On Evaporation and Dissociation. Part V. A Study of the Thermal Properties of Methyl-Alcohol

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Phil. Trans. R. Soc. Lond. A 1887 **178**, 313-334
doi: 10.1098/rsta.1887.0011

XI. *On Evaporation and Dissociation.*—Part V.* *A Study of the Thermal Properties of Methyl-Alcohol.*

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Communicated by Professor G. G. Stokes, *P.R.S.*

Received January 6,—Read January 20, 1887.

[Plates 14–18.]

In previous memoirs we have given the results of investigations of the thermal properties of ethyl-alcohol, acetic acid, and ethyl oxide (ether). The subject of the present paper is the vapour-pressures, vapour-densities, and expansion of methyl-alcohol; and from these results the heats of vaporisation have been deduced. The range of temperature is from −16° to the critical temperature 240°; and the range of pressure from 11 millims. to 60,000 millims.

Preparation of pure methyl-alcohol.†—A finely crystallised sample of methyl oxalate was distilled with ammonia; the distillate was rectified, and when partially freed from water was distilled with quicklime. The distillate was again distilled from barium oxide, and then allowed to stand for some weeks over anhydrous copper sulphate; but the boiling-point was found to be by no means constant. It was then distilled six times over small quantities of sodium; and the rise of temperature during the last distillation was less than 0·1°. The boiling-point was 64·85° at 761·9 millims. A series of determinations of vapour-pressure at low temperatures was then made, and it was decided, before employing the alcohol for determinations of vapour-density, to re-distil it. It boiled at 64·95°, under the same pressure, 761·9 millims. Preliminary experiments were then carried out, with a view to determining the critical temperature and pressure; but the volume-tube burst, and the experiments were delayed until a new volume-tube had been calibrated. As the boiling-point of the alcohol was not absolutely constant, it was repeatedly fractionated, and the

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* Parts I. and II. are published in the 'Philosophical Transactions' for 1886 (Part I.); Part III., *ibid.*, 1887; Part IV. is published in the 'Transactions of the Chemical Society,' 1886, p. 790; Part VI., in the 'Phil. Mag.,' vol. 23, 1887, pp. 435–458; vol. 24, 1887, pp. 196–212.

† See also Addendum at p. 330.

greater part was obtained, boiling at 64·7°, under 760 millims. pressure. The rise of temperature did not exceed 0·05° during the complete distillation.

The boiling-point of methyl-alcohol has been a subject of much dispute. Kopp found, with three separate samples, 65°, 65°–65·2°, 64·6°–65·2°; Pierre, 66·3°; Mendeléeff, 66°; Delffs, 66·5°; Dumas and Peligot, 66·5°; Landolt, 66·3°; and Dittmar and Stewart, 64·1°. Perkin, who dried his alcohol with copper sulphate, found 65·8°–66°; but we found that several weeks' standing over copper sulphate produced little effect. Regnault, who dried his alcohol over lime, found 66·78°; and Schiff found 64·8° at 763 millims. pressure. There can be little doubt that the last is correct.

Apparatus employed.—The apparatus for determining vapour-pressures at low temperatures was that described in the 'Phil. Trans.,' 1884, p. 37; and in the 'Chem. Soc. Trans.,' 1885, p. 42. The vapour-densities at low temperatures were determined by a modification of Hofmann's apparatus, whereby pressure, volume, and temperature could be altered at will. This apparatus has been described in our memoir on ether ('Phil. Trans.,' 1887, A, p. 59). The constants at high temperatures were determined by a modified Andrews' apparatus, of which a description is to be found in our paper on ether.

Experimental results.—Before giving experimental results, it should be noted that in every case the temperatures are those of an air thermometer; the pressures refer to the latitude of University College, Bristol (51° 27′ 25″ N.), and to 226 feet above sea-level; they are corrected according to Amagat's experiments ('Comptes Rendus,' vol. 99, p. 1153), and are measured in actual millimetres of mercury.

Vapour-pressures at low temperatures.—The thermometer employed for temperatures below 40° was graduated in tenths of a degree. By reduction of pressure an apparent fall of temperature of 0·25° for 760 millims. was observed. This apparent fall is proportional to the pressure, and correction was applied accordingly. The thermometer was standardised by a determination of the vapour-pressures of water above 0°; and it was assumed that the graduation below 0° was equally regular.

TABLE I.

Series I.				Series II.		Series III.			
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
mms.	°	mms.	°	mms.	°	mms.	°	mms.	°
11·15	−14·61	44·2	6·58	161·2	30·4	27·15	− 1·4	291·5	42·3
13·15	−12·35	55·0	10·16	189·7	33·7	29·6	0·0	334·05	45·5
13·7	−11·94	61·0	12·13	217·8	36·6	40·2	+ 4·8	384·45	48·75
15·85	−10·02	88·4	18·64	257·1	39·8	41·0	5·0	436·55	51·45
17·05	− 8·70	105·0	21·77	299·1	43·2	52·65	9·3	484·8	53·75
19·05	− 6·89	125·5	25·19	344·3	46·3	68·4	13·95	537·6	56·4
24·05	− 3·19	147·35	28·32	357·2	47·2	82·8	17·45	588·5	58·7
26·3	− 1·98	173·4	31·63	390·5	48·9	103·9	21·4	645·8	60·9
29·85	+ 0·01	200·9	34·70	449·6	52·5	139·8	27·2	699·0	62·8
32·95	1·60	235·1	37·95	494·2	54·8	166·8	30·8	743·2	64·2
36·1	3·25			541·6	56·6	197·1	34·1		
40·65	5·06			590·6	58·7	239·65	38·2		
				640·9	60·9				
				698·4	62·95				
				761·8	65·0				

These results were plotted, and curves drawn through them, showing great regularity. The first two series were determined with substance boiling at 64·85°; and the third, with the alcohol after fractionation.

Vapour-densities at low temperatures.—The weight of the methyl-alcohol taken was not determined directly, but was ascertained from vapour-density determinations at the boiling-point of chlorobenzene under a pressure of 718·95 millims., corresponding to the temperature 130°.

TABLE II.

Temperature.	Pressure.	Volume.	P. V.	Mean P. V.
°	mms.	c,cs.		
130	320·3	175	56,053	56,040
	339·9	165	56,083	
	373·2	150	55,980	
	406·1	138	56,042	
	466·8	120	56,016	

From these observations the weight was calculated to be 0·0716 gramme.

Temperature.	Pressure.	Volume.	P. V.	Vapour-density. (H = 1.)
°	mms.	c.cs.		
60	264·5	173·7	45,944	16·13
(Alcohol vapour, P = 350·3 mms.)	265·7	172·4	45,807	16·17
	292·0	157·0	45,844	16·16
	317·5	144·25	45,800	16·18
	360·6	126·6	45,652	16·23
	408·0	111·05	45,309	16·35
	474·3	95·0	45,058	16·44
	557·8	80·1	44,680	16·58
	624·4	70·0	43,708	16·95
				(condensed ?)
40	243·8	174·0	42,421	16·42
(Alcohol vapour, P = 133·7 mms.)	260·1	160·0	41,616	16·73

Condensed at smaller volumes.

The vapour-pressure at 60° is 625·1 millims.; and at 40°, 260·47 millims. The vapour-densities at 40° appear to be too high; this would be caused by the presence of dust particles, which may cause condensation at low temperatures and at pressures considerably below the vapour-pressure.

Constants at high temperatures.—Three different amounts of methyl-alcohol were employed for these experiments. The first quantity, which we shall call A, was comparatively large, and was employed for the determination of the orthobaric volumes * and of the vapour-pressures. Its volume was ascertained by direct measurement, and its weight from determinations of the specific gravity of methyl-alcohol at low temperatures. The weight of the second quantity, B, was calculated from a comparison of its volumes when gasified with those of the third quantity, under similar conditions of temperature and pressure. That of the third quantity, C, was ascertained from its density at 240°, at large volumes, when *p.v.* remained constant during considerable change of volume. In the course of the experiments the quantity C was slightly increased by rise of liquid from the lower portion of the tube. The increased weight, which we shall term C′, was ascertained by a comparison between the volumes of this portion and those given by the former.

A. *Results of experiments with large quantity. Specific gravity of methyl-alcohol.*—The specific gravity was determined by a SPRENGEL's tube of the form recommended by PERKIN ('Chem. Soc. Trans.,' 1884, p. 443).

Weight of methyl-alcohol at 22·94° . . .	16·59625 grammes.
Weight of water . . .	20·9595 ,,
Specific gravity at 22·94° (water at 4° = 1) .	0·78909 ,,
Volume of 1 gramme	1·26729 cub. centim.

(These weighings were reduced to a vacuum.)

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* We term "orthobaric volumes" the volumes occupied by 1 gramme of the liquid under the vapour-pressures corresponding to the temperatures of measurement.

The results of other observers* are :—

Dumas and Peligot, at 20°	0·798	Kopp (1847)	0·8180
Regnault, at 15–20°	0·813	Kopp (1855)	0·8142
Deville, at 9°	0·807	Pierre, at 0°	0·8207
Kopp (1845), at 0°	0·8147	Mendeléeff	0·8206

Perkin, at 15°/15°, 0·79726 ; at 25°/25°, 0·78941.

Perkin's results give, when compared with water at 4°: at 15°, 0·79658 ; at 25°, 0·78714 ; they are in close accordance with ours.

The portion of methyl-alcohol A gave the following measurements :—

	Volume.
At 18·2°	0·27622 c.c.
22·4°	0·27697 ,,
80·0°	0·29666 ,,

From these numbers a curve was constructed, and the volume at 22·94° was read ; it was 0·27701 c.c. The specific gravity at 22·94° was found to be 0·78909 ; hence the weight of portion A was 0·21858 gramme.

The volume-tube was a new one, 35 centims. long, and about 1·1 millim. internal diameter ; the external diameter was about 8 millims. It was carefully calibrated by weighing with mercury at a known temperature.

The following corrections 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 no data are available. It is probable that any correction would have been within the limits of error of reading.

For pressure.—A low-pressure and a high-pressure manometer were employed ; where possible, readings on both were taken. The manometers were calibrated by weighing with mercury, and contained air dried over phosphorus pentoxide.

Corrections.—Meniscus of mercury.
Difference of levels of mercury in volume-tube and in pressure-gauges.
Difference in temperature of water-jacket at time of filling and time of reading.
Deviation of air from Boyle's Law, as determined by Amagat.

For temperature.—The data given by us in the 'Chem. Soc. Trans.,' 1885, p. 640,

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* Lossen gives a tabulated statement of boiling-points and specific gravities in the 'Annalen der Physik und Chemie,' vol. 214, p. 104.

were employed. No correction was necessary except that the pressures under which the standard liquids boiled were read at the temperature of the room instead of at 0°, and altered accordingly. The temperatures are those of an air thermometer.

The vapour-pressures at each temperature were determined at widely different volumes. The extreme volumes are as a rule about 0·91 and 0·46 cub. centim.

A.

Jacketing vapour.	Pressure.	Temperature.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.
	mms.	°	c.cs.		mms.
Chlorobenzene	144·8	80	1·3572	0·7368	1,340 1,341 1,341 1,341
				Mean . .	1,341
”	208·35	90	1·3814	0·7239	1,896 1,898 1,898 1,896
				Mean . .	1,897
”	292·75	100	1·4015	0·7135	2,621 2,637 2,627 2,625
				Mean . .	2,627
”	402·55	110	1·4228	0·7028	3,554 3,561 3,565 3,565
				Mean . .	3,561
”	542·8	120	1·4495	0·6899	4,745 4,764 4,775 4,770
				Mean . .	4,763
”	718·95	130	1·4755	0·6777	6,257 6,245 6,234 6,224
				Mean . .	6,238

Jacketing vapour.	Pressure.	Temperature.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.
	mms.	°	c.cs.		mms.
Bromobenzene	372·65	130	1·4764	0·6773	6,257
					6,245
				Mean . .	6,251
,, ...	495·8	140	1·5039	0·6649	8,052
					8,060
					8,092
					8,076
					8,078
					8,066
					8,080
					8,077
				Mean . .	8,073
,, ...	649·05	150	1·5400	0·6494	10,309
					10,308
					10,297
				Mean . .	10,305
Aniline	283·7	150	. .	. .	10,355
					10,370
					10,358
					10,352
				Mean . .	10,359
,, ...	386·0	160	1·5821	0·6321	13,037
					13,014
					13,043
					13,029
				Mean . .	13,031
,, ...	515·6	170	1·6234	0·6160	16,295
					16,297
					16,292
					16,286
				Mean . .	16,292
,, ...	677·15	180	1·6732	0·5977	20,044
					20,067
					20,069
					20,070
				Mean . .	20,062
Methyl salicylate . . .	249·35	180	1·6758	0·5967	20,129
					20,152
					20,144
					20,157
				Mean . .	20,145

Jacketing vapour.	Pressure.	Temperature.	Volume of 1 gramme.	Specific gravity.	Vapour-pressure.
	mms.	°	c.cs.		mms.
Methyl salicylate . . .	330·85	190	1·7302	0·5780	24,556 24,611 24,634 24,658
				Mean . .	24,615
,, ,, . . .	432·35	200	1·8098	0·5525	29,759 29,776 29,827 29,833
				Mean . .	29,799
,, ,, . . .	557·5	210	1·9033	0·5254	35,739 35,753 35,779 35,808
				Mean . .	35,770
,, ,, . . .	710·1	220	2·0410	0·4900	42,678 42,735 42,739
				Mean . .	42,713
Bromonaphthalene . . .	181·75	220	. .	. .	42,617 42,670
				Mean . .	42,644
,, . . .	207·35	225	2·1367	0·4680	46,320 46,332 46,350
				Mean . .	46,334
,, . . .	235·95	230	2·2633	0·4418	50,461 50,421
				Mean . .	50,441
,, . . .	248·3	232	2·3253	0·4301	52,227 52,187
				Mean . .	52,207
,, . . .	261·2	234	2·4229	0·4127	53,988
,, . . .	274·65	236	2·5300	0·3953	55,685
,, . . .	281·6	237	2·5868	0·3866	56,955
,, . . .	288·7	238	2·6989	0·3705	57,707
,, . . .	292·3	238·5	2·7455	0·3642	58,329
,, . . .	295·95	239	. .	. .	58,810
,, . . .	299·65	239·5	. .	. .	59,141
,, . . .	303·35	240	. .	. .	59,661

No meniscus was visible at 240°. On lowering the temperature to 239·9° the meniscus appeared after a short time. The apparent critical temperature, therefore, lies between 239·9° and 240°.

Only one reading is given at high pressures. The reason for this is that the alteration of level of the mercury in the volume tube altered the level of the mercury in the gauge by only 0·1 mm.

B. The weight of this portion was ascertained by a comparison of its volumes in the gaseous state with those of C under similar conditions of temperature and pressure. It was found to be 0·02565 gramme. With this portion vapour-densities at high temperatures, and vapour-pressures, were determined.

For this series the jacketing vapour was bromonaphthalene boiling under various pressures.

Pressure of bromonaphthalene.	Temperature.	Volume of 1 gramme.	Pressure.	Vapour-density.
mms.	°	c.cs.	mms.	
181·75	220	39·934	20,645	18·58
		29·364	26,109	19·98
		23·462	30,510	21·40
		17·610	36,058	24·18
		14·713	39,016	26·68
		13·271	40,590	28·43
		12·554	41,397	29·48
		12·125	41,829	30·21
		11·840	42,178	30·68
		11·696	42,231	31·02
		Vapour-pressure	= 42,319	
207·35	225	39·938	20,999	18·45
		29·368	26,647	19·77
		23·466	31,282	21·08
		17·614	37,146	23·65
		14·717	40,536	25·94
		13·275	42,269	27·58
		11·844	44,165	29·59
		11·123	45,168	30·80
		10·410	45,907	32·38
		10·269	46,012	32·75
		10·125	46,118	33·14
		Vapour-pressure	= 46,222	
235·95	230	39·94	21,337	18·34
		29·37	27,192	19·57
		23·47	31,980	20·83
		17·62	38,191	23·23
		14·72	41,914	25·34
		13·28	43,918	26·81
		11·84	46,011	28·69
		11·13	46,894	29·96
		10·41	47,801	31·40
		9·696	48,756	33·06
		8·982	49,737	34·99
		8·674	49,884	36·12
		Vapour-pressure	= 50,262	

Pressure of bromo-naphthalene.	Temperature.	Volume of 1 gramme.	Pressure.	Vapour-density.
mms.	°	c.cs.	mms.	
248·3	232	39·94	21,545	18·27
		29·37	27,428	19·48
		23·47	32,260	20·73
		17·62	38,753	22·99
		14·72	42,457	25·11
		13·28	44,718	26·43
		11·84	46,761	28·34
		10·41	48,829	30·86
		9·696	49,820	32·48
		8·982	50,851	34·36
		8·265	51,655	36·75
		Vapour-pressure	= 52,192	
261·2	234	39·94	21,697	18·18
		29·37	27,630	19·41
		23·47	32,541	20·63
		17·62	39,086	22·88
		14·72	43,094	24·84
		13·28	45,211	26·25
		11·84	47,443	28·04
		10·41	49,727	30·42
		8·982	51,969	33·75
		8·265	52,801	36·09
		7·552	53,741	38·81
		7·267	53,796	40·29
		Vapour-pressure	= 53,890	
274·65	236	39·95	21,856	18·11
		29·38	27,881	19·19
		23·48	32,901	20·48
		17·63	39,515	22·72
		14·73	43,669	24·60
		11·85	48,375	27·60
		10·42	50,496	30·08
		8·982	52,729	33·48
		8·265	53,967	35·45
		7·552	54,726	38·26
		6·838	55,414	41·73
		Vapour-pressure	= 55,563	
288·7	238	39·95	21,951	18·11
		29·38	28,078	19·25
		23·48	33,137	20·42
		17·63	39,869	22·60
		14·73	44,154	24·43
		11·85	48,865	27·43
		10·42	51,280	29·73
		8·982	53,822	32·84
		7·552	55,972	37·56
		6·838	56,853	40·83
		6·421	57,111	43·30
		Vapour-pressure	= 57,445	

Pressure of bromo-naphthalene.	Temperature.	Volume of 1 gramme.	Pressure.	Vapour-density.
mms.	°	c.cs.	mms.	
295·95	239	39·95	22,020	18·08
		29·38	28,243	19·17
		23·48	33,232	20·40
		17·63	40,209	22·46
		14·73	44,361	24·36
		11·85	49,432	27·17
		10·42	51,849	29·46
		8·982	54,282	32 63
		7·552	56,808	37·08
		6·838	57,307	40·59
		6·127	58,328	44·52
		5·696	58,568	47·67
		Vapour-pressure	= 58,672	
299·65	239·5	11·85	49,634	27·09
		10·42	52,301	29·24
		8·982	54,568	32·49
		7·552	56,992	36·99
		6·838	57,836	40·25
		6·127	58,703	44·27
		5·410	58,776	50·08
303·35	240	39·95	22,100	18·05
		29·38	28,361	18·72
		23·48	33,454	20·30
		17·63	40,651	22·26
		14·73	44,677	24·24
		11·85	49,761	27·04
		10·42	52,406	29·21
		8·982	54,993	32·27
		7·552	57,071	36·98
		6·127	58,751	44·28
		5·410	59,590	49·45
		4·697	59,775	56·77
		3·984	60,038	65·84

C. The weight of this portion was 0·00221 gramme. It was ascertained from measurements of the volume occupied by the vapour at 230° and 240°. At 230° the change of volume was from 1·0245 cub. centim. to 0·6019 cub. centim.; the product of pressure and volume was constant, and gave for the weight 0·002211 gramme; at 240°, with the same change of volume, the weight was 0·002206 gramme. The value taken was 0·00221 gramme. The error can hardly be more than 0·5 per cent.

The following determinations were made:—

Pressure of bromo-naphthalene.	Temperature.	Volume of 1 gramme.	Pressure.	Vapour-density.
mms.	°	c cs.	mms.	
235·95	230	463·58	2,115	15·94
		340·90	2,862	16·02
		272·35	3,583	16·02
		204·44	4,747	16·11
		170·81	5,658	16·17
		137·44	7,021	16·20
		104·23	9,114	16·45
		87·65	10,754	16·59
		71·10	13,022	16·88
		54·50	16,472	17·41
		46·22	19,050	17·75
		37·90	22,421	18·40
		29·62	27,085	19·49
		21·35	33,884	21·61
		Vapour-pressure	= 50,511	
303·35	240	463·71	2,143	16·04
		428·48	2,326	16·00
		410·87	2,422	16·02
		375·72	2,650	16·01
		341·00	2,913	16·05
		272·43	3,647	16·05
		204·50	4,846	16·09
		170·86	5,775	16·16
		137·48	7,168	16·29
		104·26	9,328	16·39
		87·67	10,991	16·54
		71·12	13,350	16·79
		54·62	16,949	17·25
		46·23	19,639	17·56
		37·91	23,076	18·23
		29·63	28,068	19·17
		21·35	35,616	20·96
Methyl salicylate.				
C'. 432·35	200	453·12	2,013	16·12
		333·20	2,722	16·21
		266·20	3,391	16·28
		199·82	4,478	16·43
		166·96	5,319	16·55
		134·34	6,552	16·70
		101·88	8,491	16·99
		85·67	9,969	17·21
		69·49	12,022	17·60
		53·27	15,042	18·34
		45·18	17,279	18·83
		37·04	20,200	19·65
		29·95	23,817	21·32
		20·87	28,876	24·40
		Vapour-pressure	= 29,739	
Aniline.				
677·15	180	101·82	8,057	17·16
		85·62	9,362	17·58
		69·45	11,207	18·09
		53·24	13,912	19·01
		45·15	15,696	19·87
		37·02	18,025	21·10
		32·17	19,674	22·24
		Vapour-pressure	= 19,970	

Pressure of aniline.	Temperature.	Volume of 1 gramme.	Pressure.	Vapour-density.
mms.	°	c.cs.	mms.	
386·0	160	452·63	1,846	16·11
		332·85	2,484	16·28
		265·91	3,085	16·40
		199·61	4,049	16·65
		166·78	4,777	16·89
		134·20	5,855	17·13
		101·77	7,505	17·62
		85·58	8,707	18·06
		69·42	10,282	18·85
		61·29	11,299	19·43
		53·22	12,518	20·20
		49·97	12,965	20·77
		Vapour-pressure	= 13,011	
204·6	140	101·72	6,890	18·31
		85·53	7,878	19·05
		82·32	8,024	19·43
		77·45	8,046	20·60
		Vapour-pressure	= 8,056	
Chlorobenzene. 542·8	120	452·17	1,658	16·29
		400·64	1,860	16·39
		332·51	2,212	16·61
		282·31	2,584	16·74
		249·01	2,900	16·91
		199·41	3,539	17·31
		166·61	4,120	17·79
		142·15	4,684	18·34
		Vapour-pressure	= 4,705	
292·75	100	451·95	1,560	16·44
		400·44	1,739	16·65
		332·34	2,065	16·89
		282·17	2,391	17·18
		265·52	2,496	17·49
		248·89	2,591	18·12
		Vapour-pressure	= 2,597	

Reduction and Arrangement of Results.

1. *Vapour-pressures.*—The vapour-pressures determined by us with quantities A, B, C, and C′, as well as the vapour-pressures calculated from these observations by the formula $\log p = a + b\alpha^t + c\beta^t$, and pressures calculated by Regnault, who also employed Biot's formula, are given in the following Table :—

Temperature.	Pressure.								
	Still method.	A.	B.	C and C′.	Mean.	Calculated from formula.	Difference in millims.	Difference in degrees.	REGNAULT.
°	mms.	mms.	mms.	mms.	mms.				
−20	..	..	..	..	..	7·605	..	..	6·27
−10	15·5	..	..	..	15·5	15·402	− 0·1	+0·1	13·47
0	29·6	..	..	..	29·6	29·600	0	0	26·82
+10	54·7	..	..	..	54·7	54·224	− 0·48	+0·15	50·13
20	96·0	..	..	..	96·0	95·104	− 0·90	+0·17	88·67
30	160·0	..	..	..	160·0	160·28	+ 0·28	−0·03	149·99
40	260·5	..	..	..	260·5	260·47	− 0·03	±0	243·51
50	406·0	..	..	..	406·0	409·47	+ 3·47	−0·2	381·68
60	625·0	..	..	..	625·0	625·10	− 0·10	±0	579·93
70	..	..	..	..	..	926·60	..	..	857·10
80	..	1,341	..	..	1,341	1,340·3	− 0·7	+0·01	1238·47
90	..	1,897	..	..	1,897	1,894·6	− 2·4	+0·04	1741·67
100	..	2,627	..	2,597	2,621	2,622·5	+ 1·5	−0·02	2405·15
110	..	3,561	..	..	3,561	3,561·1	+ 0·1	0	3259·60
120	..	4,763	..	4,705	4,751	4,751·3	+ 0·3	0	4341·77
130	..	6,238 and 6,251	..	..	6,242	6,239·2	− 2·8	+0·02	5691·30
140	..	8,073	..	8,056	8,071	8,072·5	+ 1·5	−0·01	7337·10
150	..	10,305 and 10,359	..	..	10,336	10,306	− 30	+0·12	9361·35
160	..	13,031	..	13,011	13,027	12,999	− 28	+0·09	..
170	..	16,292	..	..	16,292	16,213	− 79	+0·23	..
180	..	20,062 and 20,145	..	19,970	20,089	20,016	− 73	+0·18	..
190	..	24,615	..	..	24,615	24,481	−134	+0·28	..
200	..	29,799	..	29,739	29,787	29,688	− 99	+0·18	..
210	..	35,770	..	..	35,770	35,722	− 48	+0·07	..
220	..	42,713 and 42,644	42,291	..	42,573	42,676	+103	−0·14	..
225	..	46,334	46,222	..	46,297	46,530	+233	−0·29	..
230	..	50,441	50,262	50,511	50,414	50,651	+237	−0·28	..
232	..	52,207	52,192	..	52,202	52,378	+176	−0·20	..
234	..	53,988	53,890	..	53,939	54,151	+212	−0·24	..
236	..	55,685	55,563	..	55,624	55,971	+347	−0·38	..
237	..	56,955	..	..	56,955	56,900	− 55	+0·06	..
238	..	57,707	57,445	..	57,576	57,839	+263	−0·29	..
238·5	..	58,329	..	..	58,329	58,310	− 19	+0·02	..
239	..	58,810	58,672	..	58,741	58,790	− 49	+0·05	..
239·5	..	59,141	..	..	59,145	59,268	+127	−0·13	..
240	..	about 59,660	..	..	..	59,759	..	..	..

The number of observations with quantity A was large, and the mean pressure given lays due stress on this fact. As with alcohol and ether, the formula expresses the observations very closely; the greatest divergence expressed in temperature being only 0·38° at 236°. The constants employed were calculated from observations at 0°, 55°, 110°, 165°, and 220°. To obtain the best values at these temperatures, portions of the curve were smoothed by the method of ratios (see 'Phil. Mag.,' vol. 20, 1885, p. 516 *et seq.*). The constants for the formula given were—

$$a = 22{\cdot}307096, \qquad \log \alpha = \bar{1}{\cdot}99988416,$$
$$\log b = 1{\cdot}2649587, \qquad \log \beta = \bar{1}{\cdot}99599796,$$
$$\log c = 0{\cdot}3855770.$$

b and c are both negative.

It will be remarked that Regnault's vapour-pressures are in every case much lower than ours. On reference to his memoir ('Mémoires de l'Académie des Sciences,' vol. 26, p. 456), it is evident that his low results are to be accounted for by insufficient drying of his specimen; it was only rectified several times over quicklime. He states, also, that the fluctuations of his thermometer when the dynamical method was employed were so great as to interfere with the accuracy of his results. Regnault, moreover, did not think it worth while to convert the readings of his mercury thermometer into those of an air thermometer.

The orthobaric volumes of 1 gramme of methyl-alcohol were read from a curve drawn so as to pass through the experimental points. We have not constructed a formula to represent these relations. They are given in the Table which follows :—

Orthobaric Volumes of 1 gramme of Liquid.

Temperature.	Volume.	Specific gravity.	Temperature.	Volume.	Specific gravity.	Temperature.	Volume.	Specific gravity.
°			°			°		
20	1·265	0·7905	120	1·449	0·690	220	2·041	0·490
30	1·2765	0·783	130	1·477	0·677	225	2·139	0·4675
40	1·291	0·7745	140	1·506	0·664	230	2·268	0·441
50	1·307	0·765	150	1·540	0·6495	232	2·328	0·4295
60	1·324	0·7555	160	1·577	0·634	234	2·413	0·4145
70	1·3405	0·746	170	1·623	0·616	236	2·528	0·3955
80	1·360	0·7355	180	1·672	0·598	237	2·597	0·385
90	1·379	0·725	190	1·733	0·577	238	2·699	0·3705
100	1·401	0·714	200	1·808	0·553	238·5	2·751	0·3635
110	1·4245	0·702	210	1·903	0·5255			

Orthobaric Volumes of 1 gramme of Vapour.

The following Table gives the volume of 1 gramme of saturated vapour at even temperatures :—

Temperature.	Volume.	Specific gravity.	Vapour-density.	Temperature.	Volume.	Specific gravity.	Vapour-density.
°	c.cs.			°	c.cs.		
0	17,803	0·0000562	16·10	160	50·16	0·01994	20·64
10	10,044	0·0000996	16·15	170	39·59	0·02526	21·45
20	5,899	0·0001695	16·23	180	31·40	0·03186	22·40
30	3,608	0·0002772	16·30	190	24·94	0·04010	23·57
40	2,276	0·0004394	16·41	200	19·70	0·05075	25·13
50	1,484	0·0006739	16·52	210	15·33	0·06521	27·40
60	993·8	0·001006	16·66	220	11·58	0·08635	31·00
70	682·7	0·001465	16·85	225	9·97	0·1003	33·50
80	479·8	0·002084	17·06	230	8·42	0·1187	36·80
90	344·0	0·002907	17·31	232	7·83	0·1277	38·40
100	251·0	0·003984	17·61	234	7·24	0·1381	40·30
110	186·0	0·005376	17·97	236	6·64	0·1505	42·75
120	140·0	0·007142	18·36	238	5·95	0·1681	46·25
130	106·6	0·009379	18·81	238·5	5·59	0·1789	48·70
140	82·25	0·01216	19·33	239	5·33	0·1878	50·80
150	64·00	0·01562	19·93				

The next Table gives the densities of the unsaturated vapour at even intervals of pressure and temperature. These were read from isotherms, and smoothed by constructing isobars from the isotherms, and, after joining the points to form a curve, re-transferring to isotherms.

Pressures.	Temperature.																				
	100°	120°	130°	140°	150°	160°	170°	180°	190°	200°	210°	220°	225°	230°	232°	234°	236°	238°	239°	239·5°	240°
mms.																					
2,000	16·800	16·455	16·35	16·30	16·26	16·24	16·22	16·20	16·16	16·12	..	..	..	16·01	..	..	..	..	..	..	16·00
2,500	17·325	16·70	..	..	..	16·35	..	..	..	16·19	..	..	..	..	..	..	..	..	..	..	..
4,000	..	17·65	17·27	17·00	16·80	16·64	16·57	16·46	16·40	16·33	..	..	..	16·11	..	..	..	..	..	..	16·02
6,000	..	..	18·48	17·83	17·40	17·15	16·96	16·80	16·72	16·60	..	..	..	16·22	..	..	..	..	..	..	16·16
8,000	..	..	..	19·16	18·25	17·82	17·52	17·06	17·06	16·90	..	..	..	16·42	..	..	..	..	..	..	16·30
10,000	..	..	..	..	19·55	18·69	18·12	17·74	17·43	17·22	..	..	..	16·64	..	..	..	..	..	..	16·45
12,000	..	..	..	..	..	19·86	18·90	18·32	17·92	17·59	..	..	..	16·86	..	..	..	..	..	..	16·63
14,000	..	..	..	..	..	..	19·90	19·06	18·48	18·01	..	..	..	17·15	..	..	..	..	..	..	16·85
16,000	..	..	..	..	..	..	21·18	19·97	19·08	18·50	18·14	17·80	17·62	17·43	17·39	17·31	17·22	17·18	..	..	17·14
18,000	..	..	..	..	..	..	..	21·10	19·86	19·02	18·55	18·12	17·94	17·77	17·67	17·60	17·52	17·42	..	..	17·38
20,000	..	..	..	..	..	..	..	22·40	20·80	19·73	19·00	18·45	18·24	18 04	17·98	17·89	17·81	17·74	..	..	17·66
24,000	..	..	..	..	..	..	..	..	23·40	21·32	20·05	19·33	19·05	18·80	18·70	18·60	18·52	18·41	..	..	18·35
28,000	..	..	..	..	..	..	..	..	..	23·76	21·64	20·52	20·08	19·70	19·57	19·42	19·28	19·16	..	..	19·03
32,000	..	..	..	..	..	..	..	..	..	..	24·00	22·10	21·40	20·84	20·63	20·43	20·25	20·08	..	..	19·93
36,000	..	..	..	..	..	..	..	..	..	..	28 ?	24·18	23·10	22·26	21·98	21·72	21·46	21·25	21·15	..	21·04
40,000	..	..	..	..	..	..	..	..	..	..	..	27·60	25·43	24·06	23·63	23·24	22·90	22·60	22·44	..	22·30
42,000	..	..	..	..	..	..	..	..	..	..	..	30·10	27·10	25·36	24·80	24·30	23·85	23·48	23·28	..	23·10
44,000	..	..	..	..	..	..	..	..	..	..	..	..	29·26	26·81	26·10	25·48	24·90	24·40	24·15	..	23·93
46,000	..	..	..	..	..	..	..	..	..	..	..	..	32·47	28·70	27·70	26·86	26·12	25·45	25·18	..	24·85
48,000	..	..	..	..	..	..	..	..	..	..	..	..	..	31·60	29·86	28·65	27·60	26·72	26·30	..	25·90
50,000	..	..	..	..	..	..	..	..	..	..	..	..	..	35·53	32·70	30·87	29·40	28·20	27·66	27·41	27·20
52,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	37·50	34·38	32·20	30·40	29·60	29·20	28·82
54,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	40·80	36·00	33·10	31·99	31·42	30·98
56,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	37·66	35·48	34·80	34·27
58,000	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	42·40	40·90	40·00

Heats of Vaporisation.

From the well-known thermo-dynamic equation

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

the heats of vaporisation at definite intervals of temperature were calculated. The values of dp/dt were calculated by means of the formula: $\log p = a + b\alpha^t + c\beta^t$; pressures were calculated for one-tenth of a degree above and below the required temperature, and the difference was multiplied by 5 to obtain the value for 1°. The pressures were reduced to grammes per square centimetre, and the value of J was taken as 42,500.

Temperature.		dp/dt		$s_1 - s_2$	L
° C.	° Abs.	millims.	grammes.	c.cs.	calories.
0	273	1·861	2·530	17,802	289·17
10	283	3·160	4·296	10,043	287·36
20	293	5·150	7·002	5,898	284·54
30	303	8·067	10·978	3,607	282·07
40	313	12·202	16·590	2,275	277·78
50	323	17·890	24·323	1,483	274·14
60	333	25·473	34·633	993·5	269·41
70	343	35·381	48·104	681·4	264·51
80	353	47·91	65·139	478·4	258·96
90	363	63·54	86·330	342·6	252·76
100	373	82·57	112·26	249·6	246·01
110	383	105·81	143·86	184·6	239·27
120	393	133·10	180·96	138·6	232·00
130	403	165·41	224·89	105·1	224·07
140	413	202·52	275·35	80·75	216·12
150	423	243·95	331·67	62·46	206·13
160	433	294·70	400·67	48·58	198·34
170	443	349·95	475·80	37·97	188·25
180	453	411·15	559·00	29·73	177·16
190	463	482·0	655·33	23·21	165·64
200	473	560·85	762·54	17·89	151·84
210	483	649·75	883·41	13·43	134·78
220	493	747·9	1016·8	9·54	112·53
225	498	797·5	1084·3	7·83	99·50
230	503	851·9	1158·2	6·16	84·47
232	505	875·0	1189·7	5·50	77·73
234	507	897·5	1220·2	4·82	70·15
236	509	921·0	1252·2	4·11	61·66
238	511	945·5	1285·5	3·25	50·22
238·5	511·5	951·7	1294·0	2·84	44·23

The heat of vaporisation of methyl-alcohol has been determined by ANDREWS, and by FAVRE and SILBERMANN, at the boiling-point under ordinary pressure. The former found 263·7 calories, and the latter 263·86 calories. At the boiling-point our results give 266·7 calories; this is a satisfactory agreement.

From the foregoing account of our experiments with methyl-alcohol it is evident that the views which we have already expressed regarding alcohol and ether are substantiated; there is no tendency towards the formation of complex molecules at low temperatures.

This research is not so complete as the former two. We have made no attempt to determine the compressibility of the liquid. The cause of this omission is the very high pressure exerted by the vapour of methyl-alcohol at high temperatures. During these experiments we lost a volume-tube and a gauge by bursting; and, as the labour involved in replacing them was very great, we did not choose to risk further breakage.

The approximate critical pressure of methyl-alcohol is 59,700, the approximate temperature 240°, and the approximate volume 3·683 cub. centims. It is noticeable here that the difference in temperature between the boiling-points of methyl- and ethyl-alcohols is by no means the same as the difference between their critical temperatures.

In Plate 14 the relations between pressure, temperature, and volume for saturated and unsaturated vapour are shown; the orthothermic constants for the liquid are also given. The small diagram shows these relations between the pressures 1600 millims. and 60,000 millims. The critical isothermal is also given. The large diagram represents the higher temperatures observed; the circles are actual experimental points.

Plate 15 shows the densities, compared with hydrogen, of the saturated and unsaturated vapour mapped against pressure. It is here noticeable that the density of the saturated vapour becomes normal at low pressures and corresponding low temperatures.

Plate 16 shows the orthobaric densities of the liquid and vapour mapped against temperature, and their approach towards identity at the critical point.

Plate 17 gives the vapour-densities of the saturated vapour, and the heats of vaporisation, mapped against temperature. Again the rapid increase of density and the rapid decrease of latent heat as the critical point is approached are noticeable.

ADDENDUM.

(Added July 28, 1887.)

The value of such work as the foregoing evidently depends on the purity of the substance employed; and, as it appears that our paper is deficient in this proof, we adduce further evidence of the purity of the sample of methyl-alcohol employed in experiments on its thermal constants.

The proofs submitted are:—

1. Constancy of boiling-point.

2. Agreement of statical and dynamical methods of measuring vapour-pressures. (See Regnault, 'Mémoires de l'Académie des Sciences,' vol. 26, p. 341.)
3. Comparison of results with those of most careful observers.

1. *Constancy of boiling-point.* (Extracts from Note-book.)

"Methyl-alcohol prepared from methyl oxalate by action of ammonia: dried with barium oxide; dried with anhydrous copper sulphate; stood for some weeks (see Perkin, 'Chem. Soc. Journ.,' vol. 45, p. 465). Boiling-point by no means constant.

"Dried with sodium. A good deal boiled constantly at 65·55° (corr.). Bar. = 761·9 mms. at 0°, and then temperature rose.

"Dried again with sodium. A good deal boiled constantly at 65°; temp. rose slowly to 65·8°. Bar. same.

"Dried again with sodium. Began at 64·9°; most of it came over within a tenth. Temp. rose finally to 65·3°. Bar. same.

"Dried again with sodium. Began at 64·85°; most of it came over within half-a-tenth. Temp. rose to 65·05°. Bar. same.

"Dried again with sodium. Began at 64·8° (or a trace above). Temp. rose only to 64·9° (rather below)."

(All these temperatures are those of Regnault's air thermometer.)

Vapour-pressure determinations were then made by our method ('Chem. Soc. Trans.,' 1885, January).

"Alcohol re-distilled with a little sodium; B.P. 64·95°. Bar. = 761·9 mms. (at 0°.)"

The specific gravity was then taken.

"Methyl-alcohol re-distilled and fractionated; B.P. 64·7° at 760 mms. (at 0°). Range, 0·05°."

Experiments at high temperatures and pressures were then made, and, after these were completed,

"Fractionated alcohol was re-distilled; B.P. 64·2° at 743·2* mms. (corr. to 0°). The vapour-pressures were again determined in our apparatus."

The accompanying curve on Plate 18 shows the $\left\{\begin{matrix}\text{boiling-points} \\ \text{vapour-pressures}\end{matrix}\right\}$ of the two samples of methyl-alcohol.

2. *Agreement of statical and dynamical methods of measuring vapour-pressures.*

a. At low temperatures. No special measurements were made at low temperatures by the statical method, but two observations were incidental during the determination of the volumes of 1 gramme by means of the "modified Hofmann's apparatus." These are represented on the curve by large crossed circles. The actual numbers are:

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* Value of dp/dt at 60°, 25·47; at 70°, 35·38 mms. Sufficiently correct estimate at 65°, 30 mms. Add 0·55°. Corrected B.P. at 760 mms., 64·75°.

	Calculated by formula.	Found by statical method.
°	mms.	mms.
T = 40	260·47	262·4
T = 60	625·10	624·4

b. The formula $\log p = a + b\alpha^t + c\beta^t$ is BIOT'S. The constants were calculated from all observations by dynamical method at low temperatures, and by statical method at high temperatures. We reproduce the numbers showing the transition from the one method to the other.

Temperature.	Observed.		Calculated.
	Dynamical.	Statical.	
°	mms.	mms.	mms.
30	160·0	. .	160·28
40	260·5	. .	260·47
50	406·0	. .	409·47
60	625·0	. .	625·10
70	. .	. .	926·6
80	. .	1341	1340·3
90	. .	1897	1894·6
100	. .	2621	2622·5
110	. .	3561	3561·1

As regards the value of this method of determining the purity of a substance, we quote REGNAULT :—

"J'ai déjà fait voir, dans mon Mémoire sur les forces élastiques de la vapeur aqueuse (t. 21, p. 524), que cette coïncidence est parfaite pour l'eau ; les deux méthodes, statique et dynamique, donnant des valeurs identiques aux mêmes températures. Je montrerai qu'il en est de même pour les autres liquides volatils, pourvu qu'ils soient à l'état de pureté parfaite. Mais lorsqu'un liquide renferme une portion, même extrêmement petite, d'une autre substance volatile, les deux méthodes donnent des valeurs différentes pour les forces élastiques de sa vapeur à la même température ; et c'est un moyen extrêmement délicat pour juger de l'homogénéité d'une substance volatile." ('Mémoires de l'Académie des Sciences,' vol. 26, p. 341.) Again, p. 390 : "On peut déduire également de ces expériences sur l'éther que les forces élastiques de la vapeur, déterminées par la méthode statique et par la méthode dynamique, coïncident parfaitement lorsque la substance est homogène."

3. *Comparison of physical properties with those found by most careful observers.*

a. Boiling-point. Determined by numerous observers with most discordant results.

×	Pierre	66·3°	at 759	(at 0° ?)—Sp. gr. reduced to 0°		0·8207
×	Mendeléeff . .	66·0°	?	..	,,	0·8206
×	Kopp	64·9°	at 744	?	,,	0·8180
×	Delffs	60·5°	at 748	?	,,	0·8138
×	Dumas and Peligot .	66·5°	at 761	?	,,	0·8155
×	Deville.	..	..	..	,,	0·8153
×	Kopp (1845) . . .	65·0°	at 752	..	,,	0·8147
×	Kopp (1855) . . .	64·6–65·2°	at 744	..	,,	0·8142
×	Landolt.	66·0°	at 753	..	,,	0·8137
×	Duclaux	66·0°	?	..	,,	0·8128
BaO	Grodzki and Krämer	65·75–66·25°	?	(uncor.)	,,	0·8130
Na	,, ,,	65·6–66·2°	at 764·8	(uncor.)	,,	0·8116
	(Specially remarked that Na is preferable to BaO.)					
×	Graham	66·0°	?	..	,,	0·8105
K_2CO_3	Linnemann	67·1°	?	..	,,	0·8768
$CuSO_4$	Perkin	65·8–66°	? 760	..	$\frac{15^\circ}{4}$ . . . $\frac{25^\circ}{4}$ . . .	0·79658 0·78714
CaO	Regnault	?		Thermometer varied at same pressure within several degrees. Calculated 66·78°.		
Na	Schiff (once) . . .	64·8°	at 763.			

It is almost certain that every one of these observers has dried the sample of alcohol used over lime. Those marked with a × used either lime or gave no account of the method of drying, or we have not been able to verify the reference in Bristol.

Grodzki and Krämer specially state that sodium is preferable to barium oxide. Their results are close to ours (65·6 to 66·2 at 764·8 mms., not corrected to 0°, with the stem of their thermometer in vapour up to 30°).

Schiff distilled once over sodium, and obtained a number practically identical with ours (64·8 at 763 mms.).

The other results are all higher; that of Delffs is probably a misprint. (Perhaps not: see Kopp.)

b. Specific gravity. As Dr. Perkin has recently determined the specific gravity of methyl-alcohol, taking all precautions, and as the same method has been followed by ourselves, it is striking that the agreement is absolute.

Perkin . . . . $\frac{22{\cdot}94^\circ}{4^\circ}$ = 0·78908 (calculated).
Ramsay and Young . . . ,, = 0·78909.

Such a close coincidence, however, must be regarded as accidental.

It is specially to be noticed that Regnault did not obtain coincident results by the statical and dynamical methods. He says (vol. 26, p. 461): "La courbe graphique que j'ai tracée sur la planche V, d'après les éléments de cette Table, représente parfaitement les observations de la Série 1, et celles de la Série 3, qui dépassent 100°.

Mais toutes les expériences par ébullition, qui correspondent à des températures inférieures à 100°, donnent des points qui sont très-inférieurs à la courbe, comme si la vapeur du liquide bouillant avec soubresauts était suréchauffée. Je n'ai pas jugé utile de calculer une seconde formule pour laquelle les températures seraient prises sur le thermomètre à air." He evidently did not consider his results very trustworthy; and this is borne out by the fact that he did not determine the specific heat of the liquid, or its heat of vaporisation.

In conclusion, we append a Table of comparative results, including recent determinations by DITTMAR, as well as those by PERKIN, REGNAULT, SCHIFF, and RAMSAY and YOUNG.

BOILING-POINT.

REGNAULT	(calculated)	66°·78.
PERKIN	(observed)	65·8–66·0.
SCHIFF	(observed)	64·8.
DITTMAR	(calculated)	64·97.
RAMSAY and YOUNG	(calculated)	64·90.

VAPOUR-PRESSURES.

Temperature.	REGNAULT.	DITTMAR.	RAMSAY and YOUNG.
°	mms.	mms.	mms.
0	26·82	29·7	29·60
10	50·13	53·8	54·22
20	88·67	94·0	95·10
30	149·99	158·9	160·28
40	243·57	260·0	260·47
50	381·68	409·4	409·47
60	579·93	624·3	625·10
65	707·33	761·0	763·15

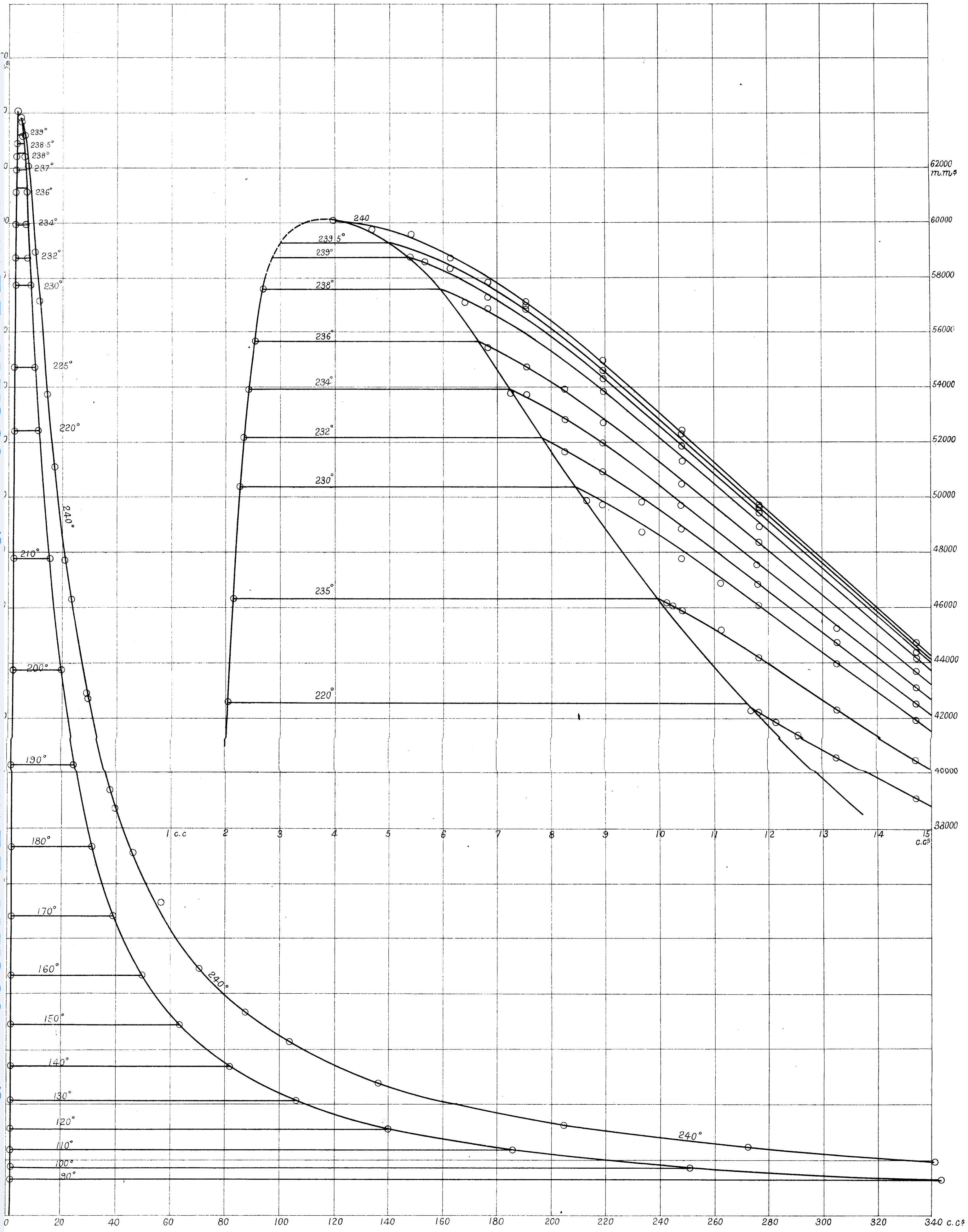
REGNAULT'S and DITTMAR'S results were obtained by the statical method; ours by the dynamical method. (See also our observations at 40° and 60° by statical method, p. 332.)

SPECIFIC gravity at 22·94°. (Water at 4° = 1·00000.)

DITTMAR	(calculated)	·78897.
PERKIN	(calculated)	·78908.
RAMSAY and YOUNG	(observed)	·78909.

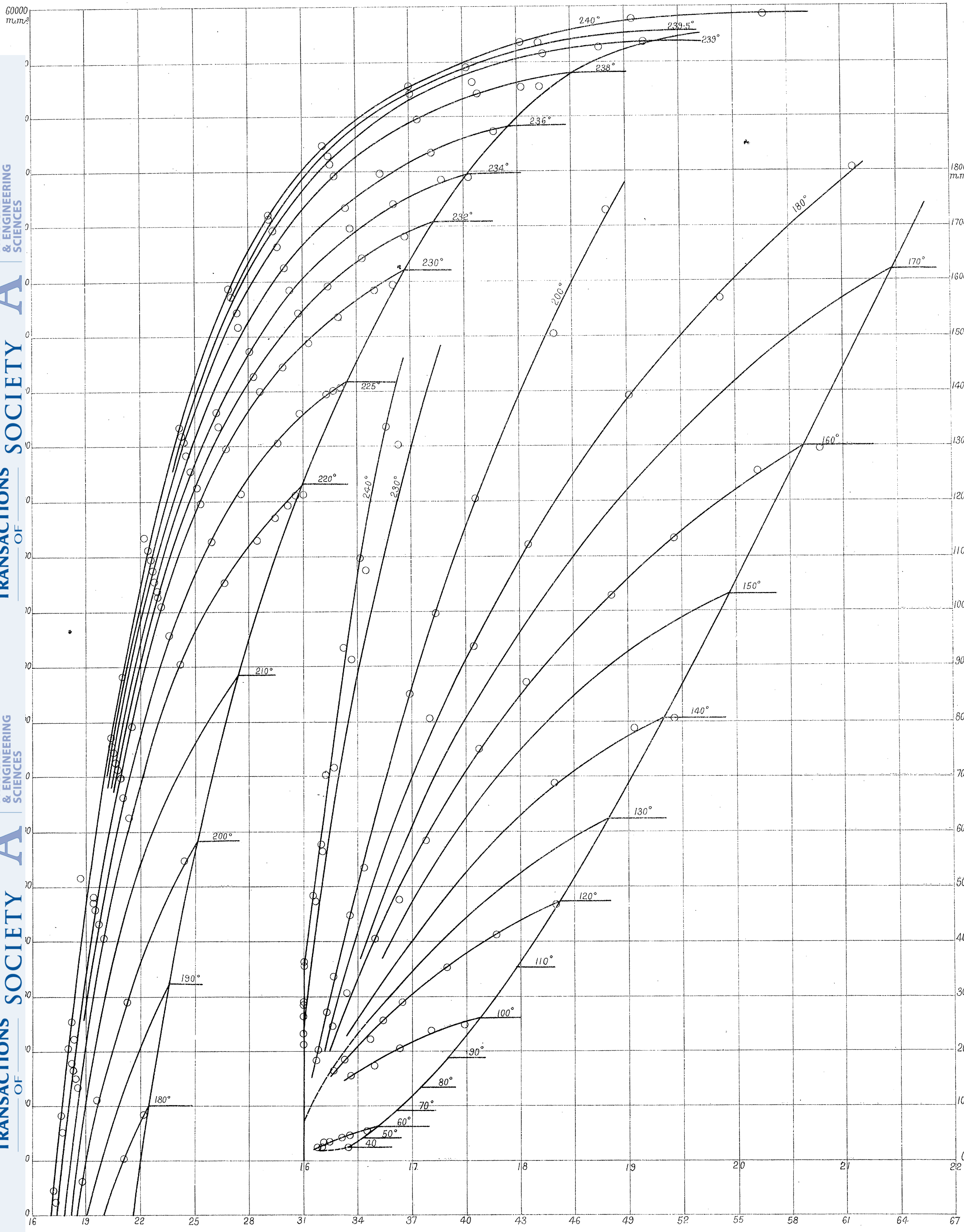
SPECIFIC gravity at 64·8°

DITTMAR	(calculated)	·74795.
SCHIFF	(observed)	·7476.



West, Newman & C° lith.

Volumes of 1 Gram Methyl Alcohol.



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Densities of Saturated and Unsaturated Vapour of Methyl Alcohol (H at t° and p. m.m^s = 1)

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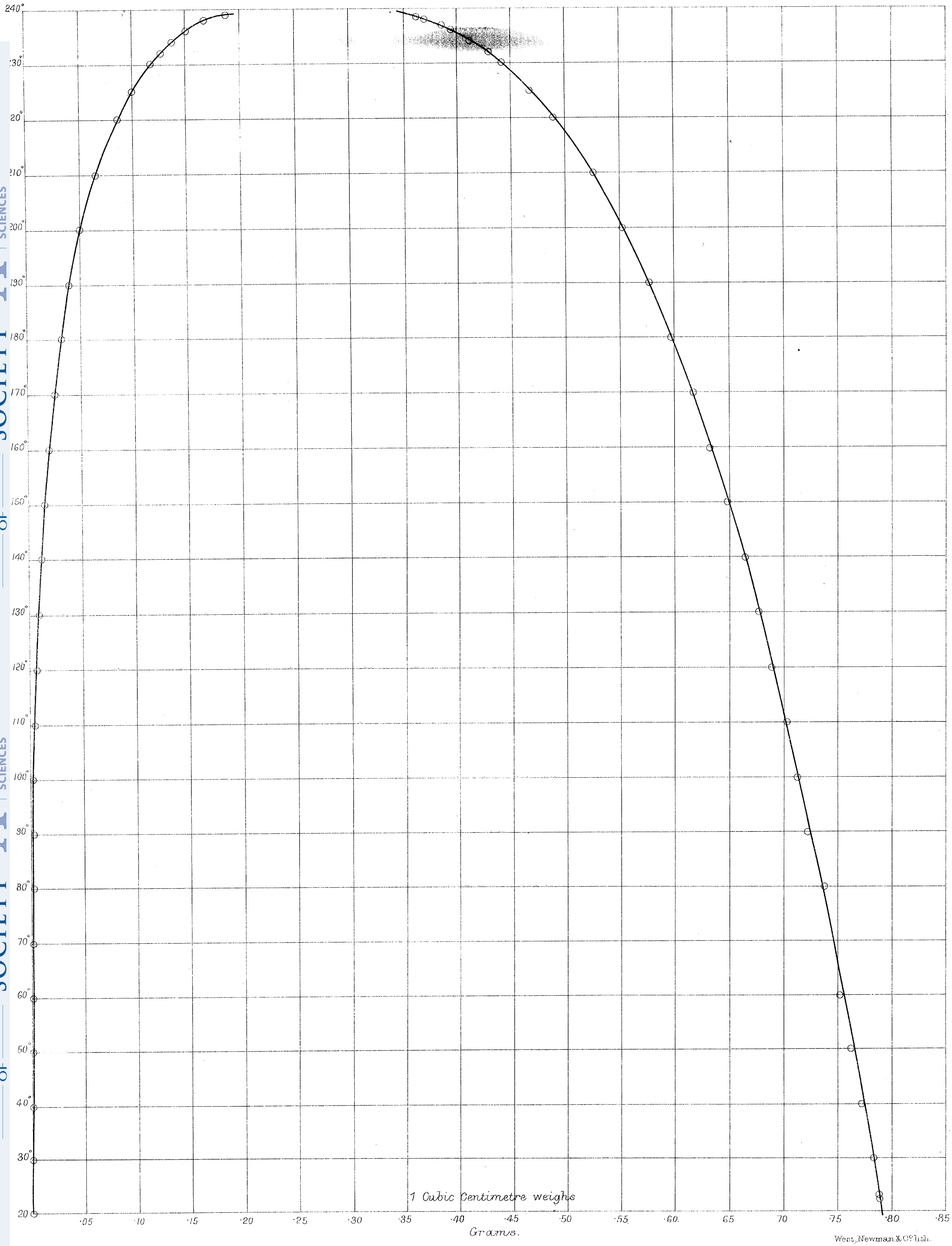

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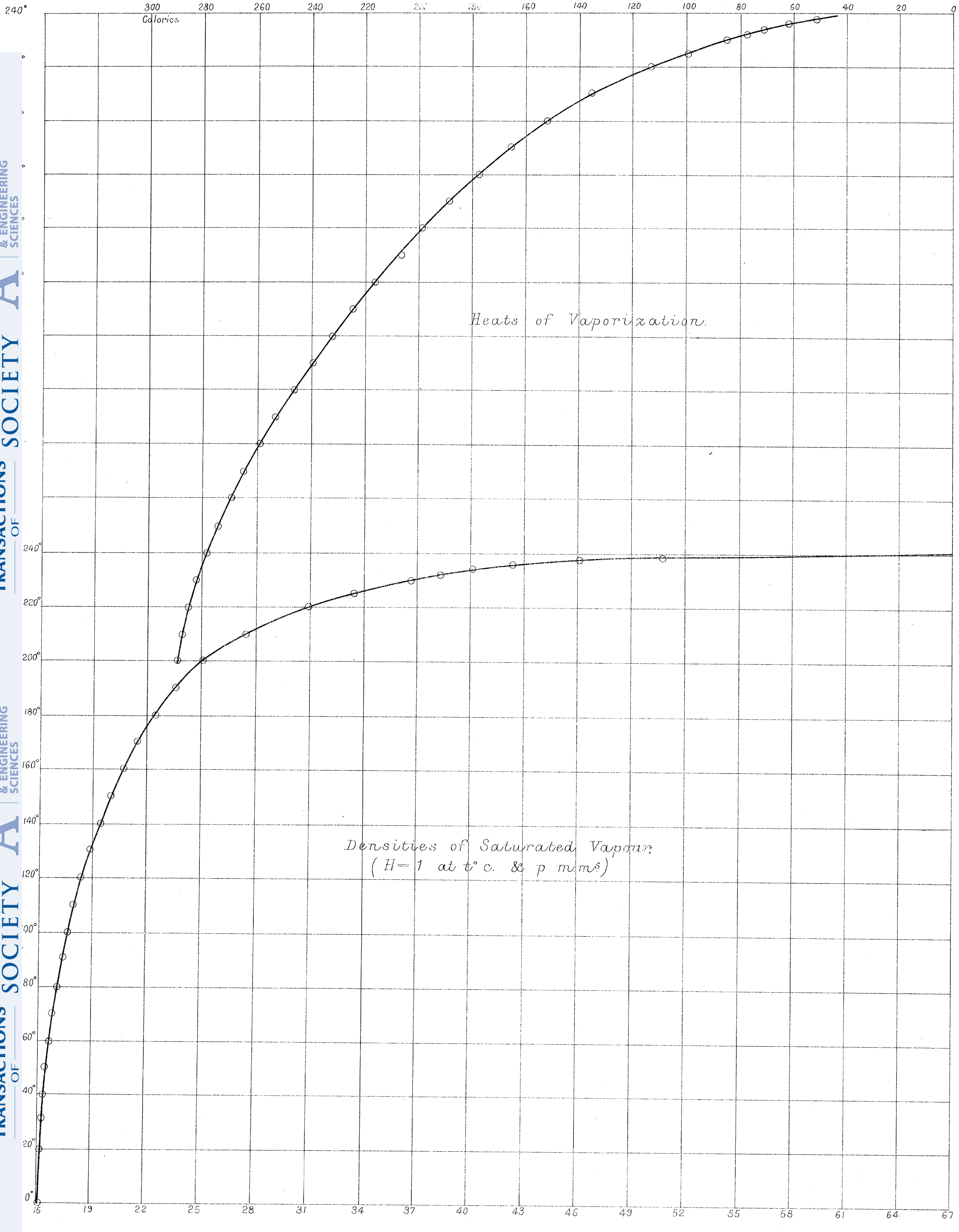

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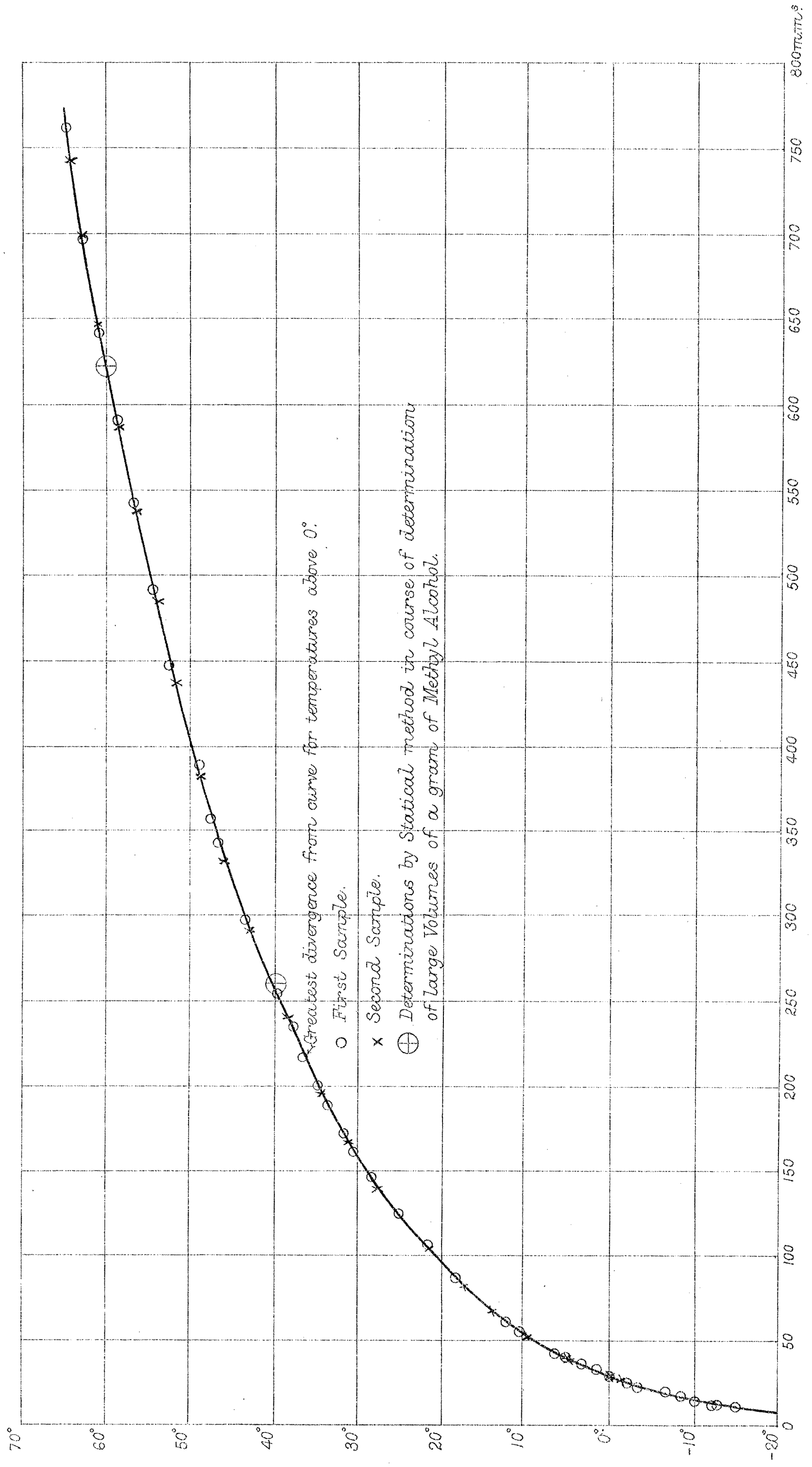

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