						c.cs.	
0·31360	0·24414	0·10907	0·03141	0·10016			
0·58620	0·18492	0·08261	0·05787	0·09872	0·09899	10·103	68·23
0·86187	0·12462	0·05568	0·08480	0·09839			
1·04445	0·08340	0·03726	0·10322	0·09883			

	Pressure of aniline.	Temperature of aniline.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
(32)	677·15	180	0·32943	2·3451	0·42642	22,131	
						21,804	
						21,745	
						21,776	21,793
						21,821	
						21,807	
	(Methyl salicylate)						
(33)	249·35	180	0·32943	2·3451	0·42642	21,942	
						21,820	
						21,804	21,756
						21,645	
(34)	287·8	185	0·34936	2·4869	0·40211	23,746	
						23,691	
						23,688	23,691
						23,695	

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·33648	2·3952	25,243
0·33299	2·3704	26,091
0·32950	2·3456	26,838
0·32602	2·3208	27,746
0·32253	2·2959	28,720
0·31905	2·2712	29,924
0·31208	2·2216	32,640
0·30860	2·1968	34,348
0·30510	2·1719	36,355
0·30161	2·1470	38,842
0·29811	2·1221	41,820

Vapour-density Determinations.

Saturated.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme vapour.	Vapour-density.
						c.cs.	
0·31308	0·24482	0·09844	0·04204	0·13428			
0·62739	0·14396	0·05788	0·08260	0·13166	0·13290	7·5245	79·85
0·89820	0·05282	0·02124	0·11924	0·13276			

Unsaturated.

Volume of vapour.	Pressure.	Weight of 1 c.c. vapour.	Volume of 1 gramme vapour.	Vapour-density.
1·1106	23,408	0·12649	7·9059	76·91
1·1990	22,947	0·11716	8·5352	72·67

	Pressure of methyl salicylate.	Temperature of methyl salicylate.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
(35)	330·85	190	0·38325	2·7282	0·36654	25,645	
						25,514	
						25,518	25,530
						25,558	

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·37836	2·6934	25,781
0·37138	2·6437	26,034
0·36440	2·5940	26,448
0·35743	2·5444	27,173
0·34696	2·4699	28,535
0·32953	2·3458	32,351
0·31908	2·2714	35,522
0·31211	2·2218	38,705

Vapour-density Determinations.

Saturated.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme vapour.	Vapour-density.
0·24674	0·27581	0·10110	0·03938	0·15960			
0·44219	0·18704	0·06856	0·07192	0·16264	0·16136	6·1973	91·44
0·69501	0·07641	0·02801	0·11247	0·16183			

Unsaturated.

Volume of vapour.	Pressure.	Weight of 1 c.c. vapour.	Volume of 1 gramme vapour.	Vapour-density.
0·91519	25,331	0·15350	6·5148	87·19
0·98687	25,107	0·14235	7·0251	81·58
1·0578	24,705	0·13280	7·5302	77·35
1·1991	23,848	0·11715	8·5359	70·69

	Pressure of methyl salicylate.	Temperature of methyl salicylate.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
(36)	349·45	192	0·40637	2·8928	0·34566	26,482	
						26,304	
						26,324	26,327
						26,354	

Compressibilities of Liquid.

Volume.	Volume of 1 gramme.	Pressure.
c.cs.	c.cs.	mms.
0·40287	2·8678	26,482
0·39589	2·8181	26,515
0·38888	2·7683	26,786
0·38189	2·7185	27,066
0·37142	2·6440	27,580
0·36444	2·5943	28,236
0·35397	2·5198	29,441
0·34700	2·4701	30,400
0·33655	2·3957	32,518
0·32957	2·3461	34,227
0·31912	2·2716	38,474
0·31215	2·2220	41,819

Vapour-density Determinations.

Saturated.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme.	Vapour-density.
						c.cs.	
0·32029	0·23773	0·08218	0·05830	0·18203			
0·47047	0·15523	0·05366	0·08682	0·18314	0·18254	5·4782	100·20
0·69794	0·03801	0·01314	0·12734	0·18245			

Unsaturated.

Volume of vapour.	Pressure.	Weight of 1 c.c. vapour.	Volume of 1 gramme.	Vapour-density.
			c.cs.	
0·91529	25,842	0·15348	6·5155	85·83
1·05800	25,172	0·13278	7·5311	76·23
1·19930	24,219	0·11714	8·5369	69·89

	Pressure of methyl salicylate.	Temperature of methyl salicylate.	Volume of liquid.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.	Mean.
	mms.	° C.	c.cs.	c.cs.		mms.	mms.
(37)	359·05	193	0·42563	3·0298	0·33006	26,851	..
						26,787	26,792
						26,797	

Vapour-density Determinations.

Saturated.

Volume of vapour.	Volume of liquid.	Weight of liquid.	Weight of vapour.	Weight of 1 c.c. vapour.	Mean.	Volume of 1 gramme.	Vapour-density.
						c.cs.	
0·43540	0·15824	0·05223	0·08825	0·20269	0·20112	4·9722	108·72
0·51645	0·11285	0·03725	0·10323	0·19956			

(38.) APPARENT Critical Point. T = 193·8° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.*	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1886	8·4612	24,466	70·08	0·48711	3·4675	27,125	..
1·1320	8·0582	24,913	72·26	0·43616	3·1047	27,279	..
1·0580	7·5315	25,372	75·92	0·41475	2·9524	27,273	..
0·98082	6·9820	25,827	80·45	0·38714	2·7559	27,842	..
0·89363	6·3614	26,316	86·66	0·37841	2·6937	28,443	..
0·75374	5·3655	26,809	100·85	0·35711	2·5421	30,407	..
0·70044	4·9976	27,044	107·34	0·33235	2·3659	34,384	..
0·62930	4·4797	27,050	119·72	0·32103	2·2853	39,579	..
0·55802	3·9723	27,079	..				

(39.) T = 195° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1992	8·5373	24,461	69·08	0·48711	3·4675	27,708	..
1·0580	7·5315	25,662	75·25	0·45192	3·2170	27,816	..
0·95122	6·7713	26,386	81·41	0·41686	2·9674	28,112	..
0·84318	6·0022	26,947	89·92	0·38189	2·7185	29,097	..
0·73595	5·2389	27,342	101·54	0·36585	2·6042	30,372	..
0·69230	4·4797	27,569	117·77	0·34142	2·4304	34,346	..
0·55802	3·9723	27,605	..	0·32504	2·3138	39,535	..

(40.) T = 197° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1994	8·5379	25,116	68·12	0·48716	3·4679	28,538	..
1·0581	7·5322	26,264	73·84	0·45196	3·2173	28,724	..
0·95130	6·7719	27,027	79·81	0·41690	2·9677	29,289	..
0·84326	6·0027	27,732	87·75	0·39941	2·8432	29,679	..
0·73601	5·2393	28,059	99·36	0·38543	2·7311	30,363	..
0·62935	4·4800	28,459	114·57	0·34947	2·4877	34,327	..
0·63807	3·9727	28,495	..	0·33065	2·3538	39,510	..

* As it is uncertain whether the substance is a vapour, this term must be accepted with an extended meaning.

(41.) T = 200° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1995	8·5387	25,545	67·39	0·55811	3·9729	29,847	123·97
1·0582	7·5329	26,740	72·98	0·48720	3·4682	30,381	..
0·95137	6·7723	27,643	78·52	0·45199	3·2175	30,725	..
0·84332	6·0032	28,511	85·89	0·41693	2·9679	31,307	..
0·73607	5·2398	29,108	96·38	0·37254	2·6519	34,318	..
0·62941	4·4804	29,663	110·60	0·34008	2·4209	39,500	..

(42.) T = 205° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1996	8·5394	26,354	66·01	0·55817	3·9734	31,873	117·30
1·0583	7·5336	27,624	71·38	0·48725	3·4685	32,623	..
0·95148	6·7732	28,664	76·52	0·45204	3·2179	33,133	..
0·84341	6·0028	29,655	83·44	0·41698	2·9682	34,334	..
0·73616	5·2403	30,484	92·99	0·38200	2·7193	36,634	..
0·62948	4·4809	31,366	105·69	0·34710	2·4708	42,731	..

(43.) T = 210° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·1997	8·5400	27,161	64·71	0·55824	3·9738	34,022	108·50
1·0584	7·5343	28,579	69·71	0·48731	3·4689	35,230	..
0·95159	6·7739	29,784	74·40	0·45210	3·2183	36,242	..
0·84351	6·0045	30,833	81·08	0·41702	2·9686	37,696	..
0·73624	5·2409	32,000	89·50	0·38204	2·7196	40,743	..
0·62955	4·4815	33,182	100·94				

(44.) T = 223° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	Vapour-density.
c.cs.	c.cs.	mms.		c.cs.	c.cs.	mms.	
1·2002	8·5436	29,231	61·72	0·55846	3·9754	39,040	99·32
1·0588	7·5371	30,954	66·07	0·52302	3·7231	40,100	103·25
0·95196	6·7766	32,426	70·15	0·48749	3·4702	41,090	108·10
0·84304	6·0069	34,067	75·33	0·45226	3·2194	42,837	111·77
0·73653	5·2430	35,591	82·61	0·41719	2·9698	45,819	113·28
0·62980	4·4832	37,493	91·71				

B. *Weight.*—The weight of portion B was ascertained by comparisons of its volume with that of A at the same temperatures and pressures. As the real pressures were in no cases the same for both, it was necessary to construct curves showing the relation of the pressures of A to its volume at constant temperatures, and to read off the volumes at the required pressures. The mean of twelve observations at various temperatures and pressures gave the number

0·01227 gramme.

(45.) T = 50° (Alcohol).

Vapour-pressure.	Mean.
mms.	mms.
1273	
1275	1275
1277	
1275	

(46.) T = 75° (Alcohol).

Vapour-pressure.	Mean.
mms.	mms.
2638	2637·5
2637	

(47.) T = 100° (Chlorobenzene).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·1610	94·63	2978	3458	41·14	0·80529	65·63	4104	3305	43·04
1·0906	88·89	3150	3435	41·40	0·76967	62·73	4265	3283	43·33
1·0201	83·14	3334	3401	41·82	0·73419	59·84	4436	3257	43·67
0·94895	77·34	3546	3365	42·27	0·69876	56·95	4618	3227	44·08
0·87710	71·48	3818	3350	42·46	0·68101	55·50	4720	3214	44·25
0·80529	65·63	4099	3301	43·09	0·66325	54·06	4820	3197	44·49
0·73419	59·84	4432	3254	43·71			L.P.G. H.P.G.		
0·69876	56·95	4636	3239	43·91	. .	. .	4865 4857		
0·66325	54·06	4815	3194	44·54	. .	. .	4868 4861	Mean	
1·1964	97·51	2893	3461	41·09	. .	. .	4841 4848	4853	. .
1·0554	86·02	3243	3423	41·55	. .	. .	4851 4853		
0·91310	74·42	3668	3349	42·47	. .	. .	4852 4844		
0·84116	68·56	3946	3319	42·88	. .	. .	4855 4847		

(48.) T = 130° (Chlorobenzene).

Volume.	Volume of 1 gramme.	Pressure. H.P.G.	P. V.	Vapour-density.	Vapour-pressure. H.P.G.	Mean.
c.cs.	c.cs.	mms.			mms.	
0·34641	28·23	8975	3109	49·43	9114	9133
0·34293	27·95	9038	3099	49·58	9127	
0·33945	27·66	9097	3088	49·77	9136	
..	..	..	..	..	9136	
..	..	..	..	..	9136	
..	..	..	..	..	9151	

(49.) T = 150° (Aniline).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·1979	97·63	3375	4043	39·90	0·38146	31·09	9,066	3458	46·64
1·1272	91·87	3564	4017	40·15	0·34661	28·25	9,809	3400	47·44
1·0568	86·13	3783	3998	40·35	0·31180	25·41	10,581	3299	48·89
0·98590	80·35	4027	3970	40·63	0·29436	23·99	11,019	3244	49·73
0·91430	74·51	4304	3935	40·99	0·27692	22·57	11,500	3185	50·65
0·84223	68·64	4561	3917	41·18	0·25946	21·15	11,998	3113	51·82
0·77064	62·81	5034	3879	41·58	0·24199	19·72	12,570	3042	53·03
0·69965	57·02	5481	3835	42·06	0·22449	18·30	13,204	2964	54·42
0·62860	51·23	6024	3787	42·60	..	..	13,265		..
0·55739	45·43	6674	3720	43·36	..	..	13,289	Mean	..
0·48657	39·66	7484	3641	44·30	..	..	13,284	13,283	..
0·41640	33·94	8497	3538	45·59	..	..	13,294		..

(50.) T = 175° (Aniline).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·19860	97·69	3589	4302	39·71	0·38170	31·11	9,906	3781	45·18
1·12790	91·93	3803	4290	39·83	0·34683	28·27	10,715	3716	45·97
1·05740	86·18	4035	4267	40·04	0·31199	25·43	11,673	3642	46·91
0·98649	80·40	4307	4249	40·21	0·27709	22·58	12,730	3527	48·43
0·91483	74·56	4626	4232	40·37	0·24214	19·73	14,021	3395	50·32
0·84276	68·69	4987	4203	40·65	0·22463	18·31	14,713	3305	51·69
0·77111	62·85	5396	4161	41·06	0·20712	16·88	15,531	3217	53·11
0·70008	57·06	5903	4133	41·34	0·18958	15·45	16,379	3105	55·02
0·62900	51·26	6485	4079	41·88	0·17204	14·02	17,304	2977	57·38
0·55774	45·46	7208	4020	42·49	0·15447	12·59	18,388	2840	60·14
0·48687	39·68	8065	3927	43·51	0·13690	11·16	19,354	2650	64·47
0·41665	33·96	9248	3853	44·34					

Vapour-pressure = 20,150.

(51.) T = 185° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·1990	97·72	3,692	4427	39·45	0·31208	25·43	12,106	3778	46·23
1·1283	91·95	3,915	4417	39·54	0·24221	19·74	14,641	3546	49·25
1·0577	86·21	4,159	4399	39·70	0·20718	16·89	16,290	3375	51·75
0·91510	74·58	4,755	4351	40·14	0·17209	14·03	18,324	3153	55·38
0·73580	59·97	5,811	4276	40·85	0·13694	11·16	20,667	2830	61·71
0·55790	45·47	7,434	4147	42·11	0·11934	9·726	21,893	2613	66·85
0·38181	31·12	10,284	3927	44·48	0·10174	8·292	22,984	2338	94·69

Vapour-pressure $= \left.\begin{matrix}23{,}522\\23{,}518\end{matrix}\right\}$ 23,520

(52.) T = 190° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·0578	86·21	4,210	4453	39·64	0·20720	16·89	16,650	3450	51·18
0·91520	74·59	4,828	4419	39·96	0·17211	14·03	18,772	3231	54·65
0·73590	59·97	5,902	4343	40·65	0·13696	11·16	21,288	2916	60·56
0·55790	45·47	7,549	4212	41·92	0·11935	9·727	22,663	2705	65·27
0·38185	31·12	10,455	3992	44·23	0·10174	8·292	24,033	2445	72·20
0·31211	25·44	12,335	3850	45·86	0·08411	6·855	25,126	2113	83·54
0·24223	19·74	14,930	3616	48·82					

Vapour-pressure = 25,462.

(53.) T = 192° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·0580	86·42	4,230	4475	39·62	0·20723	16·89	16,774	3476	51·01
0·91530	74·60	4,847	4436	39·97	0·17213	14·03	18,909	3255	54·48
0·73600	59·98	5,930	4364	40·63	0·13697	11·16	21,448	2938	60·36
0·55800	45·48	7,590	4235	41·86	0·11937	9·729	22,848	2727	65·02
0·38189	31·12	10,544	4027	44·03	0·10176	8·293	24,319	2475	71·65
0·31215	25·44	12,428	3879	45·71	0·08412	6·856	25,641	2157	82·21
0·24226	19·74	15,032	3642	48·69					

Vapour-pressure = 26,342.

(54.) T = 193° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·0580	86·42	4,244	4490	39·58	0·17213	14·03	19,035	3276	54·24
0·91530	74·60	4,859	4447	39·96	0·13697	11·16	21,660	2967	59·89
0·73600	59·98	5,941	4372	40·64	0·11937	9·729	23,091	2756	64·47
0·55800	45·48	7,618	4251	41·80	0·10176	8·293	24,498	2493	71·28
0·38189	31·12	10,577	4239	43·99	0·08412	6·856	25,878	2177	81·63
0·31215	25·44	12,462	3890	45·68	0·06648	5·418	26,659	1772	100·26
0·24226	19·74	15,115	3662	48·53	0·06294	5·130	26,764	1685	105·48
0·20723	16·89	16,883	3499	50·79					

Vapour-pressure = 26,816.

(55.) Apparent Critical Point. T = 193·8° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·0580	86·42	4,252	4498	39·57	0·17213	14·03	19,100	3288	54·14
0·91530	74·60	4,867	4455	39·96	0·13697	11·16	21,731	2977	59·80
0·73600	59·98	5,951	4380	40·64	0·11937	9·729	23,211	2771	64·25
0·55800	45·48	7,627	4256	41·82	0·10176	8·293	24,682	2512	70·87
0·38189	31·12	10,587	4043	44·03	0·08412	6·856	25,980	2185	81·45
0·31215	25·44	12,499	3902	45·62	0·06648	5·418	26,984	1794	99·22
0·24226	19·74	15,152	3671	48·49	0·05941	4·842	27,039	1607	110·80
0·20723	16·89	16,944	3511	50·69	0·05235	4·267	27,091	1418	125·51

(56.) T = 195° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·1993	97·74	3,797	4554	39·19	0·20723	16·89	17,105	3545	50·35
1·1258	91·97	4,007	4522	39 47	0·17213	14·03	19,213	3307	53·96
1·0580	86·42	4,260	4507	39·60	0·13697	11·16	21,906	3001	59·48
0·9153	74·60	4,884	4470	39·92	0·11937	9·729	23,335	2785	64·07
0·7360	59·98	5,969	4393	40·62	0·10176	8·293	24,956	2539	70·28
0·5580	45·48	7,651	4269	41·80	0·08412	6·856	26,400	2221	80·36
0·38189	31·12	10,631	4060	43·96	0·06648	5·418	27,435	1824	97·85
0·31215	25·54	12,560	3921	45·52	0·05235	4·267	27,601	1445	123·51
0·24226	19·74	15,241	3692	48·33					

(57.) T = 223·25° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·2001	97·81	4,044	4853	38·99	0·24244	19·76	16,784	4069	46·50
1·1293	92·04	4,289	4844	39·07	0·20738	16·90	18,918	3923	48·26
1·0587	86·29	4,556	4824	39·23	0·17225	14·04	21,669	3733	50·70
0·98771	80·50	4,870	4810	39·34	0·13707	11·17	24,991	3426	55·24
0·91597	74·65	5,232	4792	39·49	0·11945	9·736	27,111	3239	58·43
0·73650	60·02	6,412	4722	40·07	0·10183	8·299	29,680	3022	62·61
0·55843	45·51	8,260	4613	41·02	0·08418	6·861	32,289	2718	69·62
0·38217	31·15	11,567	4421	42·81	0·06653	5·422	35,623	2370	79·84
0·31238	25·46	13,698	4279	44·22					

C. The weight of C was deduced by comparison of the volumes with those of B at the same temperatures and pressures. The mean value was found to be

0·0035982 gramme.

(58.) T = 50° (Alcohol).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·0887	302·6	855	930·8	38·80	0·73288	203·7	1240	909·5	39·75
1·0183	283·0	909	925·6	39·02	0·71519	198·7	1263	904·0	39·99
0·98965	263·3	974	922·6	39·15	0·70458	195·8	1272	896·9	40·30
0·87533	243·3	1051	921·1	39·25	0·69751	193·8	1273	888·6	40·68
0·80384	223·4	1139	916·4	39·45					

(59.) T = 195° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·1285	313·6	1224	1381	37·89	0·27723	77·05	4,718	1308	40·01
1·0580	294·0	1301	1376	38·02	0·24226	67·33	5,356	1298	40 33
0·98700	274·3	1391	1373	38·12	0·20723	57·59	6,166	1278	40·96
0·91530	254·4	1503	1376	38·04	0·17213	47·84	7,312	1269	41·58
0·73595	204·5	1858	1367	38·27	0·13697	38·07	8,972	1229	42·59
0·55800	155·1	2431	1357	38·58	0·11937	33·17	10,108	1207	43·38
0·38189	106·13	3480	1329	39·38	0·10176	28·28	11,584	1179	44·40
0·34700	96·44	3820	1319	39·68	0·08412	23·38	13,450	1131	46·26
0·31215	86·75	4219	1317	39·74	0·06648	18·48	16,096	1070	48·91

(60.) T = 222·85° (Methyl salicylate).

Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.	Volume.	Volume of 1 gramme.	Pressure.	P. V.	Vapour-density.
c.cs.	c.cs.	mms.			c.cs.	c.cs.	mms.		
1·2001	333·5	1231	1477·3	37·53	1·0905	303·1	1354	1476·6	37·55
1·1627	323·7	1268	1476·9	37·55	1·0587	294·2	1393	1474·8	37·60
1·1293	313·8	1307	1476·0	37·57					

Reduction and Arrangement of Results.

I. *Vapour-pressures.*—The vapour-pressures experimentally observed and calculated are given in the annexed Table, as well as those calculated by REGNAULT from his observations.

Temperature.	Vapour-pressures.			Temperature.	Vapour-pressures.		
	Observed.	Calculated.	REGNAULT.		Observed.	Calculated.	REGNAULT.
−20°	. .	62·99	68·90	95°	4326	4326·69	4401·81
−15	86·00	85·22	89·31	100	4855	4859·01	4953·30
−10	112·3	111·81	114·72	105	5441	5439·35	5556·23
− 5	144·8	144·69	146·08	110	6082	6070·38	6214·63
0	184·9	184·9	184·39	115	6775	6754·93	6933·26
5	233·0	233·52	230·89	120	7513	7495·73	7719·20
10	290·8	291·78	286·83	125	8313	8295·62	
15	360·0	360·93	353·62	130	9155	9157·42	
20	439·8	442·36	432·78	135	10077	10084·0	
25	534·8	537·51	525·93	140	11051	11078·2	
30*	. .	647·93	634·80	145	12122	12142·9	
35†	771·8	775·25	761·20	150	13262	13281·0	
40	921·0	921·18	907·04	155	14514	14495·1	
45	1085·5	1087·53	1074·15	160	15778	15788·1	
50	1276	1276·11	1264·83	165	17201	17162·9	
55	1491	1488·97	1481·06	170	18671	18622·2	
60	1734	1728·13	1725·01	175	20189	20168·4	
65	2004	1995·71	1998·87	180	21775	21804·3	
70	2304	2293·91	2304·90	185	23623	23532·4	
75	2638	2625·04	2645·41	190	25513	25355·1	
80	2974	2991·40	3022·79	192	26331	26111·2	
85	3389	3395·46	3439·53	193	26800	26495·0	
90	3831	3839·71	3898·26				

* The results given up to 30°, as observed, were read from the curve mentioned on p. 62.

† This result was calculated from the boiling-point under atmospheric pressure. The remainder are the means of actual observations.

The formula which REGNAULT employed in his extensive research on vapour-pressures was suggested by BIOT. It is

$$\log p = a + b\alpha^t + c\beta^t.$$

The concordance between the found and calculated pressures through a range of temperatures so great as from $-20°$ to $180°$ shows how well this formula interprets the facts. The constants employed were calculated from the observations at 0°, 45°, 90°, 135°, and 180°. The numbers directly read were, however, not taken; but small portions of the curve about these points were previously smoothed by means of the simpler formula

$$\log p = a + b\alpha^t.$$

The constants for the larger formula are

$$a = 5 \cdot 9834771, \qquad \log \alpha = \bar{1} \cdot 99827459,$$
$$\log b = 0 \cdot 5240258, \qquad \log \beta = \bar{1} \cdot 99130336\,;$$
$$\log c = \bar{1} \cdot 5733238,$$

b and c are both negative.

The greatest difference, calculated as temperature between the found and calculated results between $-15°$ and 180°, is 0·2°; but above 180° the difference increases gradually, amounting to 0·8° at 193°; but, indeed, it is doubtful whether any formula can be expected to hold in the immediate neighbourhood of the critical point.

The vapour-pressures of ether were measured between $-20°$ and 120° by REGNAULT; though his results agree with ours at certain temperatures, yet there is, on the whole, considerable discrepancy; and, in our opinion, he himself furnishes the explanation. In only one case was the specimen of ether used by him purified from alcohol by repeated shaking with water; and this specimen appears to have been used only in determining the specific heat of the vapour. He points out that after standing much lower vapour-pressures were obtained than with freshly distilled ether; for instance, at 0° his calculated number is 184·39 mms. In the first series, in which the ether had been distilled from calcium chloride, the pressure at $-0·08°$ was 181·7 mms., corresponding to 182·5 mms. at 0°. In the third series the same ether had stood for a year, and was redistilled over lime before experiment. The vapour-pressure at 0° was 181·65 mms. The same quantity of ether was again allowed to stand in sealed flasks, and on redetermining the vapour-pressure after six months it had fallen to 174·9 mms., and after three months more to 171·93 mms. REGNAULT states that the chemical composition was unaltered, and that the alteration was of a physical nature; but LIEBEN ('Deutsch. Chem. Gesell. Ber.', *Jahrg.* 4, p. 758) states that pure ether, either alone, or in contact with potash, lime, or sodium, does not change on standing; but that the presence of water, fused sodium chloride, calcium chloride, or anhydrous copper sulphate induces a change, the liquid exhibiting the iodoform reaction. We have little doubt, therefore, that the specimen of ether used by REGNAULT contained alcohol; and it is known from Professor GUTHRIE's researches that the presence of a minute amount of an impurity has a great influence on vapour-pressures. A further argument in support of this view will be given when we consider the heats of vaporisation. It should here be pointed out, moreover, that REGNAULT's observations below 0° agree nearly as well with our formula as with his own, whereas our observations are in very close accordance with our calculated results.

II. *Compressibilities.*—The isothermals of the liquid state, showing decrease in volume with increase of pressure, were, for the purpose of smoothing, plotted on a sheet of curve-paper, and isobars were drawn representing the relations of volume to temperature. The discrepancies of individual observations were thus eliminated, and from the isobars the numbers were retransferred to the isotherms. It will be seen on inspection of the curves (Plate 6) that the smoothed curves agree well with the observations. The Table which follows shows these results, and includes some of the isotherms corresponding to the gaseous state. The volumes are those of 1 gramme.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Pressure.	Temperature.															
mms.	50°	100°	130°	150°	175°	185°	190°	192°	193°	193·8°	195°	197°	200°	205°	210°	223°
1,000	256·4															
2,000	1·4770	..	..	..	..	..	..	..	..	..	189·6	..	..	..	..	203·4
4,000	1·4705	67·58	75·72	81·05	87·35	89·86	..	..	..	..	92·17	..	..	..	..	99·45
6,000	1·4690	1·636	47·55	51·49	56·12	57·93	59·07	..	..	..	59·86	..	..	..	..	64·55
8,000	1·4675	1·632	33·06	36·52	40·47	41·91	42·72	..	..	..	43·39	..	..	..	..	47·23
10,000	1·4660	1·6305	..	27·42	30·94	32·31	32·93	..	..	33·35	33·51	..	..	..	..	36·75
12,000	1·4645	1·629	..	21·17	24·53	25·76	26·33	26·50	..	26·72	26·90	..	..	..	..	29·84
14,000	1·4635	1·627	..	1·9265	19·87	20·96	21·57	21·73	21·82	21·93	22·08	..	..	..	..	24·77
16,000	1·4625	1·6235	..	1·912	16·21	17·39	17·93	18·08	18·21	18·30	18·40	..	..	..	19·88	21·01
18,000	1·4615	1·621	..	1·9045	13·11	14·47	15·03	15·21	15·33	15·38	15·54	15·76	16·01	16·51	16·95	18·05
20,000	1·4610	1·620	..	1·8995	10·32	11·94	12·58	12·70	12·93	13·01	13·15	13·38	13·62	14·13	14·57	15·68
22,000	1·4605	1·618	..	1·893	2·202	9·59	10·40	10·68	10·79	10·90	11·04	11·26	11·62	12·11	12·58	13·69
24,000	1·4600	1·616	..	..	2·169	2·459	8·327	8·664	8·854	8·962	9·175	9·443	9·808	10·35	10·85	11·96
26,000	1·4600	1·613	..	..	2·140	2·371	2·652	6·252	6·647	6·889	7·223	7·638	8·135	8·804	9·327	10·49
28,000	1·4595	1·6105	..	..	2·119	2·317	2·498	2·611	..	2·750	3·020	5·350	6·367	7·283	7·954	9·198
30,000	1·4595	1·6095	..	..	2·099	2·270	2·411	2·490	..	2·570	2·632	2·790	3·830	5·698	6·627	8·060
32,000	1·4590	1·608	..	..	2·080	2·233	2·350	2·410	..	2·469	2·512	2·604	2·848	3·860	5·241	7·000
34,000	1·4580	1·605	..	..	2·062	2·201	2·300	2·350	..	2·400	2·440	2·509	2·659	3·040	4·073	5·990
36,000	1·4575	1·602	..	..	2·049	2·179	2·264	2·308	..	2·349	2·381	2·440	2·549	2·769	3·295	5·070
38,000	1·4570	1·600	..	..	2·036	2·157	2·237	2·276	..	2·310	2·340	2·390	2·470	2·639	2·929	4·300
40,000	1·4565	1·599	..	..	2·024	2·139	2·211	2·248	..	2·279	2·302	2·343	2·409	2·550	2·760	2·720

Above the critical point, 193·8°, the compressibility of the substance has been given, where its condition may be assumed to approximate to that of a liquid.

Isothermals at even pressures for 50° *and* 100°.—As the limits of pressure are so small, it has been thought advisable to give these isothermals separately, in order to save room.

Temperature.	Pressure.	Volume of 1 gramme.	Temperature.	Pressure.	Volume of 1 gramme.	Temperature.	Pressure.	Volume of 1 gramme.
°	mms.	c.cs.	°	mms.	c.cs.	°	mms.	c.cs.
50	900	286·3	100	2800	101·1	100	4000	67·58
	1000	256·4		3000	93·67		4200	63·83
	1100	231·7		3200	87·18		4400	60·41
	1200	211·0		3400	81·45		4600	57·26
	1276	196·9		3600	76·32		4800	54·32
				3800	71·74		4859	53·50

III. From these results the curve, which we propose to call the orthobaric curve, was constructed. It represents the relations between the volumes of a gramme of liquid and temperatures, at pressures equal to the vapour-pressures. These were obtained by direct reading, sometimes, however, at pressures slightly higher than the vapour-pressures; and also from the points of intersection of the curves representing compressibility, with the horizontal lines, indicating vapour-pressure. The numbers read from the smoothed curve, representing the latter, and also the corresponding specific gravities, are given in the following Table :—

Temperature.	Volume.	Specific gravity.	Temperature.	Volume.	Specific gravity.	Temperature.	Volume.	Specific gravity.
°			°			°		
0	1·3583	0·7362	95	1·617	0·6184	155	1·976	0·5061
40	1·4505	0·6894	100	1·638	0·6105	160	2·021	0·4947
45	1·4650	0·6826	105	1·660	0·6024	165	2·027	0·4817
50	1·4785	0·6764	110	1·684	0·5942	170	2·147	0·4658
55	1·4900	0·6711	115	1·708	0·5855	175	2·238	0·4468
60	1·5020	0·6658	120	1·735	0·5764	180	2·343	0·4268
65	1·5175	0·6590	125	1·763	0·5672	185	2·489	0.4018
70	1·531	0·6532	130	1·792	0·5580	190	2·730	0·3663
75	1·550	0·6452	135	1·823	0·5485	192	2·900	0·3448
80	1·562	0·6402	140	1·857	0·5385	193	3·030	0·3300
85	1·580	0·6329	145	1·893	0·5283			
90	1·600	0·6250	150	1·931	0·5179			

Orthobaric Volumes of 1 gramme of Vapour.—The following Table gives the volumes of 1 gramme of the saturated vapour at even temperatures, with the corresponding specific gravities and vapour-densities.

Temperature.	Volume of 1 gramme.	Specific gravity.	Vapour-density.	Temperature.	Volume of 1 gramme.	Specific gravity.	Vapour-density.
°	c.cs.			°	c.cs.		
0	1209·1	0·000827	37·95	105	47·62	0·02100	45·35
5	973·6	0·001027	38·00	110	42·57	0·02349	46·05
10	791·1	0·001264	38·10	115	38·02	0·02630	46·95
15	646·6	0·001547	38·35	120	34·09	0·02934	47·8
20	534·7	0·001870	38·5	125	31·30	0·03195	48·75
25	436·2	0·002293	38·6	130	27·49	0·03638	49·75
30	373·6	0·002677	38·9	135	24·73	0·04044	50·85
35	316·2	0·003163	39·05	140	22·28	0·04488	52·0
40	268·0	0·003731	39·4	145	20·03	0·04992	53·4
45	229·5	0·004358	39·6	150	18·01	0·05551	54·95
50	196·9	0·005079	39·95	155	16·18	0·06179	56·7
55	170·3	0·005886	40·2	160	14·47	0·06911	58·9
60	147·7	0·006771	40·5	165	12·90	0·07754	61·5
65	128·4	0·007790	41·0	170	11·45	0·08731	64·55
70	112·1	0·008920	41·45	175	10·12	0·09879	68·2
75	98·33	0·01017	41·9	180	8·815	0·1135	73·25
80	86·60	0·01155	42·35	185	7·579	0·1320	79·75
85	76·56	0·01306	42·8	190	6·172	0·1620	91·45
90	67·70	0·01477	43·4	192	5·476	0·1826	100·2
95	60·14	0·01663	43·95	193	4·970	0·2012	108·7
100	53·55	0·01867	44·55				

The curves showing the relations given in the preceding Tables between specific gravity and temperature of liquid and vapour are represented in Plate 10, and the volumes of 1 gramme of liquid and vapour are shown in Plate 9, but mapped against pressure.

Densities of Unsaturated Vapour at even Pressures.—(H = 1.)

Pressures.	Temperatures.															
	50°	100°	130°	150°	175°	185°	190°	192°	193°	193°·8	195°	197°	200°	205°	210°	223°
900	38·96	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
1,000	39·15	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
1,100	39·39	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
1,200	39·65	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
2,000	..	..	..	..	..	..	..	..	..	..	38·35	..	..	..	..	37·9
2,800	..	40·95	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3,000	..	41·25	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3,200	..	41·55	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3,400	..	41·86	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3,600	..	42·19	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3,800	..	42·52	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4,000	..	42·88	41·35	40·55	39·85	39·6	..	..	..	..	39·45	..	..	..	..	38·75
4,200	..	43·24	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4,400	..	43·61	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4,600	..	44·01	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4,800	..	44·46	..	..	..	..	..	..	..	..	..	..	..	..	..	..
6,000	..	..	43·9	42·55	41·35	40·95	40·6	..	..	..	40·50	..	..	..	..	39·8
8,000	..	..	47·35	45·00	43·0	42·45	42·1	..	..	..	41·9	..	..	..	..	40·8
10,000	..	..	..	47·95	45·0	44·05	43·7	..	..	43·5	43·4	..	..	..	..	41·95
12,000	..	..	..	51·75	47·3	46·05	45·55	45·45	..	45·25	45·05	..	..	..	..	43·05
14,000	..	..	..	..	50·05	48·5	47·65	47·5	47·4	47·25	47·05	..	..	..	..	44·45
16,000	..	..	..	..	53·7	51·15	50·15	49·95	49·7	49·55	49·4	..	..	..	47·2	45·85
18,000	..	..	..	..	59·0	54·65	53·2	52·8	52·5	52·40	52·0	51·5	51·0	50·0	49·2	47·45
20,000	..	..	..	..	67·45	59·6	57·2	56·9	56·0	55·75	55·3	54·6	53·95	52·55	51·5	49·15
22,000	..	..	..	..	..	67·1	62·9	61·5	61·0	60·50	59·9	58·95	57·5	55·75	54·25	51·2
24,000	..	..	..	..	..	..	72·0	69·5	68·15	67·45	66·05	64·45	62·45	59·8	57·6	53·6
26,000	..	..	..	..	..	..	..	88·9	83·8	81·00	77·45	73·55	69·5	64·9	61·9	56·5
28,000	..	..	..	..	..	..	..	..	..	..	..	97·5	82·45	72·85	67·4	59·85
30,000	..	..	..	..	..	..	..	..	..	..	..	..	..	86·9	75·5	63·9
32,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	89·5	68·65
34,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	108·4	74·55
36,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	82·5
38,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	94·4
40,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	104·2
42,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	110·5

These results are graphically shown on Plate 7. The curves were smoothed by constructing others showing the relations between temperature and pressure at equal vapour-densities, and then transferring back to the original sheet of curve paper. It can be judged by the position of the circles how nearly the observations agree with the smoothed curves.

IV. *Heats of Vaporisation.*—From the thermodynamic equation

$$\frac{L}{s_1 - s_2} = \frac{dp}{dt}\frac{t}{J},$$

the heats of vaporisation at definite intervals of temperature were calculated. The values of the expression dp/dt were calculated in the following manner. By means of the formula $\log p = a + b\alpha^t + c\beta^t$, the vapour-pressures at one-tenth of a degree above and below the definite temperature were calculated, and the difference was multiplied by 5 to obtain the values for 1°. This method gives results probably as nearly correct as it is possible to obtain. The pressures were reduced to grammes per square centimetre, and the value of J was taken as 42,500.

Temperature.		$\frac{dp}{dt}$	$\frac{dp}{dt}$	$\frac{dp}{dt}\frac{t}{J}$	$s_1 - s_2$	L
C.	Abs.	in mms.	in grammes.			
0°	273°	8·843	12·023	0·07723	1207·7	93·27
10	283	12·695	17·26	0·11493	789·8	90·77
20	293	17·585	23·91	0·16483	533·3	87·90
30	303	23·720	32·25	0·22992	372·2	85·60
40	313	31·160	42·37	0·31200	266·6	83·18
50	323	40·095	54·51	0·41430	195·4	80·95
60	333	50·620	68·82	0·53924	146·2	78·84
70	343	62·840	85·44	0·68932	110·58	76·42
80	353	77·005	104·70	0·86958	85·04	73·95
90	363	93·010	123·46	1·0801	66·10	71·39
100	373	110·48	150·21	1·3183	51·85	68·35
110	383	131·48	178·76	1·6113	40·95	65·98
120	393	153·95	209·3	1·9355	32·36	62·63
130	403	178·61	242·8	2·3027	25·67	59·11
140	413	205·8	279·8	2·7191	20·42	55·52
150	423	234·9	319·4	3·1786	16·10	51·18
160	433	266·65	362·5	3·6936	12·45	45·99
170	443	300·4	408·4	4·2572	9·324	39·69
180	453	336·4	457·4	4·8751	6·478	31·58
185	458	363·0	493·5	5·3186	5·035	26·78
190	463	407·0	553·4	6·0282	3·467	20·90
192	465	446·0	606·4	6·6344	2·578	17·10
193	466	472·0	641·7	7·0364	1·942	13·67

The heats of vaporisation have been determined by other observers; BRIX ('LIEBIG'S Annalen,' vol. 44, 1842, p. 169) gives determinations of the heats of vaporisation of water, alcohol, and ether. Translating Réaumur into Centigrade degrees, that of water becomes 539·6 calories; of alcohol, 214·25 calories; and of ether, 89·96 calories. Determinations were next made by ANDREWS ('Chem. Soc. Journ.,' vol. 1, 1849, p. 27), who found 90·5 calories. The sample of ether he employed boiled at 34·9° at 752 mms. pressure. FAVRE and SILBERMANN found 91·11 calories ('Annales de Chimie,' vol. 37, 1853, p. 465). REGNAULT ('Mémoires de l'Académie,' vol. 26, p. 881) gives a formula for calculating the total heat of vaporisation from 0°; it is

$$\lambda = a + bt + ct^2,$$

where $a = 94$, $b = 0{\cdot}45$, and $c = -0{\cdot}00055556$.

From this formula the heat of vaporisation at 0° = 94 calories, but for higher temperatures the specific heat of ether is required, for calculating which he gives the formula

$$Q = at + bt^2,$$

where Q is the total quantity of heat required to raise 1 grm. of ether from 0° to t; $\log a = \bar{1}{\cdot}7234538$; and $\log b = \bar{4}{\cdot}4711026$. Four experiments were made, of which the results of only three were employed in calculating the constants, although the fourth experiment was moderately concordant with the others; the range was only from −30° to +32°. Taking into consideration the small number of experiments, and the not very close agreement between the result of the second experiment and the value calculated from the formula (calculated, Q = 15·821; observed, Q = 15·930), it is doubtful whether these constants would hold good for temperatures much higher than 35°. REGNAULT made two series of experiments, of which there were seven observations in the first and four in the second, on the heats of vaporisation of ether. The ether employed in the first series was purified by the ordinary methods, and distilled from time to time with lime to remove acids and water. In the second series, including experiments at very low pressures, the ether was purified "with the greatest care," and kept in a stoppered flask. Nevertheless, on distillation, a quantity of less volatile liquid remained behind, having, as he states, the percentage composition of ether. This modification, according to him, is absent from ether recently distilled, but forms after some months (see remarks on p. 82). In the second series the weight of the residual liquid in the calorimeter was always subtracted from the total weight, the liquid having been distilled from the calorimeter. The following Table gives the individual results of REGNAULT'S experiments, and also the total heats at the same temperatures, calculated by means of his formula. The first four experiments were made with the carefully purified ether.

Temperature.	Total heat.		Temperature.	Total heat.	
	Observed.	Calculated.		Observed.	Calculated.
− 3°·7	92·235	92·343	34°·83	109·117	109·0
+ 7·51	95·370	97·35	90·05	128·900	..
12·9	97·282	99·72	93·85	130·880	..
15·5	98·801	100·84	108·80	138·196	136·38
17·15	101·278	101·56	120·90	140·781	..
21·95	104·366	..			

From some of these the heats of vaporisation were calculated by help of the formula given for calculating specific heats.

HEATS of Vaporisation.

Temperature.	Observed.	Calculated.	R. and Y.	Temperature.	Observed.	Calculated.	R. and Y.
− 3·7°	94·188	94·296	94·4	17·15°	92·12	92·40	88·8
+ 7·51	91·38	93·36	91·3	34·83	90·333	90·21	84·5
12·9	90·41	92·85	89·9	120·9	72·49	..	62·5
15·5	90·53	92·57	89·25				

It is noticeable that the agreement between REGNAULT'S observed and calculated numbers is much less good at low than at high temperatures, with the exception of the first at −3·7°; and, as the four first determinations were made with the purest sample, more stress has been laid by REGNAULT on his observations with the less pure than with the purer ether.

The heats of vaporisation thus calculated are widely different from the results obtained by us, with the single exception of that at the lowest temperature; but it is also remarkable that the individual experiments with the purer substance exhibit much closer concordance with our results.

As the results about the temperature 35° by all observers exhibit fairly close agreement with the observations of REGNAULT, but differ widely from our calculated values, it appeared desirable to submit them to proof by translating REGNAULT'S results into vapour-densities; and for this purpose the values of dp/dt were calculated by means of BIOT'S formula, using REGNAULT'S constants. By thus doing, the work is entirely REGNAULT'S. The results are given in the following Table:—

Temperature.	$\frac{dp}{dt}$	$\frac{dp}{dt}$	$\frac{dp}{dt}\frac{t}{J}$	L	s_1-s_2	s_1	Vapour-density.
°	mms.	grammes.					
0	8·44	11·47	0·07388	94·0	1272·4	1273·8	36·12
10	12·22	16·615	0·11063	93·12	841·7	843·1	36·37
20	17·175	23·35	0·16099	92·08	572·0	573·4	36·69
30	23·47	31·91	0·22749	90·86	399·4	400·8	37·01
35	27·155	36·92	0·26756	90·18	377·05	338·5	37·15

As the minimum value of the vapour-density of ether is 37, the first three results are impossible; and, on consulting the Table on p. 64, giving the results of our measurements at 12·9°, and Table 58, p. 80, it will be seen that the density of the saturated vapour rises to 38·25 at 12·9°, and 39·95 at 50°. At 35° the vapour-density read from the curve is 39·05.

Our results also receive confirmation from a number of experiments by HORSTMANN ('LIEBIG's Annalen,' Suppl. 6, 1868, p. 63), which, although not very concordant with each other, yet amply suffice to prove that the vapour-density is not constant, and that, therefore, *p.v.* is variable.

It follows from the Table already given that, if REGNAULT's results are correct, the thermo-dynamical formula does not always hold; the same discordance was noticed in his observations with alcohol.

It is possible, assuming the impurity in REGNAULT's ether to have been alcohol, which is not unlikely, inasmuch as no mention is made of the sample of ether having been purified by washing with water, to calculate the percentage which must have been present in order to raise the heat of vaporisation from 84·5, calculated by us, to 90·2, calculated from REGNAULT's formulæ; it is 4·4 per cent., and an analysis of such a mixture would give 64·3 per cent. of carbon, instead of 64·86 per cent. contained in pure ether. This does not, however, account for the composition of the high-boiling residue, which, if alcohol, should have contained 52·17 per cent. of carbon.

From these experiments it is noticeable that with ether, although the density of the saturated vapour is very abnormal, even more so than with alcohol, yet there is no tendency towards a rise with decrease of temperature. It therefore seems probable that, for the same reasons which were stated in the memoir on alcohol, combination of gaseous molecules to form complex molecules does not take place.

It is impossible to state accurately the temperature, pressure, and volume of any substance at the critical point; but the following numbers may be regarded as closely approximate for ether:—

Temperature . . .	194°.
Pressure	27,060 mms. = 35·61 atmospheres.
Volume	probably 4·06 cub. centims. for 1 gramme.

APPENDIX.

Received February 2, 1887.

Since the foregoing memoir was read, it appeared to us of importance, in consequence of some theoretical deductions, a short account of which has been communicated to the Society by Professor STOKES, to make fresh determinations of the relations between volume, temperature, and pressure of ether at higher temperatures and greater pressures than we had formerly employed.

For these experiments a fresh stock of ether was prepared; the volume tube was new; and the air-gauges were refilled. The weight was not determined directly, but was ascertained by comparison with our previous results at 175°, 185°, and 195°. It was 0·055406 gramme.

The temperature 175° was maintained by jacketing the experimental tube with aniline; methyl salicylate was used for the temperatures 185°, 195°, and 220°; and bromonaphthalene for 250° and 280°. It should be mentioned that fresh samples of aniline and methyl salicylate, carefully fractionated from impurities, were employed.

TEMPERATURE, 175°.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·608	12,729	17·199	15,392	13·154	17,994
21·254	13,304	16·524	15,822	11·821	18,943
19·901	13,960	15·847	16,207	10·493	19,930
18·552	14,673	14·496	17,163		

Vapour-pressure. P = 20,180; 20,271; 20,284; 20,277; 20,321. Mean, 20,271.

TEMPERATURE, 185°.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·615	13,248	13·158	18,988	8·530	22,956
19·907	14,549	11·825	20,115	7·880	23,451
17·204	16,061	10·496	21,346		
14·500	17,948	9·181	22,437		

Vapour-pressure. P = 23,750; 23,760; 23,774; 23,770. Mean, 23,763.

The mean of previous determinations of vapour-pressure at 175° is 20,189; and at 185° 23,623. Considering that the samples of ether, aniline, and methyl salicylate were different, and that the gauges were refilled, the agreement is satisfactory.

TEMPERATURE, 195°.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·620	13,723	10·498	22,503	5·308	27,373
19·911	15,102	9·183	23,904	4·665	27,599
17·207	16,752	7·881	25,325	4·025	27,704
14·503	18,793	7·237	25,988	3·386	27,735
13·161	19,931	6·593	26,529	2·748	28,846
11·827	21,169	5·950	27,039		

TEMPERATURE, 220°.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·635	14,886	9·189	27,584	4·028	37,740
19·925	16,451	7·887	29,708	3·389	40,278
17·219	18,357	6·598	32,123	3·069	42,630
14·513	20,772	5·954	33,325	2·749	46,921
11·836	23,763	5·311	34,715	2·622	50,342
10·505	25,542	4·669	36,201	2·558	52,753

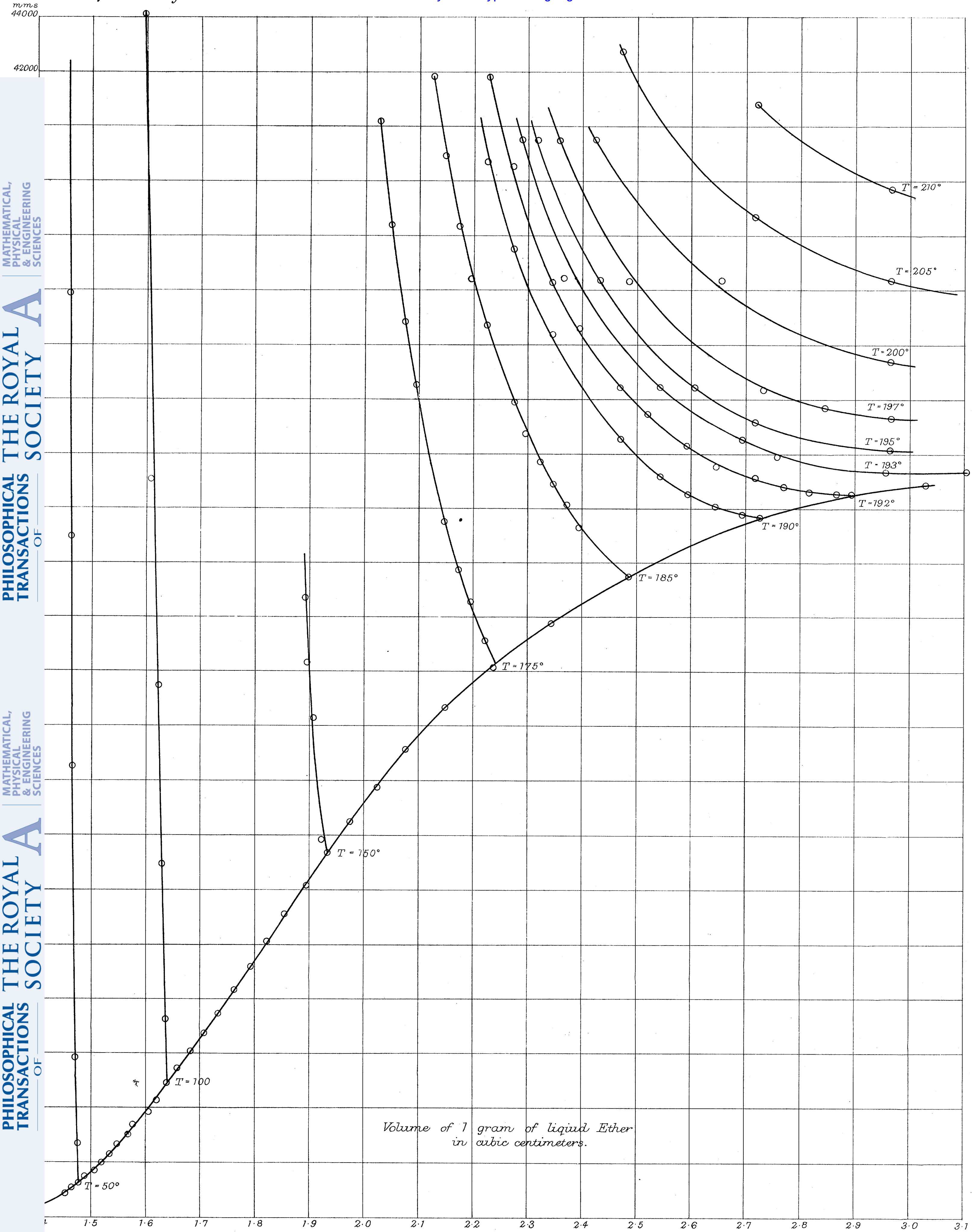
TEMPERATURE, 250°. Pressure of bromonaphthalene vapour, 386·35 mms.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·651	16,223	10·513	29,074	5·315	43,259
19·938	18,058	9·195	31,741	4·672	46,155
17·231	20,269	7·892	34,815	4·351	47,884
14·523	23,110	6·602	38,513	4·031	50,129
11·844	26,789	5·958	40,664	3·711	52,599

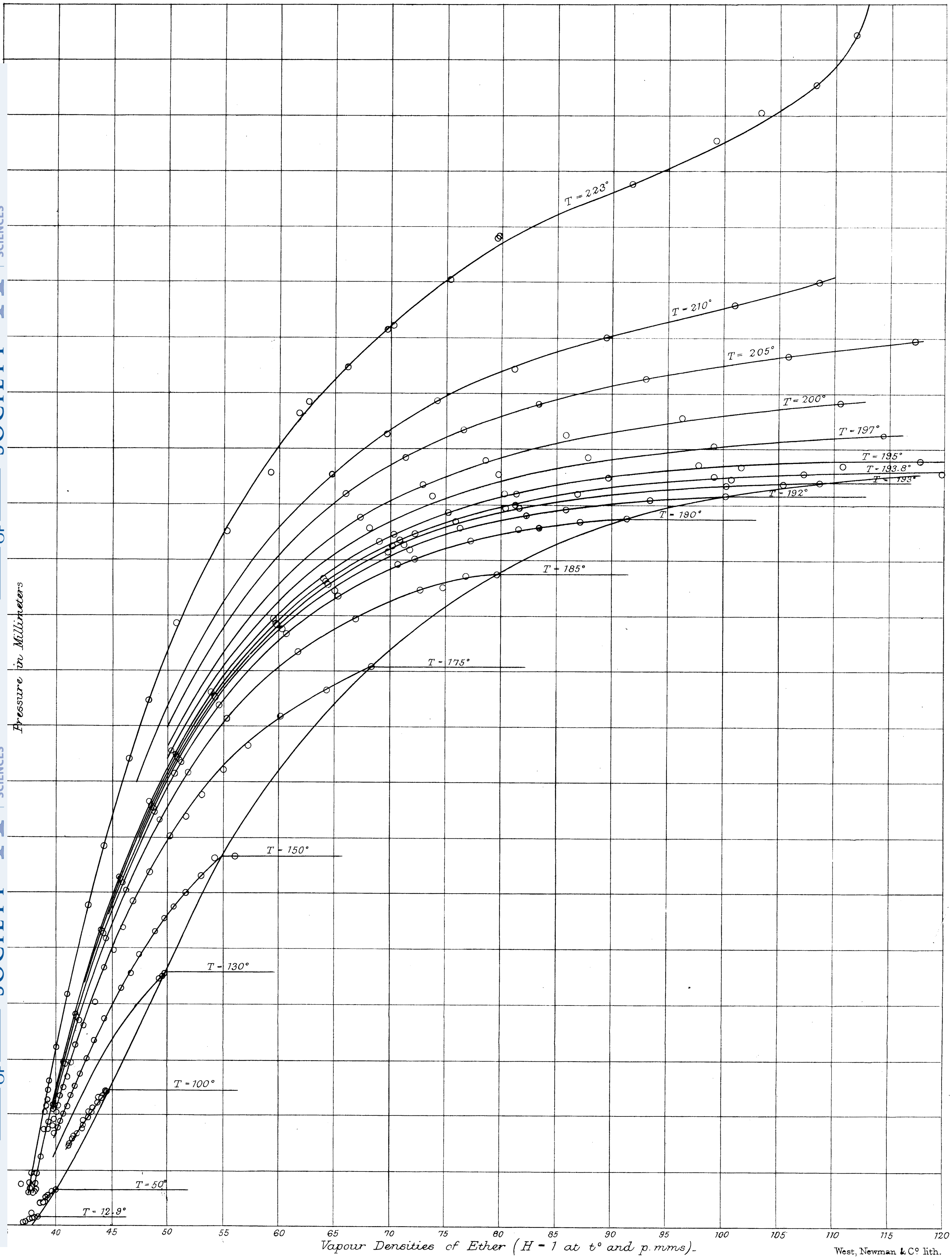
TEMPERATURE, 280·35°. Pressure of bromonaphthalene vapour, 758·2 mms.

Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.	Volume of 1 gramme.	Pressure.
c.cs.	mms.	c.cs.	mms.	c.cs.	mms.
22·669	17,806	10·521	33,349	5·963	49,552
19·954	19,881	9·203	36,777	5·642	51,598
17·245	22,499	7·899	41,084	5·319	53,841
14·535	25,834	7·253	43,537		
11·853	30,430	6·607	46,552		

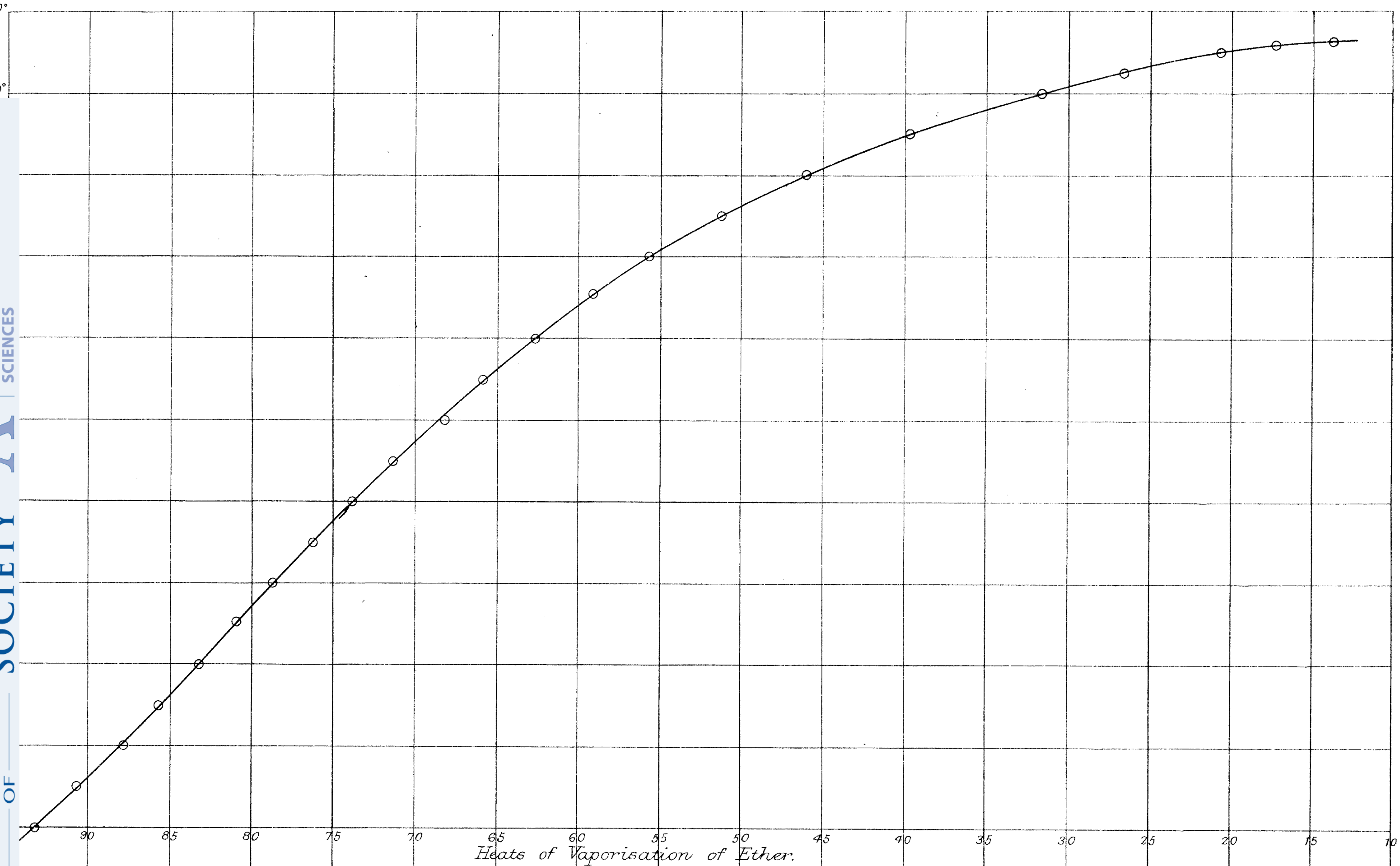
At 175° and at 280° the readings of pressure were double, one set being made with rising and the other with falling pressures; the means are given.

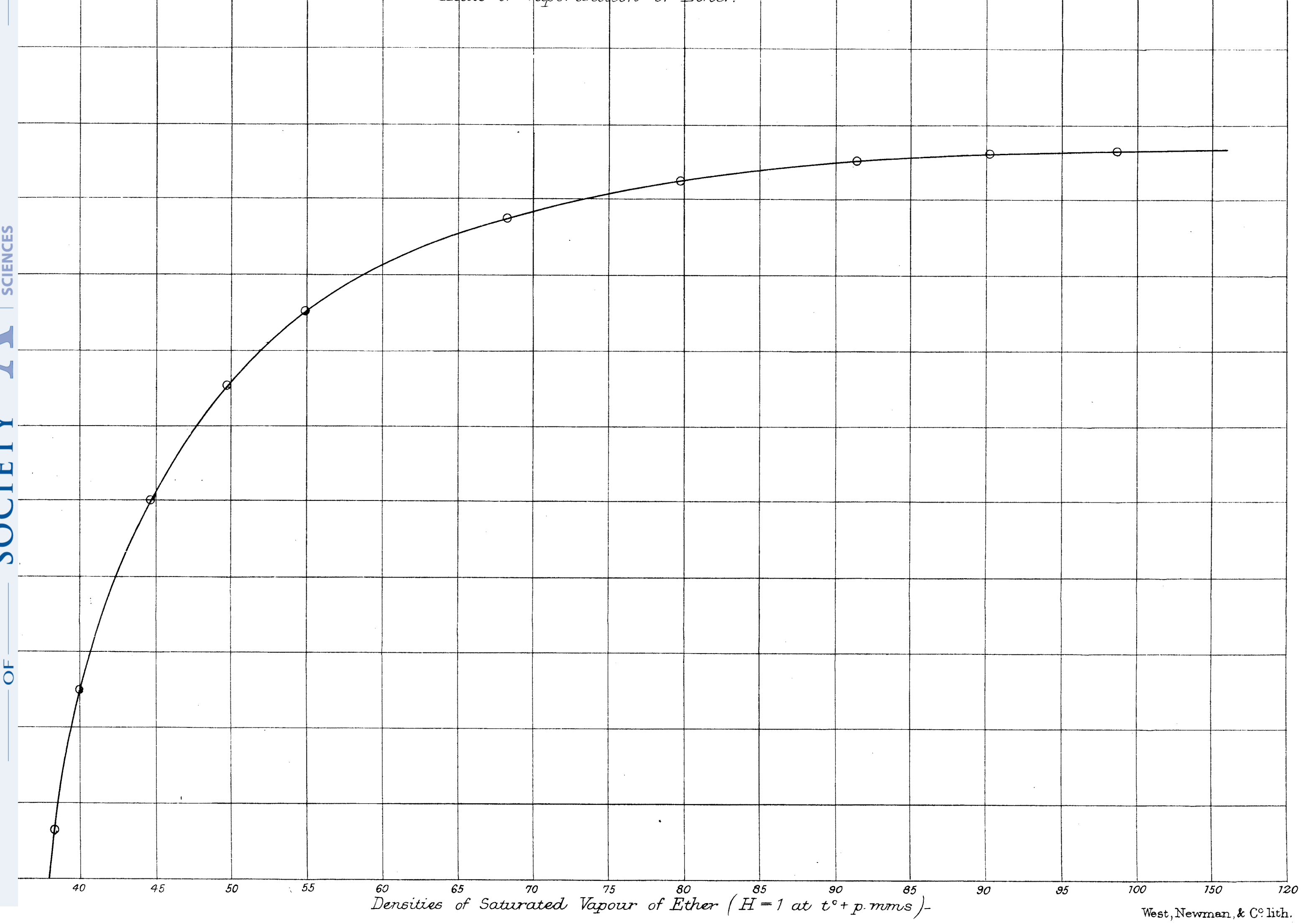


West, Newman & C° lith.



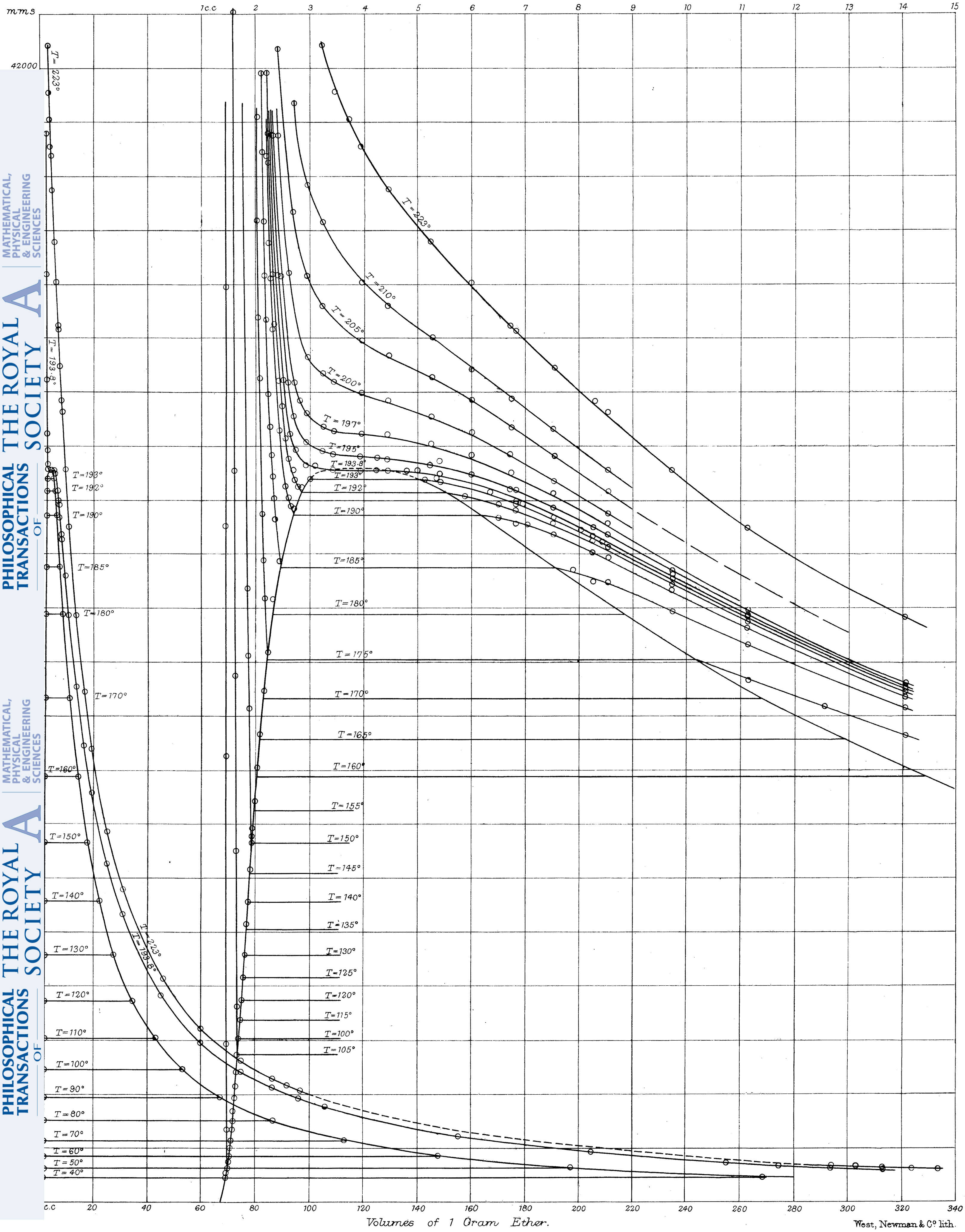
West, Newman & C° lith.



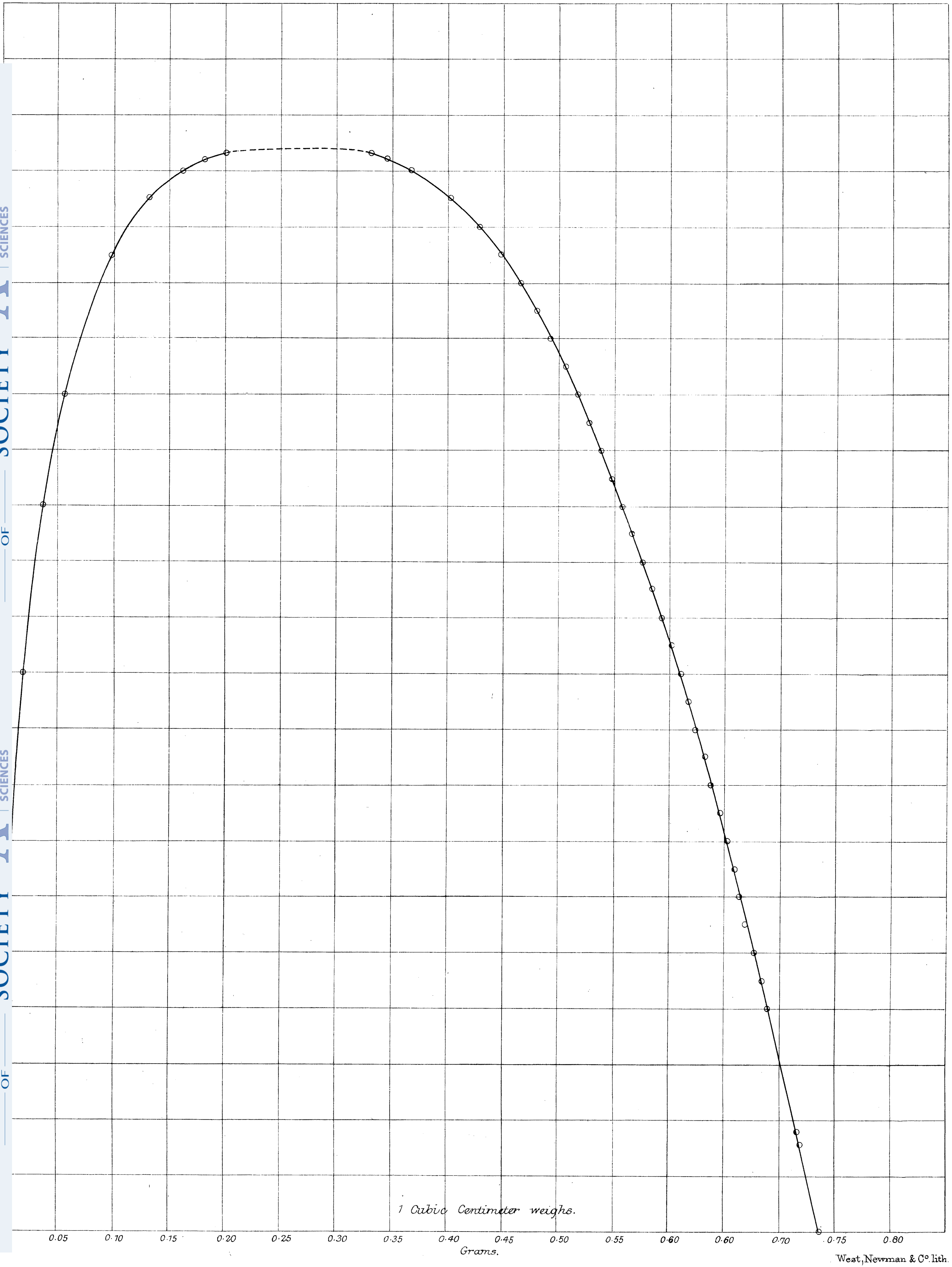


West, Newman, & Co. lith.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES



West, Newman & Co. lith.