III. *On Evaporation and Dissociation.*—Part II. *A Study of the Thermal Properties of Alcohol.*

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[Plates 3–7.]

1. The density of gases is found to increase as the temperature falls towards their condensing point. This may be explained by one of two theories :—

(1) That complex gaseous molecules are formed in increasing numbers as the temperature falls; these complex molecules consisting of congeries of the simpler molecules known to exist in gases (see Playfair and Wanklyn, Trans. Roy. Soc. Edin., xxii., (3), p. 441, and 'Annalen,' 122, p. 245; also Naumann, 'Annalen,' 155, p. 325, and 'Thermochemie,' pp. 86 *et seq.*).

(2) That mutual attraction of the molecules, caused by their greater proximity, comes into play, and reduces their mean distance from each other.

The second of these hypotheses involves a deviation from Avogadro's law; while the first does not.

Similarly, with those substances in which dissociation takes place in the gaseous state, the density of the mixture of gases increases with fall of temperature, and this is doubtless caused by the increase in number of compound molecules. That this is the case with nitrogen peroxide can hardly be questioned, from the different physical properties of the gas under different conditions of temperature; and the phenomenon is also well seen in the case of tertiary amyl bromide.

It may be pointed out that both these causes may operate at the same time. It has occurred to us that light may be thrown on this question by a study of the thermal properties of three representative compounds :—

(1) What may be called a normal substance; *i.e.*, a substance in which no chemical dissociation is generally supposed to occur. Ethyl alcohol has been chosen as a representative of such a type.

(2) A substance the vapour-density of which shows marked abnormality, and which is suspected by many chemists of forming complex molecular groups. It is generally supposed that acetic acid, $C_2H_4O_2$, tends to form double molecules of the formula $C_4H_8O_4$, and that its abnormal vapour-density is to be explained on this hypothesis. Hence we have chosen it as a subject of experiment.

(3) It is hoped that it may be possible to effect a similar investigation of a sub-

stance which undoubtedly dissociates into dissimilar molecules, or the dissociation of which is undoubted from some change in its physical properties.

2. Such a study as we propose involves the determination, within the largest possible range of temperature, of the expansion of the liquid and of its compressibility; of the density of the vapour when unsaturated as well as when in contact with its liquid; and of the heat absorbed in producing change of state from liquid to gas.

We have already accumulated a number of data dealing with a portion of this problem; and as they are necessarily very voluminous, we deem it advisable to publish those bearing on the thermal constants of alcohol.

3. It is proposed to reserve until later a detailed description of the apparatus with which this research was executed. It will be sufficient here to state that it is a modification of ANDREWS' apparatus, provided with two air-gauges, one for measuring low, and the other for measuring high pressures. The temperature of each gauge was accurately known, for they were jacketed with running water in which a thermometer was immersed.

These gauges were graduated in millimetres and calibrated by weighing with mercury, and were filled with air dried with phosphorus pentoxide.

In calculating pressure, the following data were required:—

(1) The temperature and pressure of the air when the gauge was filled.

(2) The temperature of the air when readings were taken.

(3) The coefficient of compressibility of dry air, taking into account the deviation from BOYLE's law, as determined by AMAGAT, 'Comptes Rendus,' 99, p. 1153.

(4) The error of the gauges, corrected by calibration.

(5) The difference in height of the columns of mercury in the gauges and in the tube containing the liquid.

(6) The vapour-pressure of mercury in the experimental tube. At the highest temperature employed, 246°, it amounts to 68 mms., or about $\frac{1}{800}$th of the total pressure measured. For this, in many cases, we have applied no correction, for it is doubtful whether the mercury can give off vapour when its surface is covered by a long column of liquid. From experiments on the vapour-pressure of bromo-naphthalene at 237°, at which the vapour-pressure of mercury is 55 mms., it was noticed that a considerable time was required for the vapour to rise through a comparatively short column of liquid bromo-naphthalene. It is, therefore, probable that the full pressure of mercury vapour was not exercised: and the possible error is reduced below the experimental error of reading at such high pressures; but in the case of unsaturated vapour-densities, this correction was introduced.

4. The experimental tube, containing the alcohol, confined by mercury, was 200 mms. long, and was graduated in millimetres, and calibrated by weighing with mercury. It was made of lead-glass barometer-tube, with an internal diameter of about 2 mms. The coefficent of expansion of this glass was determined between 30° and 100°, and was found to be 0·0000257 per degree. In correcting for the meniscus of the mercury, the meniscus was regarded as a hemisphere.

A similar correction was made for the surface of the alcohol, no apparent change taking place until its temperature was raised to within a few degrees of its critical point. At those temperatures it was found that the error was inappreciable.

The experimental tube was heated by the vapours of pure liquids, boiling under pressures which could be varied at will. The vapour-pressures of these liquids have been accurately determined, temperature being measured with a mercury thermometer. Several measurements were carried out with an air-thermometer, and the necessary corrections were applied to reduce the readings of the mercurial thermometers used to those of an air-thermometer. The details of this investigation have been given in the Trans. Chem. Soc., 1886, p. 37; the results which are there published constitute a guarantee of the accuracy of the determination of temperature. We can state with confidence that at the highest temperature employed (246°) the absolute error does not amount to two or three-tenths of a degree; and the temperature can be altered with certainty through 0·05° by alteration of the pressure under which the liquid is boiling. This is, we believe, the only method by which a long tube can be uniformly heated; and by which the temperature can be easily and quickly altered. All the temperatures given are, therefore, those of an air-thermometer.

5. It is unnecessary to give details as regards reading, calibration, &c., for all our results. But as it may help to explain our method of procedure, one instance shall be given, and the method may be held to apply to all the other results.

The temperature on an air-thermometer at which aniline boils at an observed pressure of 703·2 mms., the temperature of the gauge being 14° (equivalent to 701·5 mms. at 0°), is 181·4°. At this temperature, the following readings were made:—Reading in experimental tube of upper surface of mercury, 210. Reading of upper surface of liquid, 139·7. Corresponding volumes corrected for meniscus: volume of liquid plus gas $=0·65974$ cc.; volume of gas $=0·39591$ cc. Add correction for expansion of glass; for higher volume, 0·00309; for lower volume, 0·00186. Corrected volumes $=(1)$ 0·66283; (2) 0·39777 cc. Volume of liquid $=0·26506$ cc.; volume of gas $=0·39777$ cc. The volume was subsequently reduced, until only a minute bubble of vapour was left uncondensed. It was thus made certain that the liquid, as such, was not being compressed. The corrected volume was then found to be 0·28706 cc. The weight of the liquid in the tube was 0·17083 grm.; this latter number was found from several readings of the volume at known low temperatures, and the known specific gravity of alcohol at those temperatures.

The specific gravity of alcohol under pressure corresponding to that of its own vapour at $181·4° = 0·17083/0·28706 = 0·5951$. From this number is deduced the weight of the liquid (vol.) $0·26506 \times$ (sp. gr.) $0·5951 = 0·15774$ grm. The weight of the vapour = total weight − weight of liquid $= 0·17083 - 0·15774 = 0·01309$ grm.

The weight of 1 cc. of vapour therefore equals its weight divided by its volume $= 0·01309$ grm./0·39777 cc. $= 0·0329$ grm.

Vapour density:—Weight of 1 cc. H at 181·4° and 15,163 mms. pressure $= 0·001074$. Hence $0·0329/0·001074 = 30·65$.

Pressure :—Reading on high-pressure gauge, 199·35. Temperature of gauge, 12·7°. Ratio of total volume of gauge tube to that of compressed air, the correction for the meniscus of the mercury in the gauge being applied, 20·008 : 1. Ratio corrected for temperature and pressure and for temperature at which gauge was filled =20·003 atmospheres =15,202−115*=15,087 mms. Add difference in heights of mercury in gauge and in experimental tube =76 mms., 15,087+76=15,163 mms. From this example an idea may be gathered as to the methods of reduction employed, and of the corrections introduced.

6. We now proceed to give results corrected by the method above explained.

PRESSURES of Vapour.

Vapour used as jacket.	T.	Number of observations.	Mean pressure in mms.
Chlorobenzene	89·85°	4	1,188
”	110·0	3	2,356
”	130·05	3	4,344
Bromobenzene	130·10	3	4,309
”	140·25	6	5,701
Methyl salicylate	150·0	3	7,353
Bromobenzene	150·65	6	7,400
Aniline	151·40	3	7,605
”	160·25	4	9,334
Methyl salicylate	161·0	3	9,647
Aniline	161·6	6	9,775
Methyl salicylate	171·0	3	12,170
Aniline	171·75	5	12,288
Methyl salicylate	180·95	3	15,078
Aniline	181·4	6	15,184
Methyl salicylate	189·8	4	18,102
Bromonaphthalene	199·3	3	21,851
Methyl salicylate	200·0	4	22,167
Bromonaphthalene	209·75	3	26,639
Methyl salicylate	210·05	4	26,894
Bromonaphthalene	219·9	3	31,990
”	219·9	3	31,967
Methyl salicylate	220·45	4	32,425
Bromonaphthalene	225·05	4	34,972
”	230·35	5	38,416
”	232·6	5	39,821
”	234·7	5	41,485
”	235·85	5	42,186
”	236·8	5	42,864
”	237·95	5	43,645
”	239·0	9	44,673
”	240·1	6	45,579
”	241·25	5	46,386
”	242·25	4	47,095
”	242·8	4	47,088
”	242·95	3	47,832
(Apparent critical point) . .	243·1	?	47,850

7. As it is impossible to distinguish between liquid and gas at the critical point, so it is impossible to give the vapour-pressure at the critical point. The pressures

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* Correction for divergence of dry air from BOYLE'S law.

recorded will be given when treating of the compressibility of the liquid. They remained constant within the limits of reading during a considerable reduction of volume.

8. The vapour-pressure of alcohol has been measured by **Regnault** up to 150°. On examining his tabulated results by the method of differences, it was found that the third differences show irregularity at and above 110°; on taking the fourth differences minus quantities begin to appear. We find that our numbers to some extent confirm this peculiarity of **Regnault**'s results. In order to calculate the pressures corresponding to even temperatures, the difference for 20°, *i.e.*, about 10° below and about 10° above the temperature requiring reduction was taken; and by dividing by the interval of temperature, the mean change for 1° was found. This was applied to reduce the pressure at the observed temperature to what it would be were the numbers representing temperature multiples of 10°. The error introduced by this somewhat crude method must necessarily be small, inasmuch as the required change of temperature seldom exceeds 1°.

From measurements, described in a later part of this paper, the vapour-pressure at 0° was found to be 12·24 mms. From this number, and from those at 60°, 120°, 180°, and 240°, constants for a formula of the type suggested by **Biot** were calculated. The formula is:—$\log p = a + b\alpha^t + c\beta^t$. The constants are:—$a = 5{\cdot}0720301$; $\log b = \bar{2}{\cdot}6406131$; $\log c = 0{\cdot}6050854$; $\log \alpha = 0{\cdot}003377538$; $\log \beta = \bar{1}{\cdot}99682424$ (c is negative).

T.	Numbers given by Regnault.		Numbers found by R. and Y.	Δ.	Numbers from above formula.	Difference of 4th place.
°						
0	12·70*	12·83†	12·24	0	12·24	..
10	24·23	24·30	23·77	+ ·05	23·73	..
20	44·46	44·48	44·00	+ ·03	43·97	2·132
30	78·52	78·49	78·06	− ·05	78·11	2·627
40	133·69	133·64	..	..	133·42	2·994
50	219·90	219·88	..	..	219·82	3·417
60	350·21	350·26	..	..	350·21	3·570
70	541·15	541·21	..	..	540·91	3·73
80	812·91	812·76	..	..	811·81	3·61
90	1189·30	1188·43	1194·3	+ 7·8	1186·5	3·46
100	1697·55	1694·92	..		1692·3	3·26
110	2367·64	2361·63	2356	− 3·9	2359·8	2·90
120	3231·73	3219·68	..	..	3223·0	2·72
130	4323·00	4301·04	4320	+ 1·3	4318·7	2·57
140	5674·59	5637·00	5666	− 20·6	5686·6	2·75
150	7318·40	7258·73	7326	− 42·7	7368·7	2·79
160	..	..	9366	− 43·9	9409·9	3·44
170	..	..	11856	− 2·0	11858	5·94
180	..	..	14763	− 1·0	14764	3·94
190	..	..	18178	− 7·0	18185	9·0
200	..	..	22164	− 18·0	22182	12·0
210	..	..	26821	− 4·0	26825	12·0
220	..	..	32097	− 99·8	32196	21·0
230	..	..	38176	−213	38389	..
240	..	..	45504	− 15	45519	..

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* 'Mémoires de l'Institut,' vol. xxvi., p. 374.

† 'Comptes Rendus,' vol. l., 1860, p. 1067.

9. *Specific Gravities and Specific Volumes.*

In order to ascertain the specific gravity of alcohol, it was necessary to know the volumes at various temperatures, and the total weight of substance. As the weight was not the same throughout, losses having occurred through breakage, it was not possible to obtain the weight directly. It was, therefore, necessary to deduce the weight from the volume and the known specific gravity at low temperatures.

The results given by different observers are, however, not uniform. We quote some of these; in all cases comparison is made with water at 4° as unity.

	Sp. gr.	Sp. vol.
Pierre ('Annalen,' 56, p.142, and 'Annales,' 15, p. 325) . . .	0·81510	1·2268
Kopp ('Annalen,' 64, p. 213)	0·80950	1·2351
Mendelejeff ('Annalen,' 119, p. 7)	0·80832	1·2371
Perkin (Chem. Soc. Journ., 45, p. 465)	0·80696	1·2392
Mendelejeff (Roscoe and Schorlemmer, vol. iii., pt. 1, p. 299) .	0·80625	1·2403
Squibb (Chem. News, 51, p. 21)	0·80573	1·2411

In calculating our results, the number 1·2403 was taken; it will be seen that the mean of the last three results, which are probably the best, is 1·2402. The alcohol employed had been frequently distilled over lime, and was finally dried by distillation with a little sodium. It boiled with perfect constancy.

10. During these experiments, an accident occurred, by which we lost the first portion of alcohol; the tube was therefore refilled. We shall name the first portion A, and the second B, in giving data.

	T. °	V.	Wt.	Mean.
A.	16·5	0·21557	0·17082	0·17083
	16·7	0·21564	0·17084	
B.	15·0	0·21954	0·17420	

11. In the following table, the pressure under which the liquid was measured, was in general the vapour-pressure corresponding to the temperature. The asterisked figures are corrected to this standard from observation on the compressibility.

A.	T.	Volume.	Sp. gr.	Sp. vol. $=\frac{1}{\text{sp. gr.}}$ =vol. of 1 grm.	Volume, $V_0=1·0$.
		cub. centims.			
	110°	0·24119	0·70606	1·4163	..
	130·05	0·25150	0·6792	1·4723	1·1871
	140·25	0·25821	0·6616	1·5115	1·2187
	150·65	0·26454	0·6458	1·5486	1·2486
	161·60	0·27038	0·6318	1·5828	1·2761
	171·75	0·27830	0·6138	1·6291	1·3135
	181·40	0·28706	0·5951	1·6804	1·3548
	189·80	0·29474	0·5796	1·7254	1·3911
	200·00	0·30671	0·5570	1·7954	1·4475
	210·05	0·32292	0·5290	1·8903	1·5241
	220·45	0·34572	0·4941	2·0238	..
*	,,	..	0·4943	2·0232	1·6312
	225·05	0·35731	0·4781	2·0917	1·6864
	230·35	0·37479	0·4558	2·1940	..
*	,,	..	0·4535	2·2051	..
	232·60	0·38482	0·4439	2·2527	..
*	,,	..	0·4420	2·2626	..
	234·70	0·39890	0·4282	2·3351	..
*	,,	..	0·4280	2·3367	..
	235·85	0·40449	0·4223	2·3678	..
*	,,	..	0·4214	2·3729	..
	236·80	0·41457	0·4121	2·4269	..
*	,,	..	0·4112	2·4317	..
	237·95	0·41906	0·4076	2·4531	..
*	,,	..	0·4055	2·4659	..
	239·0	0·42819	0·3989	2·5066	..
*	,,	..	0·3954	2·5291	..

B.	T.	Volume.	Sp. gr.	Sp. vol. (V. of 1 grm.)	Volume, $V_0=1·0$.	Mean of A and B volume, $V_0=1·0$.
		cub. centims.				
	160°·25	0·27523	0·6329	1·5800	1·2739	..
	230·35	0·38567	0·4517	2·2140	..	1·7814
	232·60	0·39539	0·4406	2·2698	..	1·8271
	234·70	0·40784	0·4271	2·3412	..	1·8858
	235·85	0·41382	0·4210	2·3755	..	1·9142
	236·80	0·42129	0·4135	2·4184	..	1·9551
	237·95	0·43188	0·4034	2·4792	..	1·9935
	239·00	0·44346	0·3928	2·5457	..	..
	239·00	0·44624	0·3904	2·5617	..	..
*	,,	..	0·3898	2·5654	..	2·0533
	240·10	0·46006	0·3786	2·6410	..	..
*	,,	..	0·3802	2·6303	..	..
	240·10	0·45481	0·3830	2·6108	2·1128	..
	241·25	0·47426	0·3673	2·7225	..	..
	241·25	0·47087	0·3699	2·7030	2·1871	..
	242·25	0·50610	0·3442	2·9053	..	..
	242·25	0·49528	0·3517	2·8432	2·2956	..
	242·80	0·52291	0·3331	3·0019	..	..
	242·80	0·51619	0·3375	2·9632	2·4046	..
	242·95	0·56026	0·3109	3·2162	2·5930	..

12. *Compressibility.*

The compressibility was measured by increasing the pressure, and after some time reading the volume of the liquid. It was noticed that heat was developed by compression, hence time was allowed for the heat to dissipate before reading. The following are the results :

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
110°	2,358	0·24119	1·4163	230·35°	38,914	0·38331	2·2004
,,	13,432	0·23970	1·4076	,,	39,722	0·37958	2·1790
,,	38,065	0·23784	1·3967	,,	41,156	0·37573	2·1569
130·05	4,344	0·25150	1·4723	,,	42,695	0·37201	2·1355
,,	6,720	0·25057	1·4668	,,	44,464	0·36816	2·1134
,,	14,694	0·24971	1·4618	,,	46,647	0·36442	2·0919
,,	21,268	0·24926	1·4591	,,	48,591	0·36071	2·0707
,,	38,055	0·24758	1·4493	,,	50,675	0·35701	2·0494
140·25	5,760	0·25821	1·5115	,,	53,522	0·35326	2·0279
,,	6,707	0·25784	1·5094	,,	55,264	0·35139	2·0265
,,	8,643	0·25779	1·5091	232·60	40,143	0·38482	2·2527
,,	13,634	0·25736	1·5065	,,	41,360	0·37959	2·2220
,,	22,088	0·25653	1·5017	,,	46,650	0·36444	2·1334
,,	39,331	0·25391	1·4864	,,	61,536	0·34259	2·0054
150·65	7,460	0·26454	1·5486	232·60	39,918	0·39539	2·2698
,,	15,198	0·26286	1·5387	,,	40,963	0·39090	2·2440
,,	21,900	0·26173	1·5321	,,	41,758	0·38719	2·2226
,,	38,993	0·26034	1·5240	,,	42,906	0·38333	2·2005
160·25	9,190	0·27523	1·5800	,,	43,949	0·37959	2·1790
,,	20,828	0·27262	1·5650	,,	45,590	0·37575	2·1570
,,	37,058	0·27000	1·5499	,,	47,037	0·37202	2·1356
,,	61,037	0·26702	1·5328	,,	48,851	0·36817	2·1135
161·60	9,804	0·27038	1·5828	,,	51,433	0·36443	2·0920
,,	21,977	0·26852	1·5719	,,	53,441	0·36073	2·0708
,,	39,130	0·26553	1·5544	,,	55,905	0·35703	2·0496
171·75	12,366	0·27830	1·6291	234·70	41,571	0·39890	2·3351
,,	22,090	0·27606	1·6160	,,	46,614	0·37578	2·1997
,,	39,158	0·27270	1·5964	,,	61,749	0·34807	2·0376
,,	64,235	0·26860	1·5724	234·70	41,566	0·40784	2·3412
181·40	11,465	0·28817	1·6869	,,	42,379	0·40224	2·3091
,,	15,149	0·28706	1·6804	,,	43,022	0·39845	2·2873
,,	38,545	0·28099	1·6449	,,	43,902	0·39467	2·2656
,,	63,482	0·27577	1·6143	,,	44,696	0·39093	2·2442
189·80	18,011	0·29474	1·7254	,,	45,837	0·38721	2·2228
,,	63,769	0·28264	1·6545	,,	46,958	0·38335	2·2006
200	22,207	0·30671	1·7954	,,	48,084	0·37962	2·1792
,,	63,838	0·29166	1·7074	,,	49,631	0·37578	2·1571
210·05	26,976	0·32292	1·8903	,,	51,584	0·37205	2·1357
,,	61,911	0·30429	1·7813	,,	52,861	0·36820	2·1137
220·45	32,336	0·34572	2·0238	,,	55,631	0·36446	2·0922
,,	62,157	0·31950	1·8703	235·85	42,278	0·40449	2·3678
225·05	34,932	0·35731	2·0917	,,	46,685	0·38075	2·2288
,,	46,548	0·33980	1·9891	,,	61,836	0·35070	2·0530
,,	61,664	0·32695	1·9139	235·85	42,309	0·41382	2·3755
230·35	38,802	0·37479	2·1940	,,	42,942	0·40971	2·3520
,,	46,430	0·35524	2·0795	,,	43,496	0·40599	2·3306
,,	61,524	0·33810	1·9792	,,	44,170	0·40225	2·3092
230·35	38,386	0·38567	2·2140	,,	44,641	0·39846	2·2873

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
°				°			
235·85	45,228	0·39468	2·2657	240·1	45,567	0·46006	2·6410
,,	46,316	0·39094	2·2442	,,	52,511	0·39695	2·2787
,,	47,356	0·38722	2·2228	,,	61,065	0·37420	2·1481
,,	48,834	0·38336	2·2007	240·1	45,347	0·45481	2·6108
,,	50,032	0·37963	2·1793	,,	45,861	0·44720	2·5671
,,	51,761	0·37579	2·1572	,,	46,225	0·43973	2·5243
,,	53,535	0·37206	2·1358	,,	46,662	0·43240	2·4822
,,	55,309	0·36821	2·1137	,,	47,366	0·42475	2·4383
236·80	42,951	0·41457	2·4269	,,	48,295	0·41721	2·3950
,,	46,703	0·38860	2·2748	,,	49,566	0·40975	2·3522
,,	61,858	0·35368	2·0704	,,	51,194	0·40229	2·3093
236·8	42,888	0·42129	2·4184	,,	52,783	0·39472	2·2659
,,	43,421	0·41718	2·3948	,,	55,540	0·38726	2·2231
,,	43,752	0·41346	2·3734	241·25	46,452	0·47426	2·7225
,,	44,202	0·40972	2·3520	,,	52,641	0·40492	2·3245
,,	44,892	0·40600	2·3307	,,	61,218	0·37899	2·1756
,,	45,722	0·40226	2·3092	241·25	46,107	0·47087	2·7030
,,	46,333	0·39847	2·2874	,,	46,230	0·46227	2·6537
,,	47,179	0·39469	2·2657	,,	46,476	0·45482	2·6109
,,	48,025	0·39095	2·2442	,,	46,863	0·44721	2·5672
,,	49,125	0·38723	2·2229	,,	47,369	0·43974	2·5244
,,	50,435	0·38337	2·2007	,,	47,767	0·43241	2·4823
,,	51,973	0·37964	2·1793	,,	48,655	0·42476	2·4383
,,	53,433	0·37580	2·1573	,,	49,713	0·41722	2·3951
,,	55,349	0·37207	2·1358	,,	50,898	0·40976	2·3522
237·95	43,840	0·41906	2·4531	,,	52,785	0·40230	2·3094
,,	46,724	0·39507	2·3127	,,	54,739	0·39473	2·2659
,,	62,881	0·35704	2·0901	,,	55,716	0·39099	2·2445
237·95	43,742	0·43188	2·4792	242·25	47,137	0·50610	2·9053
,,	43,962	0·42846	2·4596	,,	52,498	0·41685	2·3929
,,	44,089	0·42473	2·4381	,,	61,025	0·38342	2·2010
,,	44,527	0·42092	2·4163	242·25	47,000	0·49528	2·8432
,,	45,119	0·41719	2·3949	,,	47,066	0·48849	2·8042
,,	45,714	0·41347	2·3735	,,	47,257	0·47722	2·7395
,,	46,318	0·40973	2·3521	,,	47,644	0·46603	2·6752
,,	46,960	0·40601	2·3307	,,	48,173	0·45483	2·6110
,,	47,610	0·40227	2·3092	,,	48,723	0·44349	2·5453
,,	48,274	0·39848	2·2875	,,	49,716	0·43242	2·4823
,,	49,395	0·39470	2·2658	,,	51,048	0·42096	2·4165
,,	50,419	0·39096	2·2443	,,	52,943	0·40977	2·3523
,,	51,643	0·38724	2·2230	,,	55,717	0·39852	2·2877
,,	52,922	0·38338	2·2008	242·60	47,282	0·52291	3·0019
,,	54,445	0·37965	2·1794	,,	47,528	0·49603	2·8475
,,	56,054	0·37580	2·1573	,,	47,795	0·47723	2·7396
239·0	44,774	0·42819	2·5066	,,	48,322	0·45857	2·6324
,,	46,724	0·40619	2·3778	,,	49,588	0·43976	2·5245
,,	61,882	0·36078	2·1119	,,	51,526	0·42097	2·4166
239·0	44,978	0·44624	2·5617	,,	55,216	0·40231	2·3095
,,	52,318	0·39097	2·2444	243·10	47,631	0·54458	3·1262
,,	60,958	0·37158	2·1330	,,	47,669	0·53336	3·0618
239·0	44,665	0·44346	2·5457	,,	47,706	0·51469	2·9546
,,	44,776	0·43599	2·5028	,,	47,971	0·49603	2·8475
,,	45,359	0·42847	2·4596	,,	48,298	0·47723	2·7396
,,	46,220	0·42093	2·4164	,,	49,203	0·45857	2·6324
,,	47,240	0·41348	2·3736	,,	50,284	0·43976	2·5245
,,	48,436	0·40602	2·3308	,,	52,286	0·42097	2·4166
,,	50,133	0·39849	2·2875	,,	56,745	0·40231	2·3095
,,	51,976	0·39097	2·2443	243·1	47,127	0·92225	5·2942
,,	54,820	0·38339	2·2008	,,	47,178	0·88520	5·0815

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
°				°			
243·10	47,242	0·86672	4·9754	243·55	61,121	0·38803	2·2275
,,	47,297	0·84818	4·8690	244·35	48,278	0·88522	5·0816
,,	47,360	0·82964	4·7626	,,	48,269	0·84820	4·8691
,,	47,423	0·81111	4·6562	,,	48,386	0·81096	4·6553
,,	47,471	0·79268	4·5504	,,	48,627	0·77421	4·4444
,,	47,528	0·77419	4·4443	,,	48,935	0·73760	4·2342
,,	47,523	0·75589	4·3392	,,	49,054	0·70118	4·0251
,,	47,587	0·73758	4·2341	,,	49,105	0·66387	3·8104
,,	47,653	0·79198	4·1258	,,	49,215	0·62653	3·5966
,,	47,659	0·70086	4·0233	,,	49,205	0·58937	3·3833
,,	47,654	0·66228	3·9166	,,	49,195	0·55205	3·1691
,,	47,649	0·66385	3·8108	,,	49,316	0·51472	2·9548
,,	47,644	0·64516	3·7026	,,	50,088	0·47724	2·7396
,,	47,639	0·62651	3·5965	,,	52,452	0·43976	2·5251
,,	47,634	0·60795	3·4900	,,	61,144	0·39585	2·2724
,,	47,629	0·58937	3·3833	246·0	49,483	0·88526	5·0818
,,	47,624	0·57070	3·2761	,,	49,673	0·84824	4·8693
,,	47,620	0·55204	3·1690	,,	49,791	0·81100	4·6555
,,	47,614	0·53336	3·0618	,,	49,917	0·77425	4·4446
,,	47,679	0·51469	2·9546	,,	49,977	0·73763	4·2344
,,	47,813	0·49603	2·8475	,,	50,030	0·70121	4·0253
,,	48,215	0·48097	2·7610	,,	50,020	0·66390	3·8111
243·55	48,148	0·88520	5·0815	,,	50,010	0·62656	3·5968
,,	48,131	0·81094	4·6552	,,	50,268	0·58941	3·3835
,,	48,159	0·73758	4·2341	,,	50,668	0·55208	3·1692
,,	48,395	0·66385	3·8109	,,	50,934	0·51474	2·9549
,,	48,433	0·58937	3·3833	,,	52,042	0·47727	2·7397
,,	48,476	0·51471	2·9547	,,	54,607	0·43979	2·5246
,,	48,915	0·47723	2·7113	,,	61,007	0·40152	2·3049
,,	51,216	0·43976	2·5245				

The graphic representation of these numbers shows that the compressibility at low temperatures is nearly constant through a large range of pressure; but at high temperatures it varies, decreasing rapidly as pressure rises, and near the critical point, as observed by ANDREWS, the liquid is much more compressible than a gas.

13. By plotting these results in curves, we are enabled to give the volumes occupied by liquid alcohol at constant pressures, with variation of temperature. To do so, however, required a somewhat tedious process. The actual results were plotted on curve paper, and by means of engineers' curves (circles of different radii), lines were drawn, occupying as nearly as could be judged a mean position among the observed points. From these curves the volumes for certain definite pressures were read off, intervals of 5000 mms. at low temperatures, and 2500 or 1250 mms. at high temperatures being chosen. From these numbers fresh curves were constructed, showing relations between temperature and volume for a series of pressures. These curves were also smoothed, and the results obtained by their means retransferred to the first set of curves. The curves published in Plate 3 show these doubly-smoothed curves, and the actual observations are also shown by circles, which will enable the amount of error to be estimated. The temperatures of the isothermals are written

on the horizontal lines which represent change of volume without increase of pressure, where vapour in contact with liquid is being condensed.

14. The temperatures given are those read directly, with two exceptions, viz., 242·8° was altered to 242·6°, and 243·25° was altered to 243·55°. The reason for this alteration was that in drawing the isobaric curves, deduced from the isothermals, the observed points at those temperatures differed from the curve in every case by the same amount. This error is really a very small one at such high temperatures, and may depend on some mistake in reading the pressure under which the bromonaphthalene used as a jacket was boiling.

It is to be remarked that by this double method of smoothing any great irregularity of temperature would at once be detected; this is shown by the corrections above referred to.

15. From the isobaric curves we give results deduced for definite intervals of temperature and pressure.

T.	5000 mms.	10,000.	15,000.	20,000.	25,000.	30,000.	35,000.	40,000.	42,500.	45,000.	47,500.	50,000.	52,500.	55,000.	57,500.	60,000.	62,500.
110	1·414	1·411	1·408	1·405	1·402	1·400	1·399	1·398	..	1·396	..	1·395	..	1·394	..	1·393	..
120	1·441	1·437	1·433	1·430	1·428	1·426	1·424	1·421	..	1·420	..	1·418	..	1·416	..	1·413	..
130	1·470	1·466	1·462	1·459	1·456	1·452	1·450	1·449	..	1·446	..	1·444	..	1·442	..	1·441	..
140	..	1·499	1·494	1·490	1·486	1·483	1·480	1·478	..	1·477	..	1·472	..	1·470	..	1·468	..
150	..	1·536	1·530	1·524	1·519	1·517	1·512	1·510	..	1·508	..	1·504	..	1·501	..	1·500	..
160	..	1·577	1·569	1·562	1·558	1·554	1·550	1·547	..	1·542	..	1·540	..	1·537	..	1·534	..
170	..	..	1·616	1·607	1·600	1·597	1·591	1·588	..	1·582	..	1·580	..	1·576	..	1·572	..
180	..	..	1·666	1·660	1·653	1·647	1·642	1·636	..	1·631	..	1·625	..	1·620	..	1·615	..
190	..	..	..	1·724	1·714	1·706	1·699	1·690	..	1·681	..	1·676	..	1·669	..	1·661	..
200	..	..	..	..	1·790	1·779	1·767	1·755	..	1·745	..	1·736	..	1·727	..	1·719	..
210	..	..	..	..	..	1·869	1·850	1·834	1·828	1·820	1·813	1·809	1·801	1·797	1·791	1·788	1·781
215	..	..	..	..	..	..	1·909	1·882	1·872	1·863	1·857	1·850	1·842	1·837	1·831	1·827	1·820
220	..	..	..	..	..	..	1·982	1·946	1·930	1·919	1·908	1·898	1·890	1·881	1·877	1·870	1·862
225	..	..	..	..	..	..	2·092	2·039	2·015	1·998	1·979	1·963	1·950	1·939	1·930	1·920	1·911
230	..	..	..	..	..	..	..	2·163	2·129	2·099	2·072	2·050	2·029	2·009	1·998	1·982	1·970
232	..	..	..	..	..	..	..	2·240	2·191	2·150	2·120	2·090	2·067	2·041	2·027	2·010	1·999
234	..	..	..	..	..	..	..	..	2·265	2·210	2·171	2·135	2·104	2·078	2·059	2·040	2·025
236	..	..	..	..	..	..	..	..	..	2·290	2·232	2·188	2·150	2·117	2·097	2·073	2·053
238	..	..	..	..	..	..	..	..	..	2·400	2·311	2·250	2·203	2·161	2·140	2·110	2·088
240	..	..	..	..	..	..	..	..	..	..	2·428	2·328	2·268	2·214	2·189	2·156	2·131
242	..	..	..	..	..	..	..	..	..	..	..	2·441	2·351	2·284	2·248	2·208	2·176
244	..	..	..	..	..	..	..	..	..	..	..	..	2·493	2·380	2·325	2·270	2·222
246	..	..	..	..	..	..	..	..	..	..	..	..	..	2·497	2·418	2·341	2·280

16. A set of determinations have been made by ZUK (Z. Rusk. Chim. Obs., 13 (2), p. 239) of the volumes of alcohol under the critical pressure observed by SAJOTCEWSKY of 62·1 atmospheres (=47,196 mms.). We are now in a position to compare our results with his. ZUK adopts the specific gravity 0·80614 at 0°, a number close to that adopted by us, 0·80625. The comparison is as follows:—

T.	$V_{0°}=1$.	
	R. and Y.	Zuk.
°		
124·3	1·153	1·1667
132·5	1·170	1·1828
140·2	1·189	1·2004
150·6	1·216	1·2291
169·8	1·274	1·2914
181·0	1·317	1·3387
190·5	1·357	1·3815
200·5	1·406	1·4398
211·6	1·473	1·5228
218·5	1·524	1·5983

It is evident that there are considerable differences between the two sets of results. These are probably to be accounted for by differences in temperature. It should be remarked that ZUK employs as the temperature of the critical point 233·7°. The formula used by ZUK is one given by AVENARIUS, viz.:—

$$V=220{\cdot}59-50{\cdot}91\log(233{\cdot}7-t).$$

As this formula is entirely empirical, there is nothing to be gained by its use, although it appears to give an approximation to the found results.

17. We are now able to give the specific volumes and specific gravities of liquid alcohol at definite intervals of temperature and at pressures equal to the vapour-pressures at those temperatures. They are given in the following table. They are read from a smoothed curve representing individual observations of temperature and volume, and checked by means of the curves representing compressibility for known rise of pressure at constant temperature. In Plate 3, the observations shown by circles determine the direction of each curve. The curve connecting their terminals, which exhibits relations between the volume of the liquid, the temperatures, and the pressures equal to the vapour-pressures at those temperatures, was constructed by correcting the volumes when not read at the true vapour-pressures to the true volumes at those pressures. The curve was drawn through the points thus obtained, and it was seen that the points of intersection of these curves confirmed the position of points on a curve representing the relations between volumes and temperatures at the vapour-pressures corresponding to the temperatures. We would suggest the

name "orthobaric" as applicable to such a curve, and "orthothermic" to denote the curve representing relations between volumes and pressures at temperatures corresponding to the vapour-pressures of the substance.

18. It would be possible to obtain the volumes of 1 gram of the liquid at definite temperatures and at corresponding vapour-pressures directly from the "orthobaric" curve, or by constructing new isothermals, by means of the isobaric curves, for such temperatures and reading the points of intersection of such curves with the "orthothermic" curve. Since the results for the temperatures of observation were practically identical, it was judged sufficient to read them directly from the "orthobaric" curve.

19. The numbers thus read are as follows;—

SPECIFIC Volumes * and Specific Gravities of Alcohol at Definite Temperatures, and at the Vapour-pressures corresponding to these Temperatures.

T.	Sp. v.	Sp. gr.	T.	Sp. v.	Sp. gr.
°			°		
110	1·417	0·7057	225	2·094	0·4775
120	1·444	0·6925	230	2·198	0·4550
130	1·473	0·6789	232	2·250	0·4444
140	1·508	0·6631	234	2·314	0·4292
150	1·541	0·6489	236	2·390	0·4184
160	1·580	0·6329	237	2·435	0·4107
170	1·622	0·6165	238	2·483	0·4027
180	1·671	0·5984	239	2·541	0·3935
190	1·7295	0·5782	240	2·614	0·3825
200	1·796	0·5568	241	2·699	0·3705
210	1·890	0·5291	242	2·820	0·3546
220	2·017	0·4958	242·5	2·925	0·3419

20. For the sake of comparison, we give HIRN'S ('Annales,' (4), 10, p. 32) and MENDELEJEFF'S (*loc. cit.*) numbers.

MENDELEJEFF . . $T=130{\cdot}9^\circ$ ($V_0=1$); 1·1895. Found (R. and Y.) 1·190.
HIRN. . . . . $T=150{\cdot}0^\circ$ ($V_0=1$); 1·24074. Found (R. and Y.) 1·243.

ZUK also, *loc. cit.*, gives numbers for the volumes of alcohol. These have already been considered.

Specific Volumes and Specific Gravities of Saturated Vapour of Alcohol.

21. It has been explained in § 5 how the volume of the saturated vapour was measured, and the various corrections introduced. We now proceed to give the experimental numbers.

---

* As some confusion has been introduced by the use of the phrase "specific volume" as synonymous with "atomic" or "molecular volume," it should here be stated that the expression is employed to denote the volume of 1 grm. of the substance.

In calculating the weight of 1 cub. centim. of saturated vapour, it has been pointed out, in § 5, that this constant depends on the specific gravity of the liquid. Now the specific gravity of the liquid may be taken, (1) as directly read, or (2) from the smoothed orthobaric curve. Both of these have been made use of, and the results are compared in the following table:—

T.	Weight of 1 cub. centim. vapour.		Weight of 1 cub. centim. of vapour smoothed by curve.	Vol. of 1 gram. of vapour.
	(1.)	(2.)	(3.)	
°	grms.	grms.		cub. centims.
110·0	0·00713	0·00728	0·00577 0·00650	173 154
130·05	0·01025	0·01041	0·01055 0·01090	94·8 91·7
140·25	0·01403	0·01370	0·01365 0·01370	73·3 73·0
150·65	0·01743	0·01743	0·01705	58·6
160·25	0·02278	0·02255	0·02090	47·8
161·6	0·01969	0·02044	0·02140	46·7
171·75	0·02608	0·02608	0·02615	38·2
181·4	0·03233	0·03135	0·03200	31·2
189·8	0·03882	0·03882	0·03860	25·9
200·0	0·04907	0·04916	0·04955	20·2
210·05	0·06578	0·06620	0·0655	15·3
220·45	0·08606	0·08676	0·0862	11·6
225·05	0·09711	0·09738	0·0977	10·2
230·35	0·11446	0·11431	0·1145	8·73
232·6	0·12324	0·12331	0·1235	8·10
234·7	0·13426	0·13434	0·13325	7·50
235·85	0·13870	0·13909	0·1394	7·17
236·8	0·14569	0·14554	0·1450	6·90
237·95	0·15184	0·15225	0·1529	6·54
239·0	0·16209 0·16092	0·16119 0·16080	0·1615	6·19
240·1	0·17271	0·17277	0·1727	5·79
241·25	0·18643	0·18719	0·1870	5·35
242·25	0·20294	0·20294	0·2050	4·88
242·6	0·22431	0·22522	0·2250	4·44

The chief differences in the numbers in these columns are at low temperatures, where a small alteration in the specific gravity of the liquid causes a large change in the weight of 1 cc. of saturated vapour.

22. From the data already given, the densities compared with hydrogen under similar conditions of temperature and pressure were calculated. In these calculations the data given in columns 1, 2, and 3 of the preceding table have been employed, and the corresponding vapour-densities are similarly numbered. The vapour-densities found were then plotted on a curve, and the 4th column shows the smoothed results.

DENSITIES of Saturated Vapour (H=1).

T.	(1.)	(2.)	(3.)	(4.)
°				
110·0	36·0	36·7	29·1 32·8	29·5 32·8
130·05	29·6	29·9	30·4 31·5	29·5 31·5
140·25	31·6	30·9	30·7 30·9	29·5 30·7
150·65	30·3	30·3	29·6	29·45 30·0
160·25	32·85	32·55	30·15	29·45 29·6
161·6	27·2	28·2	29·5	29·35 29·5
171·75	29·3	29·3	29·4	29·4
181·4	30·0	29·1	29·7	29·8
189·8	30·8	30·8	30·65	30·7
200·0	32·6	32·6	32·9	33·1
210·05	36·7	36·9	36·55	36·4
220·45	40·75	41·05	40·85	40·85
225·05	43·1	43·2	43·3	43·4
230·35	46·7	46·7	46·7	46·85
232·6	48·8	48·8	48·9	48·9
234·7	51·2	51·2	50·8	50·9
235·85	52·15	52·25	52·35	52·35
236·8	54·0	53·8	53·7	53·8
237·95	55·4	55·55	55·75	55·55
239·0	57·9 57·5	57·6 57·4	57·7	57·7
240·1	60·55	60·55	60·55	60·55
241·25	64·3	64·6	64·5	64·5
242·25	69·1	69·1	69·8	69·8
242·6	76·45	76·75	76·65	76·65

23. It is evident, on inspection of this and the preceding table, that the results at lower temperatures are not nearly so accurate as those at higher. The cause of this is that an error in the specific gravity of the liquid, which would have almost no effect on the vapour-densities at higher temperatures exercises a serious influence, for it will be remembered that the weight of the vapour is deduced from the total weight of substance and the weight of the liquid, while the weight of the liquid is deduced from its specific gravity and its volume. As the difference between the total weight and the weight of the liquid is very small, the ratio of the error in the weight of the liquid, and therefore of the vapour, to the total weight of vapour is a large one.

24. The preceding table also shows that the vapour-density decreases very rapidly at first, and afterwards more and more slowly with fall of temperature, from the highest temperature to about 180°. Below that temperature the results were not certain enough to enable us to decide positively whether the density of the saturated vapour remains constant during a considerable fall of temperature or whether it begins to increase slowly. Determinations shall be described further on which elucidate this point. It is one of extreme importance, for an increase of vapour-density

would imply the probable formation of complex molecular groups; that this is the case with acetic acid vapour will be shown in a subsequent memoir.

25. In concluding this part of the subject we give a table taken from the curves, showing specific volumes, specific gravities, and vapour-densities at definite intervals of temperature.

SPECIFIC Gravity, Specific Volume, and Density of Saturated Vapour at definite Intervals of Temperature.

T.	Sp. gr.	Sp. vol.	V. dens.	T.	Sp. gr.	Sp. vol.	V. dens.
°		cub. centims.		°		cub. centims.	
110	0·00577	173	29·5	200	0·0495	20·2	33·1
	0·00650	154	32·8	210	0·0651	15·4	36·4
120	0·00800	125	29·5	220	0·0854	11·7	40·75
	0·00850	118	32·1	225	0·0976	10·25	43·4
130	0·0105	95·2	29·5	230	0·1135	8·81	46·7
	0·0108	92·6	31·4	232	0·1209	8·27	48·3
140	0·0135	74·1	29·5	234	0·1296	7·72	50·15
	0·0136	73·5	30·7	236	0·1401	7·14	52·5
150	0·0170	58·8	29·45	237	0·1463	6·83	53·9
			30·05	238	0·1532	6·53	55·65
160	0·0208	48·1	29·45	239	0·1615	6·19	57·7
			29·6	240	0·1715	5·83	60·2
170	0·0253	39·5	29·4	241	0·1835	5·45	63·5
180	0·0310	32·3	29·7	242	0·1990	5·02	67·3
190	0·0388	25·8	30·85	242·5	0·2164	4·62	74·25

The bracketed numbers express the limits between which these constants appeared to fall.

26. *Heats of Vaporisation of Alcohol.*

From the foregoing data it is possible to calculate the heats of vaporisation of alcohol by means of the formula

$$L=(s_1-s_2).\frac{t}{J}\frac{dp}{dt}.$$

$L=$ Heat of vaporisation.

s_1 and $s_2=$ Volumes of saturated vapour and liquid respectively.

$t=$ Absolute temperature.

$J=$ Mechanical equivalent of heat. $=42500$.

$\frac{dp}{dt}=$ Rate of change of pressure, measured in grammes per square centimetre.

27. This rate of change was ascertained from the vapour-pressures of alcohol, calculated by BIOT'S formula, two points being chosen, 0·1° above and 0·1° below the temperature required, and the difference between these pressures was multiplied by 5. From 231° to 239° inclusive the values were read from a curve constructed to show relations of $\frac{dp}{dt}$ to temperature; the number at 240° is calculated, but at 241°, 242°, and 242·5° the curve was again employed. The results are given in the following table:—

Values of $\frac{dp}{dt}$ for definite Temperatures.

T.	$\frac{dp}{dt}$.	T.	$\frac{dp}{dt}$.	T.	$\frac{dp}{dt}$.
°0	0·840	°130	122·45	°232	684·0
10	1·516	140	151·75	233	692·5
20	2·616	150	185·41	234	701·0
30	4·332	160	223·72	235	710·5
40	6·898	170	266·75	236	721·0
50	10·575	180	315·45	237	731·0
60	15·750	190	369·70	238	741·0
70	22·75	200	430·80	239	751·5
80	31·85	210	499·3	240	763·7
90	43·61	220	576·6	241	774·5
100	58·17	225	620·0	242	785·0
110	75·95	230	664·0	245·5	790·0
120	97·33	231	674·5		

28. Values of L.

T (Cent.).	T (Abs.).	$\frac{T}{J^*}$.	$\frac{dp\dagger}{dt}$.	s_1-s_2.	L in calorics.
°	°				
110	383	0·00901	103·26	171·6 152·6	159·67 141·99
120	393	0·00925	132·33	123·6 116·6	157·82 142·67
130	403	0·00948	166·48	93·7 91·1	147·92 143·82
140	413	0·00972	206·32	72·6 72·0	145·59 144·39
150	423	0·00995	252·08	57·25	143·6
160	433	0·01019	304·17	46·5	144·1
170	443	0·01042	362·67	37·9	143·3
180	453	0·01066	428·9	30·6	139·9
190	463	0·01089	502·65	24·1	132·0
200	473	0·01113	585·7	18·4	119·9
210	483	0·01136	678·85	13·5	104·15
220	493	0·01160	783·9	9·7	88·2
225	498	0·01172	842·9	8·16	80·6
230	503	0·01184	902·8	6·61	70·6
232	505	0·01188	930·0	6·02	66·6
234	507	0·01193	953·1	5·41	61·5
236	509	0·01198	979·4	4·75	55·7
237	510	0·01200	993·9	4·40	52·5
238	511	0·01202	1007·5	4·05	49·0
239	512	0·01205	1021·8	3·65	47·5
240	513	0·01207	1038·3	3·22	40·3
241	514	0·01209	1053·0	2·75	35·0
242	515	0·01212	1067·3	2·20	28·4
242·5	515·5	0·01213	1074·1	1·695	22·1

(For correct values below number 210° refer to § 40.)

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* The value of J was taken as 42500.

† In grammes per square centimetre.

29. It will be seen from these numbers that the values of L increase regularly to 180° with fall of temperature. They then appear to remain approximately constant. It is at this temperature also that the vapour-densities become uncertain, and show a tendency to rise. From the nature of the equation used to obtain the values of L any discrepancy in the vapour-densities will affect the values of L. At temperatures below 180°, as explained in § 23, the error introduced becomes considerable, and the experimental results are evidently no longer trustworthy. But above this temperature the ratios of the specific gravity of the liquid to that of the gas becomes sufficiently small to give accurate results; and the accuracy is confirmed by the regularity of the deduced curve.

30. There are already data as regards the heat of vaporisation of alcohol. ANDREWS (Chem. Soc. Journ., I., p. 27) gives the value of L for 77·9°, under a pressure of 760 mms., as 202·4 cal. FAVRE and SILBERMANN ('Annales' (3), 37, p. 465) give at the boiling-point under normal pressure 208·92 cal. REGNAULT ('Mémoires de l'Institut,' xxvi., pp. 819 and 262) gives a number of values of the total heats, from which the heats of vaporisation may be calculated by subtracting the specific heats of the liquid, calculated according to the formula given by him :—

$$\log \text{Sp. Ht.} = \bar{1}\cdot7384166 + \bar{3}\cdot0499296t + \bar{6}\cdot3436027t^2.$$

These numbers are as follows, and we append the volumes of saturated vapour and the resulting vapour-densities calculated from his numbers. They are shown graphically on the accompanying curve in Plate 4 (1) :—

T.	Total heat.	Latent heat.	$\frac{dp}{dt}$	Vol. of 1 gram. of vapour.	Vap. density.
°	centims.				
0	236·5	236·5	0·854	33,435	21·08
10	244·4	238·8	1·525	17,297	21·00
20	252·0	240·6	2·565	10,008	20·48
30	258·0	240·5	4·23	5,866·8	20·45
40	262·0	238·2	6·82	3,489	20·865
50	264·0	233·5	10·635	2,126	21·50
60	265·0	227·6	15·975	1,338	22·11
70	265·2	220·6	23·14	877·5	22·26
80	265·2	213·1	32·43	583·0	23·16
90	266·0	206·0	44·19	402·6	23·57
100	267·3	199·1	58·73	285·4	23·94
110	269·6	192·9	75·60	209·5	24·01
120	272·5	186·8	97·0	154·5	24·47
130	276·0	181·0	123·35	119·7	24·22
140	280·5	175·8	152·05	89·02	25·42
150	285·3	170·5	186·5	69·11	26·01

As alcohol cannot without dissociating possess a vapour-density less than 23, the numbers below 80° are manifestly wrong.

ANDREWS' measurement gives a vapour-density of 23·51 ; and FAVRE and SILBER-

MANN'S, 23·25; both of which agree well with our results. In these calculations our values of $\frac{dp}{dt}$ were employed.

31. HERWIG gives a formula by which the volume of 1 gram. of saturated vapour of various liquids may be calculated from the known value of PV when constant. This formula is

$$v_1 = \frac{v}{s} = \frac{\text{PV}}{0 \cdot 0595 \sqrt{a + t.ps}}$$

Where v_1 is the volume of 1 gram; s the mass of substance; a, 273; t, temperature centigrade; and p, vapour-pressure at temperature t. Although this formula does not hold in the least at high temperatures, we give the results for alcohol calculated by HERWIG, at temperatures within the limits of which HERWIG states that his law holds good. (HERWIG states that the alcohol he used contained a trace of water.)

T.	P. (HERWIG)	v_1	$\frac{dp}{dt}$ (from REGNAULT)	L.	V.D.
23°	50·23	7977·9	2·99	225·85	22·97
30·5	77·58	5237·9	4·34	219·15	23·23
36·4	108·0	3798·4	5·80	216·4	23·46
41·9	144·7	2828·9	7·46	211·06	23·93
47·8	196·5	2125·0	9·68	209·55	23·90
57·8	315·8	1342·7	14·52	204·72	24·28
62·9	396·83	1076·6	17·81	204·39	24·48
69·9	537·63	802·4	22·98	200·55	24·76

If the vapour-densities were continued to lower temperatures they would manifestly fall below the lowest possible. Had our values of $\frac{dp}{dt}$ been substituted for those of REGNAULT, the discrepancy would have been even greater.

The numbers of ANDREWS, and of FAVRE and SILBERMANN, are fairly concordant, and appear to indicate a vapour-density of 23·25 to 23·5 at normal pressure; and it will be seen that a continuation of the curve obtained by us might hit this number at 78·4°.

It appeared desirable to confirm this view by further experiments in which different methods were employed.

32. *Densities of Unsaturated and Saturated Alcohol Vapour.*

For higher temperatures the process was essentially the same as that already described. A much smaller amount of alcohol was used, so that it was possible to convert it into gas, and to increase volume until its density became normal at a high temperature. Three sets of experiments were made. In the first too large an amount of alcohol was taken to enable the vapour to acquire normal density, even with the largest volume which could be given. The volume of the liquid was therefore measured at 220° and 225°, and its weight was calculated from the data obtained, and from the determinations of the specific gravity of alcohol which have already been described. In the second and third series the density was normal under the greatest volumes given, for the product of pressure into volume remained constant during change of volume.

SERIES I.

Weight of Substance.

I.	Volume at 220°	0·04323 cc.
	Sp. Gr.	0·4958.
	Weight	0·02143 gram.
II.	Volume at 225°	0·04514 cc.
	Sp. Gr.	0·4775.
	Weight	0·02155 gram. Mean, 0·02149.

T.	Volume.	Sp. vol. (vol. of 1 grm.)	P.	P. V.	Vapour density.
			mms.		
220°	0·88473	41·27	14,181	12,548	26·23
,,	0·84773	39·54	14,714	12,476	26·39
,,	0·81051	37·80	15,238	12,352	26·66
,,	0·77379	36·09	15,869	12,278	26·81
,,	0·73719	34·38	16,505	12,170	27·05
,,	0·70211	32·75	17,188	12,069	27·27
,,	0·66350	30·95	17,958	11,917	27·63
,,	0·62618	29·21	18,776	11,757	28·00
,,	0·58901	27·47	19,670	11,585	28·42
,,	0·55175	25·73	20,635	11,387	28·91
,,	0·51441	23·99	21,679	11,152	29·53
,,	0·47697	22·25	22,813	10,882	30·26
,,	0·43953	20·50	24,140	10,610	31·04
,,	0·41098	18·75	25,560	10,275	32·06
,,	0·36433	16·99	27,004	9,840	33·48
,,	0·32709	15·26	28,656	9,372	35·14
,,	0·30880	14·40	29,408	9,080	37·29
,,	0·29107	13·57	30,278	8,813	37·37
,,	0·27268	12·72	31,182	8,503	38·73
,,	0·26151	12·20	31,861	8,332	39·53
,,	0·25140	11·85	32,153	8,170	40·31
,,	0·24668	11·51	32,162	7,934	Liquid present.
,,	0·23549	10·98	32,188	7,580	Liquid present.
,,	0·21687	10·11	32,183	6,979	Liquid present.

SERIES II.

33. A quantity of the alcohol was removed and a fresh set of determinations made at 220°. A curve was then constructed from the results of Series I., showing relation between volume and pressure; the volumes on this curve corresponding to the pressure on the second series were then read, and the ratios between the volumes in the two series at the same pressures were determined. By this method the weight of the alcohol used in Series II. was found to be 0·004751 grm. It will be seen that with this smaller quantity of substance the vapour-density at the higher temperatures and largest volumes becomes constant at 23, and this affords sufficient confirmation of the correctness of the weight given.

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
120°	0·88243	185·7	2725	2405	24·13
,,	0·84553	178·0	2826	2390	24·28
,,	0·80841	170·2	2942	2379	24·40
,,	0·77177	162·4	3061	2363	24·55
,,	0·75353	158·6	3117	2350	24·69
,,	0·74619	157·1	3142	2346	24·73
,,	0·73894	155·5	3167	2342	24·78
,,	0·73528	154·8	3176	2337	24·83
,,	0·73156	154·0	3185	2326	24·94
130	0·84575	178·0	2930	2478	24·01
,,	0·69884	147·1	3479	2433	24·45
,,	0·62471	131·5	3838	2399	24·81
,,	0·58762	123·7	4037	2374	25·08
,,	0·57273	120·6	4117	2360	25·22
,,	0·56529	119·0	4168	2357	25·24
,,	0·55785	117·4	4220	2355	25·27
,,	0·55414	116·6	4244	2352	25·29
,,	0·55045	115·9	4261	2346	25·36
,,	0·54668	115·1	4279	2340	25·43
140	0·84598	178·1	3012	2549	23·92
,,	0·73567	154·8	3445	2536	24·05
,,	0·62489	131·5	3978	2487	24·52
,,	0·51335	108·0	4749	2439	25·01
,,	0·43862	92·32	5428	2381	25·60
,,	0·42740	89·96	5533	2365	25·78
,,	0·41990	88·38	5606	2355	25·90
,,	0·41615	87·59	5653	2353	25·92
150	0·84618	178·0	3127	2646	23·60
,,	0·73583	155·0	3567	2625	23·80
,,	0·62503	131·5	4128	2581	24·20
,,	0·51348	108·0	4933	2534	24·65
,,	0·40136	84·48	6165	2475	25·23
,,	0·36366	76·55	6632	2412	25·89
,,	0·34509	72·64	6916	2386	26·17
,,	0·32649	68·72	7231	2362	26·45
,,	0·32279	67·94	7276	2349	26·59
,,	0·31907	67·16	7334	2341	26·68
,,	0·31540	66·39	7353	2320	26·92
160	0·84639	178·1	3214	2721	23·50
,,	0·73602	155·0	3661	2696	23·72
,,	0·62519	131·6	4272	2672	23·93

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
160°	0·51360	108·1	5,105	2623	24·38
,,	0·36376	76·57	6,915	2515	25·42
,,	0·29061	61·17	8,334	2424	26·38
,,	0·27225	57·30	8,780	2391	26·74
,,	0·25740	54·18	9,140	2354	27·17
,,	0·25370	53·40	9,254	2349	27·22
,,	0·25002	52·61	9,344	2338	27·35
,,	0·24572	51·72	9,390	2309	27·70
170	0·84662	178·1	3,301	2796	23·39
,,	0·66263	155·0	4,158	2757	23·72
,,	0·51375	108·1	5,261	2704	24·19
,,	0·36386	76·59	7,131	2596	25·20
,,	0·25377	53·41	9,704	2462	26·56
,,	0·23519	49·50	10,283	2418	27·05
,,	0·21659	45·59	10,950	2372	27·58
,,	0·20542	43·24	11,388	2339	27·96
,,	0·19795	41·67	11,663	2309	28·33
,,	0·19425	40·89	11,816	2295	28·49
180	0·84684	178·1	3,381	2864	23·35
,,	0·66280	155·0	4,277	2835	23·60
,,	0·51388	108·2	5,400	2776	24·10
,,	0·40167	84·55	6,780	2723	24·57
,,	0·29076	61·20	8,990	2615	25·58
,,	0·21664	45·60	11,484	2488	26·89
,,	0·17943	37·77	13,183	2366	28·27
,,	0·16829	35·42	13,774	2318	28·85
,,	0·16091	33·87	14,188	2283	29·29
,,	0·15722	33·09	14,446	2271	29·45
,,	0·15350	32·31	14,648	2249	29·74
,,	0·14975	31·52	14,725	2205	30·33
190	0·84707	178·2	3,486	2954	23·14
,,	0·73661	155·0	3,993	2942	23·24
,,	0·62569	131·7	4,647	2909	23·50
,,	0·43919	92·44	6,498	2854	23·96
,,	0·25390	53·44	10,553	2679	25·51
,,	0·17948	37·78	13,805	2479	27·58
,,	0·16096	33·88	15,006	2416	28·30
,,	0·14237	29·97	16,364	2325	29·59
,,	0·13498	28·41	16,974	2291	29·83
,,	0·13123	27·62	17,279	2268	30·15
,,	0·12384	26·07	17,846	2205	31·01
,,	0·12017	25·29	18,104	2176	31·42
200	0·84727	178·2	3,559	3016	23·15
,,	0·73684	155·0	4,076	3003	23·25
,,	0·62584	131·7	4,758	2978	23·46
,,	0·43929	92·46	6,628	2911	23·98
,,	0·25396	53·46	10,863	2760	25·31
,,	0·17952	37·79	14,444	2642	26·94
,,	0·16100	33·89	15,701	2527	27·63
,,	0·14240	29·97	17,140	2441	28·15
,,	0·13501	28·41	17,815	2406	29·03
,,	0·12757	26·85	18,494	2359	29·60
,,	0·12020	25·29	19,295	2320	30·11
,,	0·10507	22·12	20,814	2187	31·94
,,	0·10158	21·38	21,336	2167	32·23
,,	0·09784	20·59	21,798	2133	32·74
,,	0·09418	19·82	22,015	2073	33·68
210	0·84750	178·2	3,628	3075	23·20
,,	0·73699	155·1	4,144	3055	23·34
,,	0·62601	131·7	4,873	3051	23·38

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
210°	0·43941	92·47	6,791	2984	23·90
,,	0·25403	53·47	11,193	2843	25·08
,,	0·17957	37·80	14,942	2683	26·58
,,	0·16104	33·90	16,324	2629	27·13
,,	0·14244	29·98	17,899	2550	27·97
,,	0·12390	26·08	19,769	2452	29·12
,,	0·10510	22·12	21,992	2312	30·86
,,	0·09421	19·82	23,699	2233	31·94
,,	0·08664	18·24	24,723	2142	33·30
,,	0·08289	17·45	25,458	2111	33·79
,,	0·07911	16·65	25,933	2052	34·76
,,	0·07533	15·86	26,532	1999	35·68
220	0·88473	186·2	3,515	3111	23·40
,,	0·84773	178·4	3,658	3102	23·47
,,	0·81051	170·6	3,823	3099	23·49
,,	0·73719	155·2	4,173	3077	23·65
,,	0·66350	139·7	4,628	3071	23·70
,,	0·58901	124·0	5,205	3066	23·74
,,	0·51441	108·3	5,916	3043	23·92
,,	0·47697	100·4	6,357	3032	24·01
,,	0·43953	92·49	6,851	3011	24·17
,,	0·40198	84·61	7,468	3002	24·24
,,	0·36433	76·68	8,168	2976	24·46
,,	0·32709	68·85	9,006	2947	24·70
,,	0·29107	61·26	10,030	2920	24·92
,,	0·25410	53·48	11,366	2888	25·20
,,	0·21687	45·65	13,014	2823	25·78
,,	0·17962	37·81	15,214	2733	26·63
,,	0·14248	29·99	18,355	2615	27·83
,,	0·10513	22·13	22,964	2414	30·15
,,	0·06785	14·28	29,632	2011	36·21
,,	0·03041	6·40	31,708	964	Liquid visible.
225	0·88481	186·2	3,531	3126	23·52
,,	0·84782	178·4	3,684	3123	23·54
,,	0·81059	170·6	3,863	3132	23·48
,,	0·73726	155·2	4,224	3115	23·61
,,	0·66356	139·7	4,681	3107	23·67
,,	0·58906	124·0	5,249	3093	23·78
,,	0·51446	108·3	5,968	3070	23·95
,,	0·47702	100·4	6,402	3058	24·04
,,	0·43957	92·52	6,916	3040	24·18
,,	0·40213	84·64	7,519	3024	24·31
,,	0·36437	76·69	8,251	3007	24·45
,,	0·32712	68·85	9,117	2983	24·65
,,	0·29110	61·27	10,168	2961	24·84
,,	0·27270	57·40	10,755	2933	25·07
,,	0·25413	53·49	11,488	2920	25·19
,,	0·23552	49·57	12,238	2883	25·51
,,	0·21689	45·65	13,160	2855	25·76
,,	0·19823	41·72	14,266	2829	26·00
,,	0·17963	37·81	15,436	2773	26·51
,,	0·16110	33·91	16,921	2727	26·97
,,	0·14249	29·99	18,729	2668	27·55
,,	0·12395	26·09	20,809	2580	28·51
,,	0·10514	22·13	23,365	2457	29·93
,,	0·08667	18·24	26,546	2301	31·96
,,	0·06785	14·28	30,601	2077	35·42
,,	0·06043	12·72	32,389	1957	37·57
,,	0·05300	11·16	34,154	1810	40·62
,,	0·04929	10·38	34,780	1715	42·89

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
225°	0·03042	6·40	34,792	1058	Liquid visible.
230	0·88493	186·3	3,576	3165	23·47
,,	0·84793	178·5	3,722	3157	23·53
,,	0·81070	170·6	3,898	3154	23·55
,,	0·70065	147·5	4,489	3146	23·62
,,	0·58914	124·0	5,308	3127	23·75
,,	0·47709	100·4	6,495	3099	23·97
,,	0·40207	84·63	7,639	3071	24·18
,,	0·32717	68·86	9,257	3029	24·52
,,	0·29114	61·28	10,318	3004	24·72
,,	0·25416	53·50	11,635	2958	25·06
,,	0·21692	45·66	13,367	2900	25·61
,,	0·17966	37·81	15,733	2826	26·27
,,	0·16112	33·91	17,202	2772	26·80
,,	0·14251	29·99	19,082	2720	27·31
,,	0·12396	26·09	21,190	2627	28·27
,,	0·10515	22·13	23,827	2506	29·64
,,	0·08668	18·24	27,144	2353	31·57
,,	0·06786	14·28	31,636	2147	34·59
,,	0·06044	12·72	33,751	2040	36·41
,,	0·05301	11·16	35,650	1890	39·29
,,	0·04559	9·595	37,556	1712	43·38
,,	0·03042	6·403	38,093	1158	64·10
232	0·88497	186·3	3,604	3190	23·37
,,	0·84797	178·5	3,759	3189	23·39
,,	0·81074	170·6	3,935	3191	23·37
,,	0·66368	139·7	4,772	3167	23·54
,,	0·51455	108·3	6,089	3133	23·80
,,	0·40209	84·63	7,690	3092	24·12
,,	0·29115	61·28	10,377	3022	24·67
,,	0·21693	45·66	13,480	2925	25·50
,,	0·17967	37·81	15,759	2849	26·17
,,	0·14252	29·99	19,108	2724	27·38
,,	0·10516	22·13	24,100	2535	29·41
,,	0·08668	18·24	27,448	2379	31·34
,,	0·06786	14·28	32,091	2178	34·24
,,	0·05670	11·93	35,055	1988	37·52
,,	0·04930	10·38	37,311	1840	40·53
,,	0·04559	9·596	38,071	1736	42·96
,,	0·04179	8·849	38,961	1629	45·80
,,	0·03042	6·403	39,650	1206	Liquid visible.
234	0·88501	186·3	3,673	3251	23·03
,,	0·81077	170·6	3,999	3243	23·14
,,	0·66371	139·7	4,862	3227	23·20
,,	0·51458	108·3	6,210	3196	23·43
,,	0·36445	76·71	8,628	3144	23·80
,,	0·25419	53·50	11,969	3042	24·61
,,	0·17968	37·81	16,135	2901	25·80
,,	0·14253	29·99	19,458	2773	26·99
,,	0·10516	22·13	24,504	2577	29·12
,,	0·08669	18·24	27,740	2405	31·13
,,	0·06787	14·28	32,721	2221	33·71
,,	0·05670	11·93	36,030	2043	36·65
,,	0·04930	10·38	38,092	1878	39·88
,,	0·04559	9·596	39,104	1872	41·99
,,	0·04204	8·849	40,048	1683	44·46
,,	0·03802	8·002	40,711	1548	48·36
,,	0·03042	6·403	40,894	1244	Liquid visible.
236	0·88507	186·3	3,690	3266	23·00

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
236°	0·81083	170·6	4,029	3267	23·00
„	0·66376	139·7	4,891	3246	23·15
„	0·51461	108·3	6,249	3116	23·37
„	0·36448	76·71	8,669	3160	23·78
„	0·25420	53·50	12,073	3069	24·49
„	0·17969	37·81	16,249	2919	25·74
„	0·14254	29·99	19,694	2806	26·78
„	0·10517	22·13	24,872	2616	28·73
„	0·08670	18·24	28,371	2460	30·56
„	0·06787	14·28	33,106	2247	33·45
„	0·05670	11·93	36,477	2068	36·34
„	0·04931	10·38	38,701	1909	39·38
„	0·04560	9·597	39,733	1812	41·49
„	0·04204	8·849	40,705	1712	43·91
„	0·03802	8·002	41,593	1578	47·52
„	0·03042	6·403	42,245	1285	Liquid visible.
237	0·88508	186·3	3,693	3269	23·04
„	0·81083	170·6	4,022	3262	23·09
„	0·66376	139·7	4,892	3247	23·19
„	0·51461	118·3	6,270	3224	23·36
„	0·36448	76·71	8,676	3162	23·81
„	0·25420	53·50	12,094	3075	24·49
„	0·17969	37·81	16,336	2935	25·66
„	0·14254	29·99	19,802	2823	26·68
„	0·10517	22·13	24,980	2627	28·66
„	0·08670	18·24	28,612	2480	30·36
„	0·06787	14·28	33,338	2263	33·28
„	0·05670	11·93	36,634	2077	36·25
„	0·04931	10·38	38,983	1922	39·18
„	0·04560	9·597	39,906	1819	41·39
„	0·04204	8·849	41,123	1729	43·56
„	0·03802	8·002	42,274	1607	46·85
„	0·03042	6·403	43,083	1311	Liquid visible.
238	0·88510	186·3	3,699	3275	23·04
„	0·81085	170·7	4,030	3268	23·08
„	0·66377	139·7	4,896	3250	23·21
„	0·51462	108·3	6,274	3226	23·39
„	0·36449	76·71	8,673	3161	23·87
„	0·25421	53·50	12,087	3073	24·56
„	0·17970	37·81	16,322	2933	25·73
„	0·14254	30·00	19,910	2837	26·59
„	0·10517	22·14	24,988	2628	28·70
„	0·08670	18·25	28,746	2492	30·28
„	0·06787	14·29	33,767	2293	32·92
„	0·05671	11·93	36,854	2090	36·10
„	0·04931	10·38	39,253	1935	38·98
„	0·04560	9·597	40,186	1832	41·10
„	0·04204	8·849	41,412	1741	43·33
„	0·03802	8·002	42,448	1614	46·75
„	0·03422	7·202	43,282	1481	50·94
„	0·03043	6·404	43,694	1329	Liquid visible.
239	0·88514	186·3	3,708	3283	23·03
„	0·81089	170·6	4,029	3268	23·13
„	0·62647	131·9	5,185	3248	23·26
„	0·43973	92·56	7,301	3213	23·54
„	0·25422	53·50	12,161	3091	24·46
„	0·17971	37·81	16,408	2949	25·64
„	0·14254	30·00	19,999	2851	26·52
„	0·10517	22·13	25,262	2657	28·45
„	0·08670	18·24	28,785	2495	30·30

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
239°	0·06788	14·28	33,890	2300	32·86
,,	0·05671	11·93	37,410	2122	35·63
,,	0·04931	10·38	39,504	1948	38·81
,,	0·04560	9·597	40,815	1861	40·62
,,	0·04205	8·849	41,947	1764	42·86
,,	0·03802	8·002	42,954	1633	46·28
,,	0·03422	7·202	43,853	1501	50·38
,,	0·03043	6·404	44,285	1348	56·11
240	0·88516	186·3	3,712	3287	23·04
,,	0·81091	170·7	4,046	3281	23·08
,,	0·62648	131·9	5,198	3257	23·26
,,	0·43975	92·51	7,305	3212	23·58
,,	0·25423	53·50	12,188	3098	24·45
,,	0·17972	37·81	16,500	2979	25·43
,,	0·14255	30·00	19,959	2845	26·62
,,	0·10518	22·13	25,303	2662	28·46
,,	0·08671	18·25	29,037	2518	30·09
,,	0·06788	14·28	33,900	2301	32·92
,,	0·05671	11·93	37,401	2122	35·70
,,	0·04931	10·38	39,865	1966	38·53
,,	0·04560	9·597	41,075	1873	40·44
,,	0·04205	8·850	42,353	1781	42·53
,,	0·03802	8·002	43,585	1657	45·70
,,	0·03422	7·202	44,299	1516	49·97
,,	0·03043	6·404	45,039	1370	55·28
241	0·88518	186·3	3,715	3290	23·07
,,	0·81092	170·7	4,055	3289	23·07
,,	0·62650	131·9	5,212	3260	23·27
,,	0·43976	92·56	7,319	3218	23·58
,,	0·25423	53·50	12,207	3103	24·46
,,	0·17972	37·82	16,535	2971	25·54
,,	0·14255	30·00	20,013	2853	26·50
,,	0·10518	22·13	25,482	2680	28·31
,,	0·08671	18·25	29,277	2538	29·89
,,	0·06788	14·28	34,150	2318	32·74
,,	0·05671	11·93	37,630	2133	35·57
,,	0·04931	10·38	40,087	1977	38·38
,,	0·04560	9·598	41,324	1885	40·27
,,	0·04205	8·850	42,623	1793	42·34
,,	0·03802	8·002	43,866	1668	45·50
242	0·88520	186·3	3,719	3293	23·10
,,	0·81094	170·7	4,062	3294	23·08
,,	0·62651	131·9	5,216	3268	23·27
,,	0·43977	92·56	7,321	3220	23·62
,,	0·25424	53·51	12,238	3111	24·45
,,	0·17973	37·82	16,566	2978	25·54
,,	0·14256	30·00	20,216	2883	26·39
,,	0·10518	22·14	25,554	2688	28·30
,,	0·08671	18·25	29,372	2546	29·86
,,	0·06788	14·29	34,093	2314	32·86
,,	0·05671	11·94	37,769	2142	35·50
,,	0·04932	10·38	40,321	1989	38·24
,,	0·04560	9·598	41,487	1892	40·19
,,	0·04205	8·850	42,658	1724	42·39
,,	0·03802	8·002	44,056	1676	45·39
243·1	0·88522	186·3	3,721	3295	23·12
,,	0·81097	170·7	4,053	3288	23·18
,,	0·66387	139·7	4,951	3287	23·18
,,	0·51470	108·3	6,332	3259	23·08
,,	0·36454	76·71	8,793	3206	23·77

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
243°·1	0·25424	53·51	12,260	3117	24·45
,,	0·17973	37·82	16,611	2985	25·53
,,	0·14256	30·01	20,158	2888	26·39
,,	0·10518	22·14	25,570	2689	28·33
,,	0·08671	18·25	29,438	2552	29·85
,,	0·06788	14·29	34,546	2345	32·50
,,	0·05671	11·94	38,192	2165	35·28
,,	0·04932	10·38	40,753	2015	37·83
,,	0·04560	9·598	41,876	1909	39·91
,,	0·04205	8·850	43,228	1818	41·92
,,	0·03803	8·002	44,367	1687	45·17
244·35	0·88525	186·3	3,751	3322	23·00
,,	0·81100	170·7	4,090	3317	23·02
,,	0·62656	131·9	5,259	3295	23·18
,,	0·43980	92·57	7,387	3249	23·51
,,	0·25426	53·52	12,313	3123	24·46
,,	0·17974	37·83	16,704	3002	25·44
,,	0·14256	30·01	20,269	2889	26·43
,,	0·10519	22·14	25,664	2700	28·30
,,	0·08671	18·25	28,991	2562	29·81
,,	0·06789	14·29	34,657	2353	32·46
,,	0·05672	11·94	38,671	2178	34·92
,,	0·04932	10·38	41,114	2027	37·67
,,	0·04561	9·599	42,394	1934	39·50
,,	0·04205	8·851	43,788	1841	41·48
246·0	0·88528	186·3	3,750	3321	23·08
,,	0·81102	170·7	4,091	3318	23·09
,,	0·62657	131·9	5,276	3306	23·18
,,	0·43981	92·57	7,465	3284	23·34
,,	0·25426	53·52	12,381	3155	24·29
,,	0·17975	37·83	16,817	3023	25·35
,,	0·14257	30·01	20,430	2913	26·31
,,	0·10519	22·14	25,936	2729	28·09
,,	0·08672	18·25	29,929	2596	29·53
,,	0·06789	14·29	34,928	2371	32·31
,,	0·05672	11·94	38,795	2200	34·82
,,	0·04932	10·38	41,358	2040	37·56
,,	0·04561	9·599	42,658	1945	39·22
,,	0·04205	8·851	44,053	1853	41·36

SERIES III.

34. The amount of alcohol used for the determinations of which the results are given above was too large to admit of values at lower temperatures; a fresh portion was removed, and the weight of the remainder was ascertained by determining the value of P. V. at a temperature at which it became constant at the highest volumes. This temperature was 130°, and the mean value obtained for P. V. was 950·8. From this the weight of alcohol was calculated to be 0·001747 grm.

The following measurements were made :—

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
90°	0·84487	483·5	993	839·7	23·47
,,	0·77117	441·4	1085	837·3	23·54
,,	0·73470	420·5	1135	834·4	23·62
,,	0·71638	410·0	1163	833·7	23·65
100	0·84509	483·7	1026	867·7	23·34
,,	0·62423	357·3	1385	865·0	23·43
,,	0·53019	304·1	1598	849·9	23·83
,,	0·51280	293·5	1650	846·7	23·92
110	0·84532	483·8	1062	898·4	23·15
,,	0·62440	357·4	1429	892·6	23·30
,,	0·43828	250·8	1996	875·2	23·76
,,	0·38213	218·7	2259	863·7	24·08
,,	0·36330	207·9	2342	851·2	24·43

35. The results of all these determinations of vapour-density are represented, so far as it is possible without introducing confusion, on Plate 4; the ordinates represent pressures, and the abscissæ vapour-densities compared with hydrogen under similar conditions of temperature and pressure; the smaller curve represents the results of the experiments at lower temperatures on a larger scale. The lines are isothermals; and the curve connecting their terminal points gives the densities of the saturated vapour at the corresponding temperatures and pressures. From inspection of this curve it is evident that these results for densities of saturated vapour confirm those obtained by direct measurement at temperatures above 180°; but the previous results are incorrect, below that temperature, for reasons already given. So far as can be judged from these results, the density of the saturated vapour of alcohol decreases with fall of temperature, and corresponding fall of pressure.

36. But from experiments with acetic acid, this is found not to be the case with that substance. On the contrary, the density of its saturated vapour increases rapidly with fall of temperature and pressure. Hence, it appeared necessary to carry out experiments on the density of saturated alcohol-vapour at still lower temperatures, for it was deemed possible that after reaching a minimum density, fall of temperature would produce an increase. The apparatus, which will be fully described in an account of the experiments with ether, consisted of a HOFMANN'S vapour-density apparatus, so modified as to admit of alteration of pressure. The desired temperature was produced by jacketing with running water.

The following results were obtained at 13·0°:—

Volume.	Pressure.	P. V.
ccs.	mms.	
106	15·55	1648
86·7	18·85	1634
77·5	20·85	1616
69·0	23·6	1628
64·0	25·7	1645
62·2	26·35	1639

At a volume of 59 cub. centims. liquid was present.

37. This method involves three readings of heights of mercury, and calculation of a fourth; and as an error of 0·1 mm. makes an alteration in the value of P. V. of 6 to 10 units, the results, although irregular, are well within the limits of experimental error. They show that the product of pressure into volume remained practically constant up to a very small distance from the volume at which condensation began to occur.

38. From measurements at the boiling-point of alcohol under atmospheric pressure, an attempt was made to ascertain the weight of the extremely minute amount of alcohol present.

Volume.	Pressure.	P. V.
ccs.	mms.	
125·9	15·75	1983
123·5	15·85	1958
118·8	16·80	1996
114·9	17·10	1965

From the mean of these results, 1976, the weight of alcohol was calculated to be 0·004166 grm.

Using this weight to calculate the vapour-density at 13°, the number 22·65 was obtained. This result is not unsatisfactory, considering the experimental difficulties; and, in our opinion, it proves that the density of the saturated vapour is practically normal at low temperatures.

39. The densities of the saturated vapour can be deduced from the curves showing the densities of unsaturated vapour; they are represented by the points of intersection of these curves with the horizontal lines which exhibit change of volume of gas in presence of liquid, while pressure remains constant. They were read from the smoothed curve given in Plate 4, and they are as follows:—

T.	Sp. gr.	Sp. vol.	V. D.	T.	Sp. gr.	Sp. vol.	V. D.
°				°			
0	0·000033	30137	23·00	110	0·00486	205·9	24·50
13	0·000073	13655	23·00	120	0·00658	151·9	24·95
20	0·000111	9004	23·00	130	0·00877	114·0	25·43
30	0·000191	5241	23·00	140	0·01152	86·8	25·99
40	0·000315	3170	23·00	150	0·01488	67·2	26·55
50	0·000506	1977	23·10	160	0·01916	52·19	27·40
60	0·00079	1274	23·20	170	0·02446	40·88	28·40
70	0·00119	842·2	23·40	180	0·03115	32·11	29·70
80	0·00174	575·0	23·50	190	0·0397	25·18	31·43
90	0·00250	399·5	23·80	200	0·0508	19·69	33·65
100	0·00351	285·2	24·02	210	0·0655	15·27	36·65

On comparing the results of this table with that previously given in § 22, it will be seen that above 180° the agreement is close, but that, as was expected, the results diverge widely at lower temperatures; above 210° the agreement was perfect.

The values at 0°, and between 13° and 90° are obtained by interpolation on curve 2, Plate 5.

40. *Heats of Vaporisation of Alcohol.*

From these numbers the heats of vaporisation were calculated by the method already mentioned. They are given in the table which follows:—

T. (cent.)	T. (Abs.)	$\frac{t.}{J.}$	$\frac{dp^*}{dt}$	$s_1 - s_2$.	L in calorics.
0°	273°	0·00642	1·142	30136	220·9
10	283	0·00666	2·061	16113	221·2
20	293	0·00689	3·557	9003	220·6
30	303	0·00713	5·890	5240	220·1
40	313	0·00736	9·378	3169	218·7
50	323	0·00760	14·38	1976	216·0
60	333	0·00783	21·41	1273	213·4
70	343	0·00807	30·93	840·9	209·9
80	353	0·00831	43·30	573·7	206·4
90	363	0·00854	59·29	398·1	201·6
100	373	0·00878	79·09	283·8	197·1
110	383	0·00901	103·26	204·5	190·3
120	393	0·00925	132·33	150·5	184·2
130	403	0·00948	166·48	112·5	177·6
140	413	0·00972	206·32	85·3	171·1
150	423	0·00995	252·08	65·66	164·7
160	433	0·01019	304·17	50·61	156·9
170	443	0·01042	362·67	39·26	148·4
180	453	0·01066	428·9	30·44	139·2
190	463	0·01089	502·65	23·45	128·4
200	473	0·01113	585·7	17·89	116·6
210	483	0·01136	678·85	13·38	103·2

(For temperatures above 210° reference must be made to § 28.)

41. The relations between temperature and heats of vaporisation are graphically represented in the two curves on Plate 5, fig. 1, curve No. 2, represents this relation for vapour-density. The points experimentally determined are indicated by circles. Between 90° and 13° the dotted line shows the probable course of the curve. It is obvious that the error must be extremely small, and it is probable that the vapour-density attains its minimum at a temperature somewhat below 50°.

42. The curve representing latent heats is similarly indicated by circles and dots. That part of it deduced from the interpolated portion of our observations of vapour-density seems to point to a constant value for heat of vaporisation below about 20°, the temperature at which vapour-density becomes normal being about 40°. This would imply that below that temperature the difference between the specific heats of the saturated liquid and saturated vapour is inversely proportional to the absolute temperature; for in the equation $\gamma = c' + \frac{dL}{dt} - \frac{L}{t}$ the expression $\frac{dL}{dt}$ vanishes.

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* In grams. per square centimetre.

43. As it was difficult to understand the reason of the great divergence between the heats of vaporisation found by REGNAULT and those calculated from our results we thought it possible that some error in REGNAULT'S determinations of the vapour-pressures of alcohol, which were at first used as the basis of our calculations, might be the cause of this discrepancy. It has already been noticed that the vapour-densities calculated from REGNAULT'S results with heats of vaporisation are impossible; and by taking the vapour-density as normal the calculated curve of heats of vaporisation approaches as near REGNAULT'S as is possible. Now, as the vapour-pressure of alcohol is a datum for the calculation of the value of s_1, and as this value, as also that of $\frac{dp}{dt}$, occurs in the equation

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

an error in REGNAULT'S determinations of vapour-pressure, which we have at first employed, would have influenced all the foregoing results, and most markedly those at lower temperatures. We, therefore, thought it advisable to make a fresh series of determinations of the vapour-pressure of alcohol, and used for this purpose the apparatus described in the Trans. Chem. Soc., Jan., 1885. The temperatures are corrected for the change in volume of the bulb of the thermometer by diminution of pressure, which, with the particular thermometer employed, one graduated in 10ths of degrees, by NEGRETTI and ZAMBRA, amounted to an apparent fall of 0·2° on lowering pressure from 763 mms. to 20 mms.

44. The results are as follows :—

T.	P.	T.	P.	T.	P.
°		°		°	
−5	8·60	0·99	13·00	16·69	35·90
−4·67	8·75	1·28	13·15	17·65	37·90
−4·27	9·20	1·63	13·75	18·55	40·00
−3·36	9·80	2·31	14·20	19·96	43·95
−2·50	10·25	2·78	14·85	20·86	46·55
−1·63	10·75	3·47	15·45	22·55	51·45
−1·60	10·90	4·67	16·90	23·43	53·95
−1·10	11·05	5·43	17·75	24·46	57·60
−0·92	11·35	6·55	18·85	25·37	60·50
−0·79	11·60	7·65	20·15	26·46	64·70
−0·39	11·85	9·15	22·15	27·25	67·60
−0·13	12·05	10·72	24·90	28·03	69·90
+0·09	12·45	12·39	27·60	29·36	75·75
0·54	12·70	14·09	30·60	32·60	90·6
0·70	12·85	15·87	34·00		

45. From these results a curve was constructed, and from it values at definite temperatures were read off. They are compared with those given by REGNAULT in the 'Mémoires de l'Institut,' vol. xxvi., p. 374.

T.	P. (REG.)	P. (R. and Y.)
° 0	12·70	12·24
5	17·62	17·15
10	24·23	23·50
15	32·98	32·10
20	44·46	43·95
25	59·37	59·50
30	78·52	78·05

46. It will be seen from these results that our pressures are uniformly lower than those given by REGNAULT, except at 25°, where there is manifestly a misprint in his figures. The difference in pressure is approximately constant, and is equal to 0·46 mm. The value of $\frac{dp}{dt}$ is considerably changed by this alteration, and the numbers given, except where the contrary is stated, have been derived from the formula, the constants of which were calculated by us for vapour-pressures.

The Critical Point of Alcohol.

47. In the 'Philosophical Transactions' for 1869, p. 583, ANDREWS gives a diagram showing, to some extent, relations between the pressure and volume of carbon dioxide at temperatures near its critical point. From our observations on alcohol we are enabled to give similar diagrams on Plate 6, showing the volumes of 1 gramme. The first of these (fig. 1) comprises observations between 90° and 243·1°. The scale is necessarily a small one. The isothermal for 243·1° has been mapped, and it is to be noticed that all other isothermals between these limits of temperature would fall between that line and the one representing volumes of saturated vapour. The numbers deduced from observations are represented by circles. Fig. 2 shows similar relations at temperatures between 220° and 246° on an enlarged scale, and it also exhibits the compressibility of the liquid. The highest temperature at which it was possible to measure both liquid and gas was 242·25°; above that temperature measurement of gas was uncertain, owing to the slow rate at which condensation or evaporation proceeded. A successful measurement of the volume of the liquid was made at 242·6°, but it was still possible to distinguish liquid from gas at 243·0°; at 243·1° the meniscus appeared to broaden and became indistinct. It disappeared absolutely on the least decrease of volume, owing to heat developed by compression, and it reappeared on increasing volume. The apparent critical point was therefore at this temperature, but the pressure remained perfectly constant during considerable change of volume. A similar phenomenon has been noticed by ANSDELL, and we agree with him that the real critical point must lie somewhat higher. In the diagram on Plate 6 a dotted line has been drawn connecting the curves showing the volumes of

saturated vapour and of liquid. The summit of this surface, which represents volumes of gas in contact with liquid, if correctly drawn, would give the relation between temperature, pressure, and volume at the critical point. It appears to us impossible to obtain direct measurements of this portion of the curve. There must, therefore, necessarily be some uncertainty as regards all three.

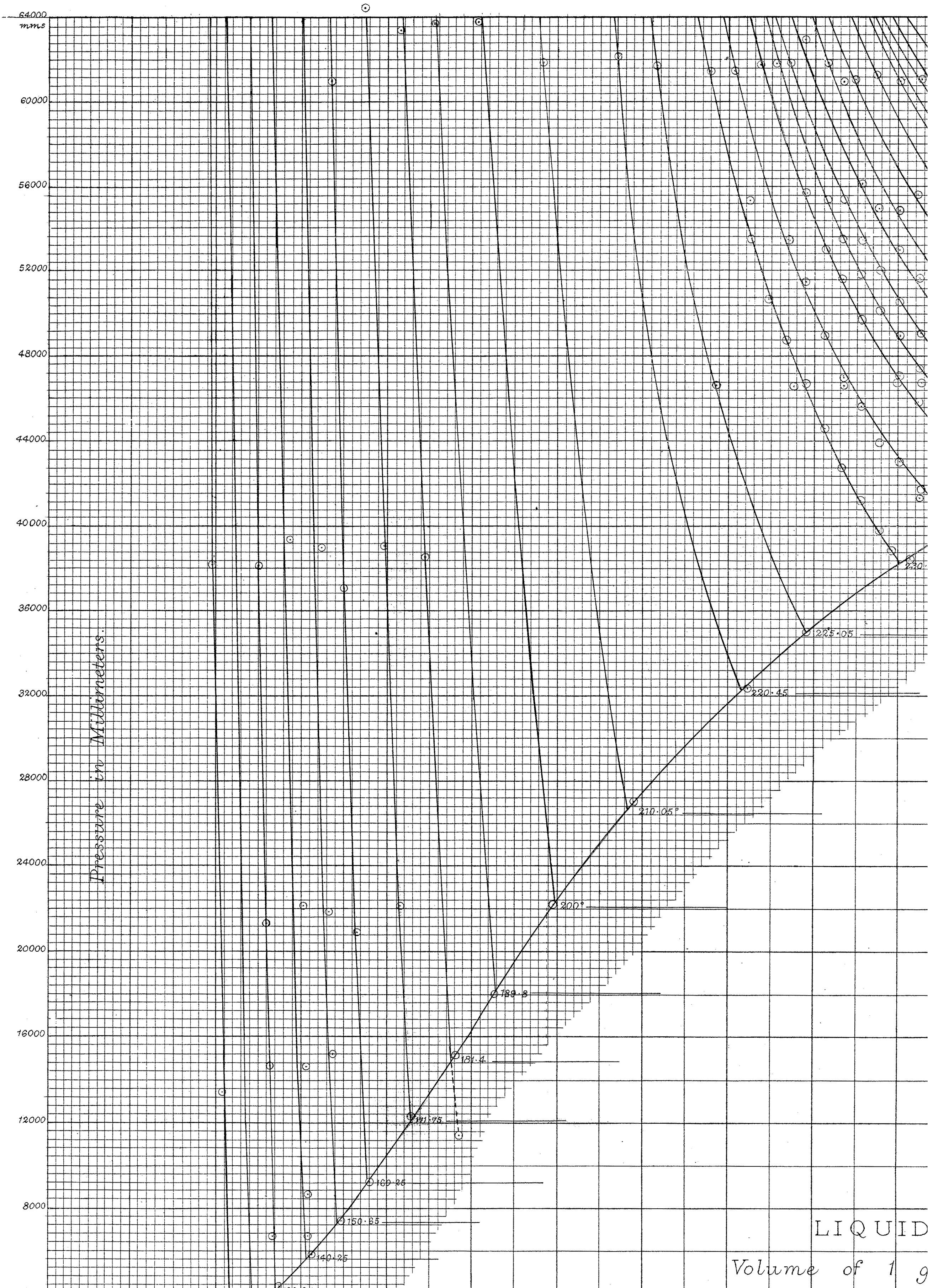
On Plate 7 the relations between the weight of one cubic centimetre of saturated vapour and liquid are shown. Curve No. 1 exhibits this relation between 40° and 242·5°; and curve No. 2 between 225° and 242·5° on an enlarged scale.

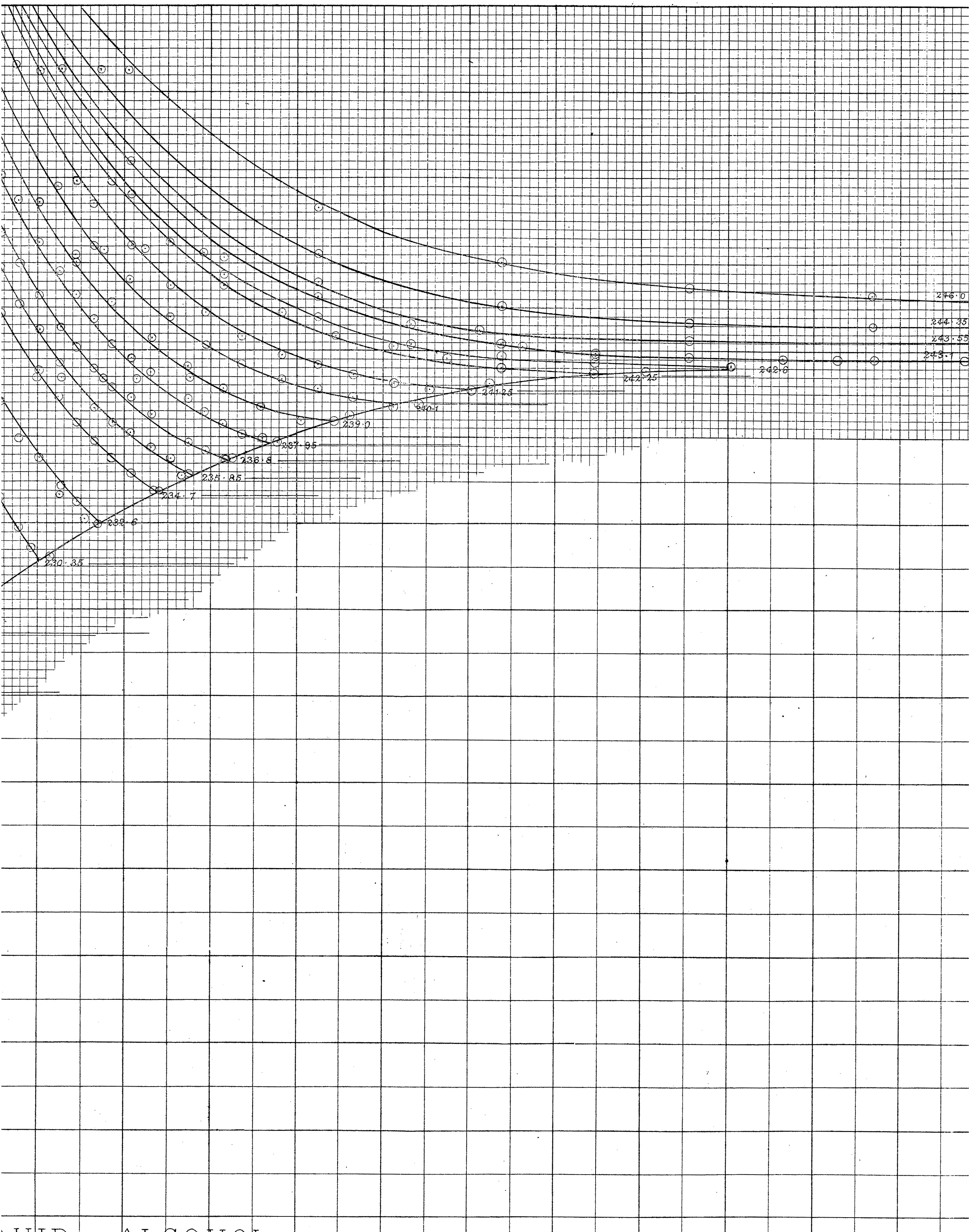
It is evident, however, from these results that the critical temperature must lie within 0·5 of a degree above or below 243·6°, that the critical pressure must be nearly 47,700 mms., and that the critical volume cannot be far from 3·5, *i.e.*, one gramme of alcohol at the critical point must occupy about 3·5 ccs.; otherwise expressed, the specific gravity at the critical point is nearly 0·28.

NOTE.

After this memoir had been read (May, 1885), an account of experiments by AMAGAT (Compt. Rend., xcix., p. 1153) on the compressibility of air was noticed. AMAGAT'S reputation and the method he adopted are a sufficient guarantee for their accuracy; and, although these results differ considerably from REGNAULT'S, which, moreover, had reference only to pressures below 20,000 mms., and were therefore not available for our purpose, we have felt justified in making use of them. This has necessitated a recalculation of all the pressures, values of *p.v.*, and vapour-densities given in this paper, and has led us to modify some of the conclusions in the memoir as read in 1885. It was also thought advisable to use BIOT'S formula, and to substitute numbers for pressure calculated by its help, instead of by the method of differences which was at first employed. The use of this formula enabled us to obtain more accurate values for $\frac{dp}{dt}$ than was possible by any graphical means, and, as a result of these alterations, the curve representing heats of vaporisation is much more regular than we at first supposed; besides, it passes between the points obtained from direct measurement by ANDREWS, and by FAVRE and SILBERMANN. The diagrams have also been reconstructed so as to represent accurately the corrected numbers.

Ramsay & Young.

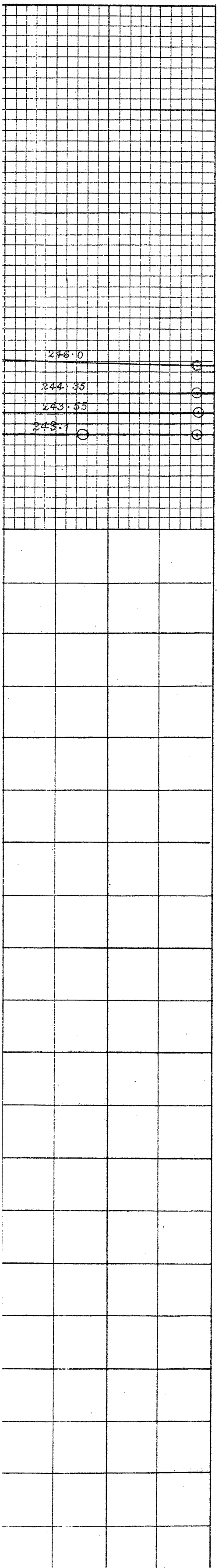


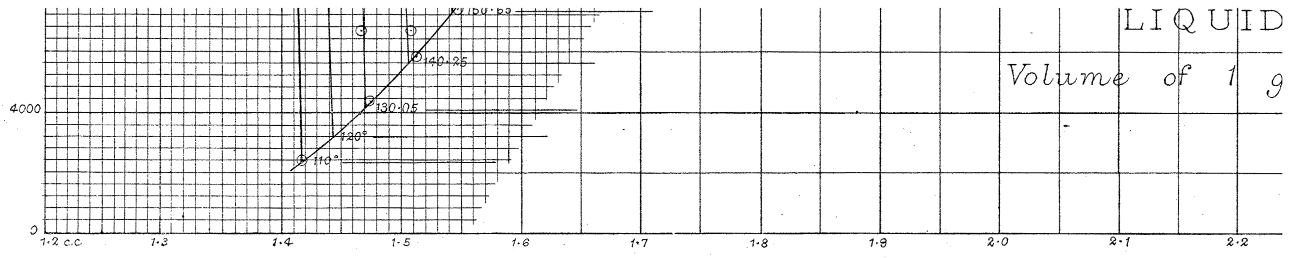


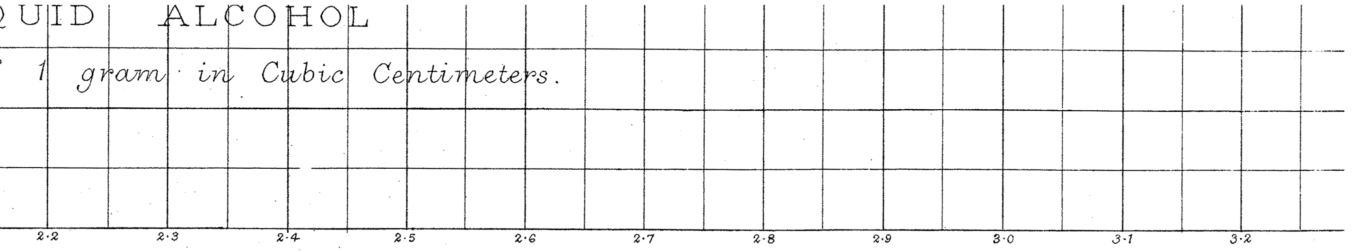
QUID ALCOHOL

1 gram in Cubic Centimeters.

86. *Plate* 3.

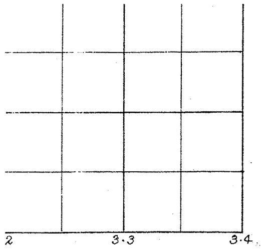



LIQUID
Volume of 1 g
4000
0
1·2 c.c.
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
110°
120°
130·05
140·25
150·65


QUID ALCOHOL

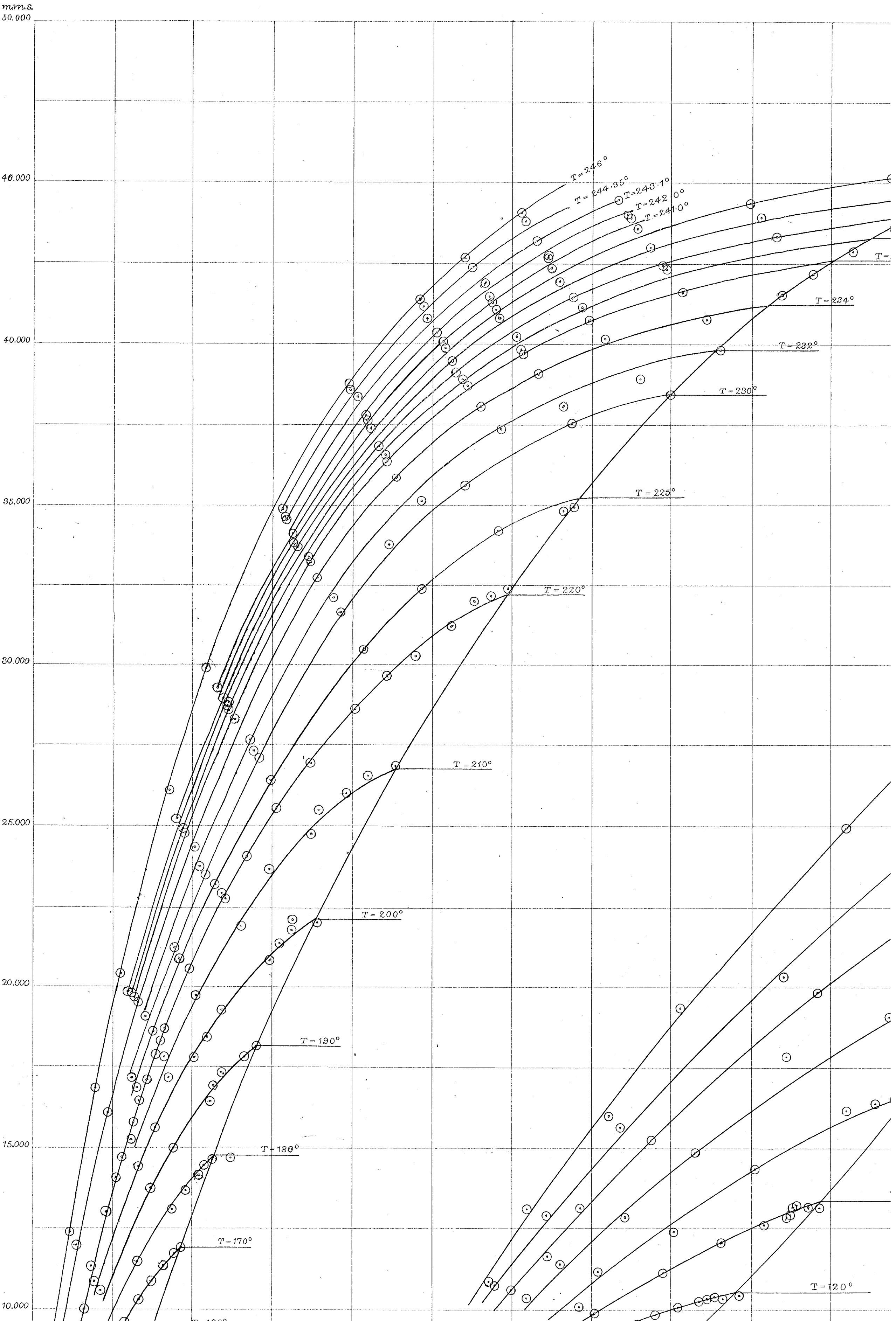
f 1 gram in Cubic Centimeters.

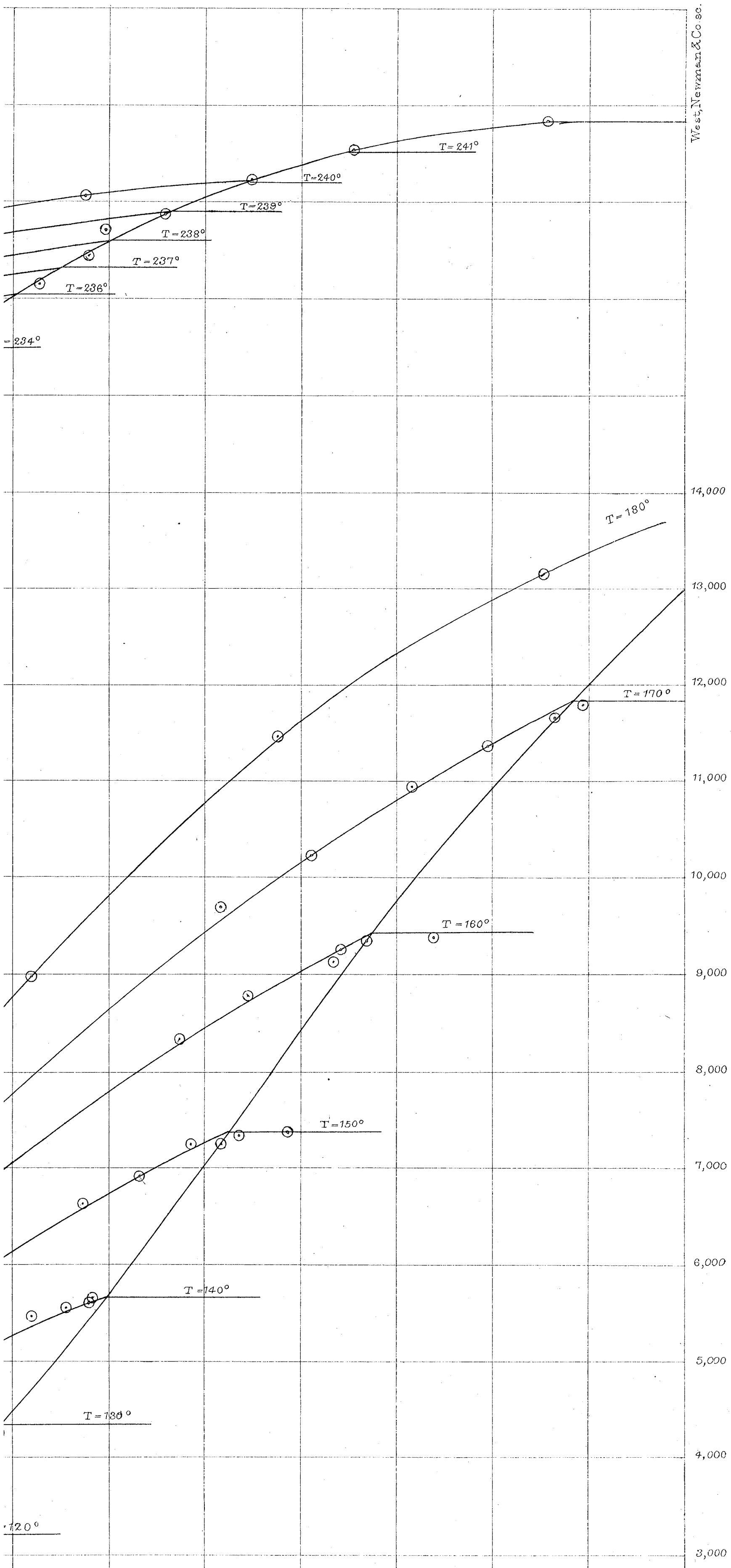
West Newma

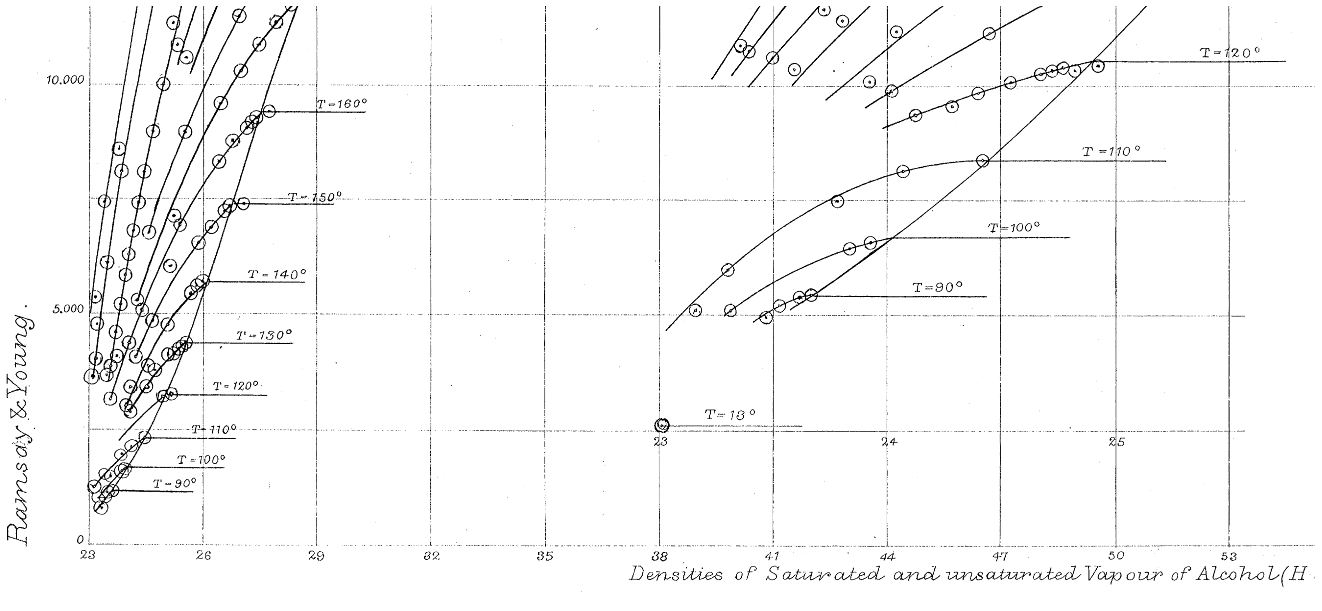


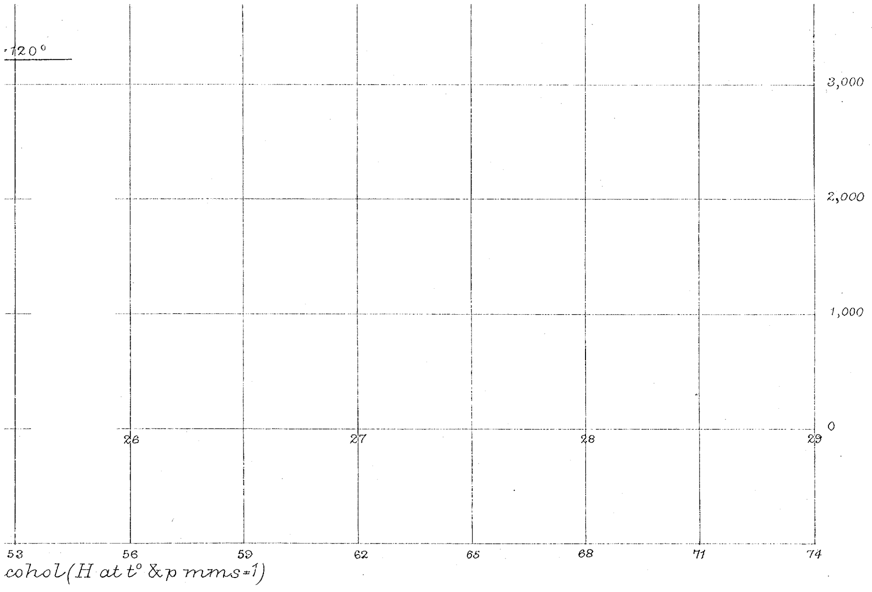
West Newman & C° lith.

Phil. Trans. 1886. Plate 4.




West,Newman&Co.sc.
T=241°
T=240°
T=239°
T=238°
T=237°
T=236°
=234°
14,000
T=180°
13,000
12,000
T=170°
11,000
10,000
T=160°
9,000
8,000
T=150°
7,000
6,000
T=140°
5,000
T=130°
4,000
120°
3,000


Ramsay & Young.
10.000
5.000
0
T = 160°
T = 150°
T = 140°
T = 130°
T = 120°
T = 110°
T = 100°
T = 90°
T = 120°
T = 110°
T = 100°
T = 90°
T = 18°
23
24
25
23
26
29
32
35
38
41
44
47
50
53
Densities of Saturated and unsaturated Vapour of Alcohol (H


120°
3,000
2,000
1,000
0
26
27
28
29
53
56
59
62
65
68
71
74
cohol(H at t° & p mms=1)

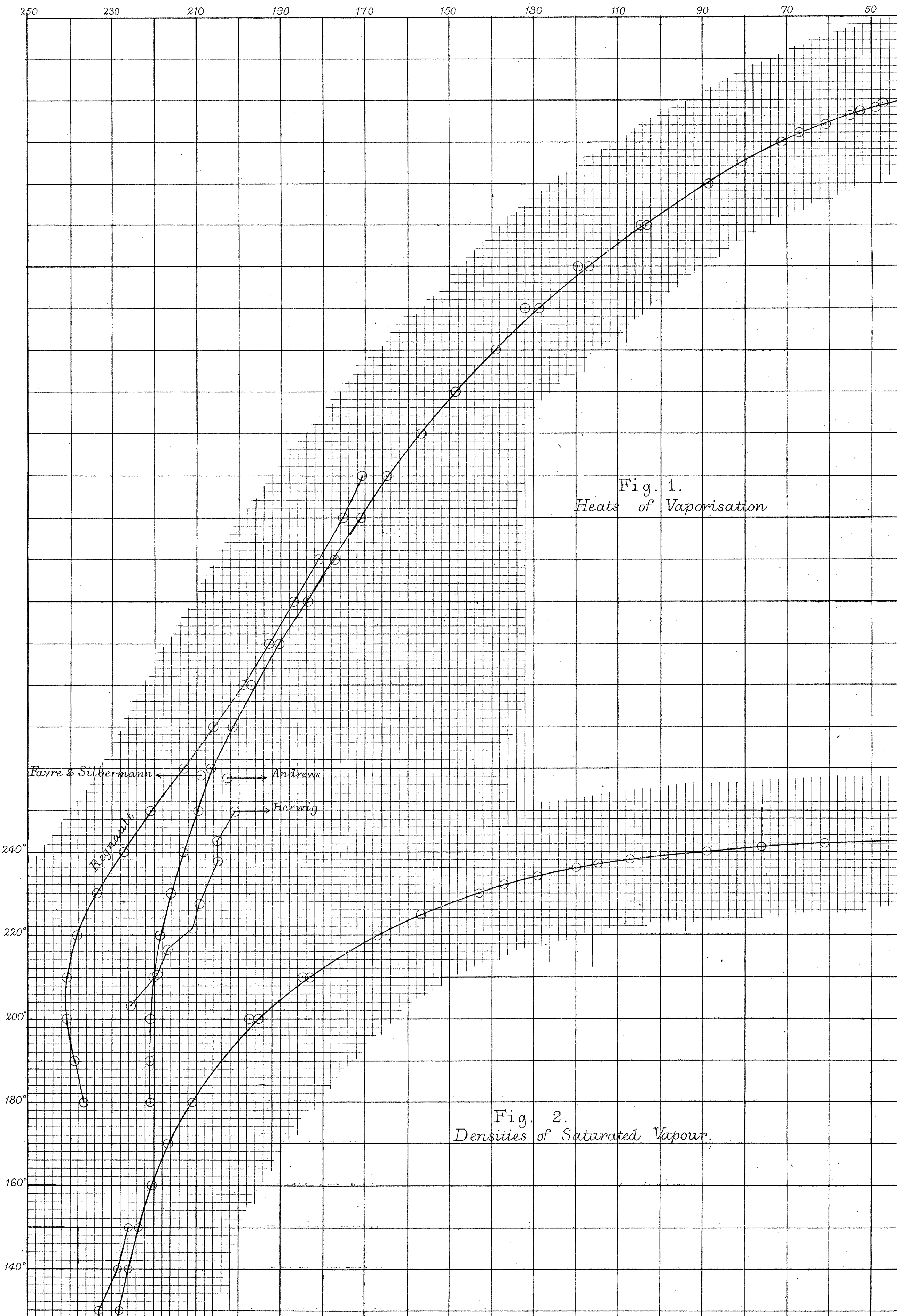
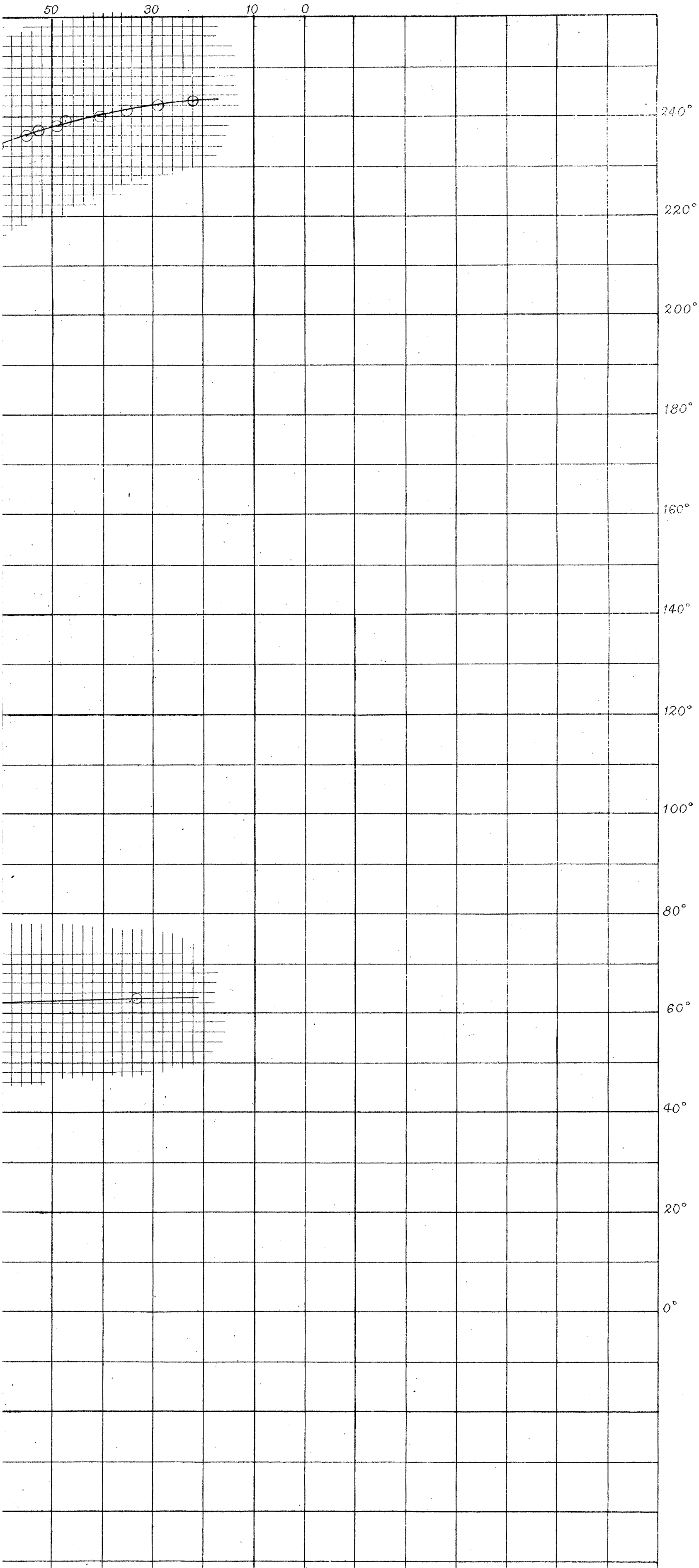
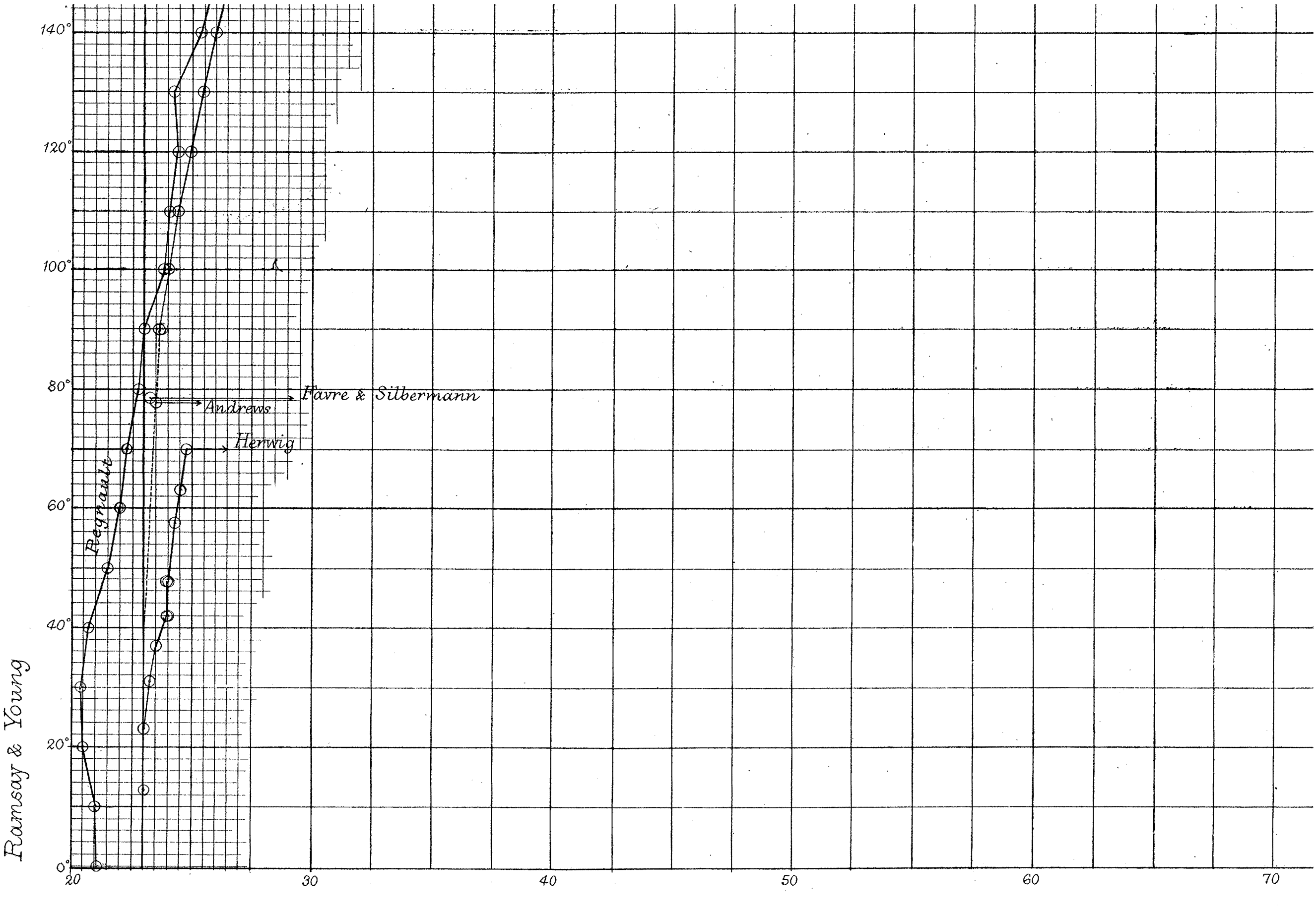


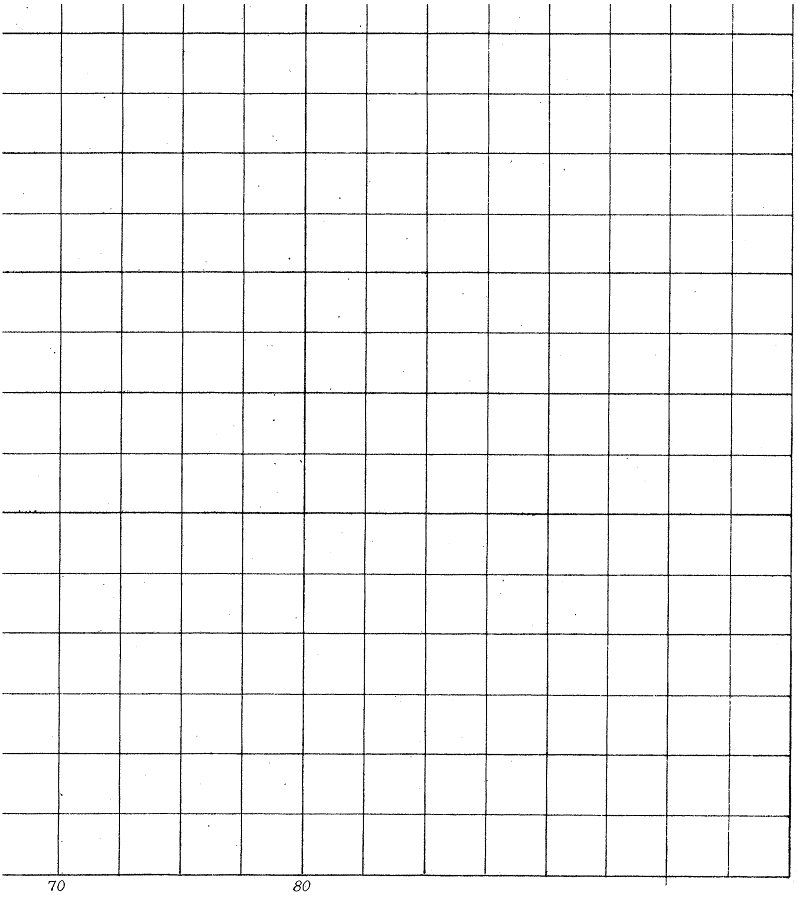
Fig. 1.
Heats of Vaporisation

Fig. 2.
Densities of Saturated Vapour.

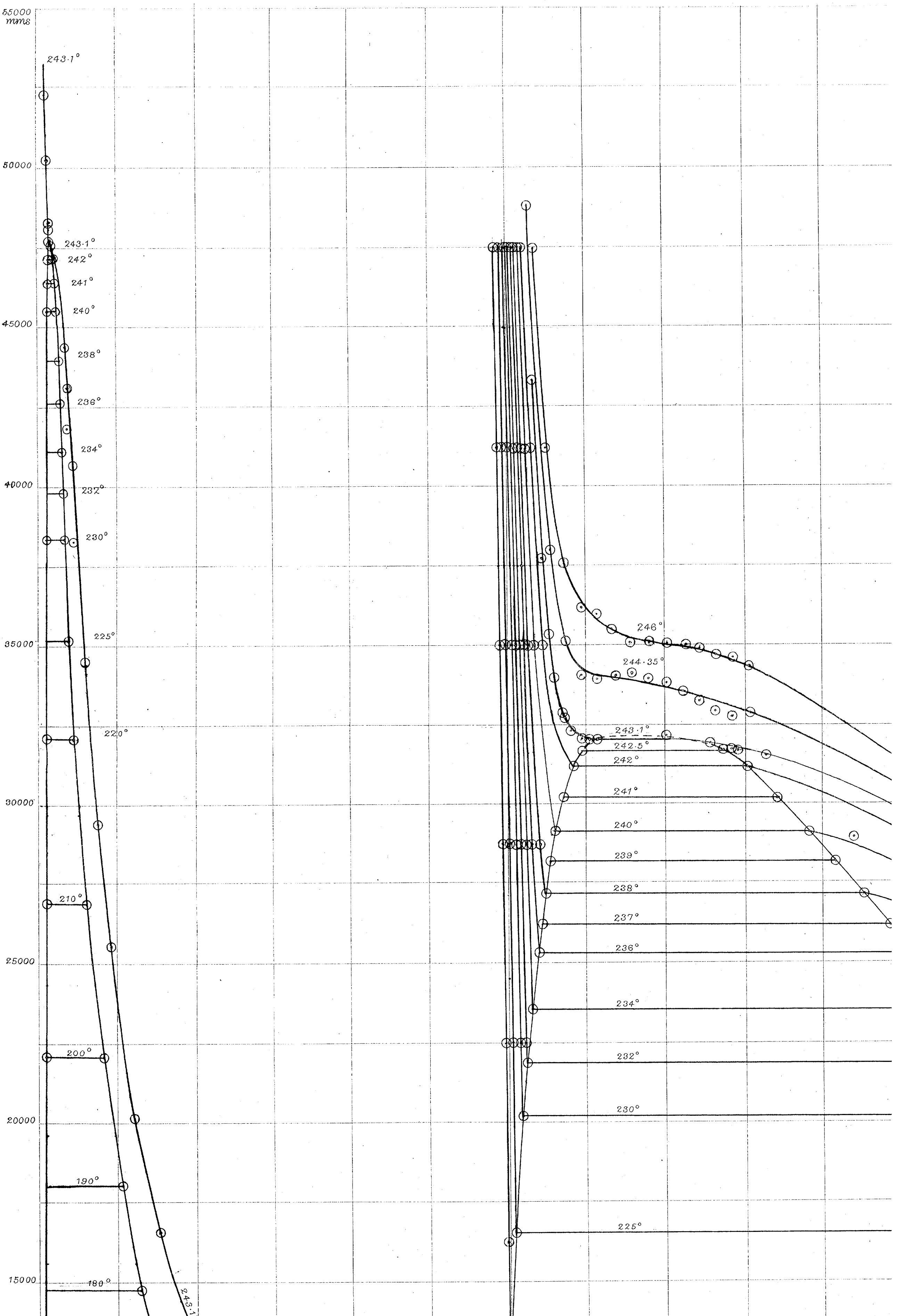


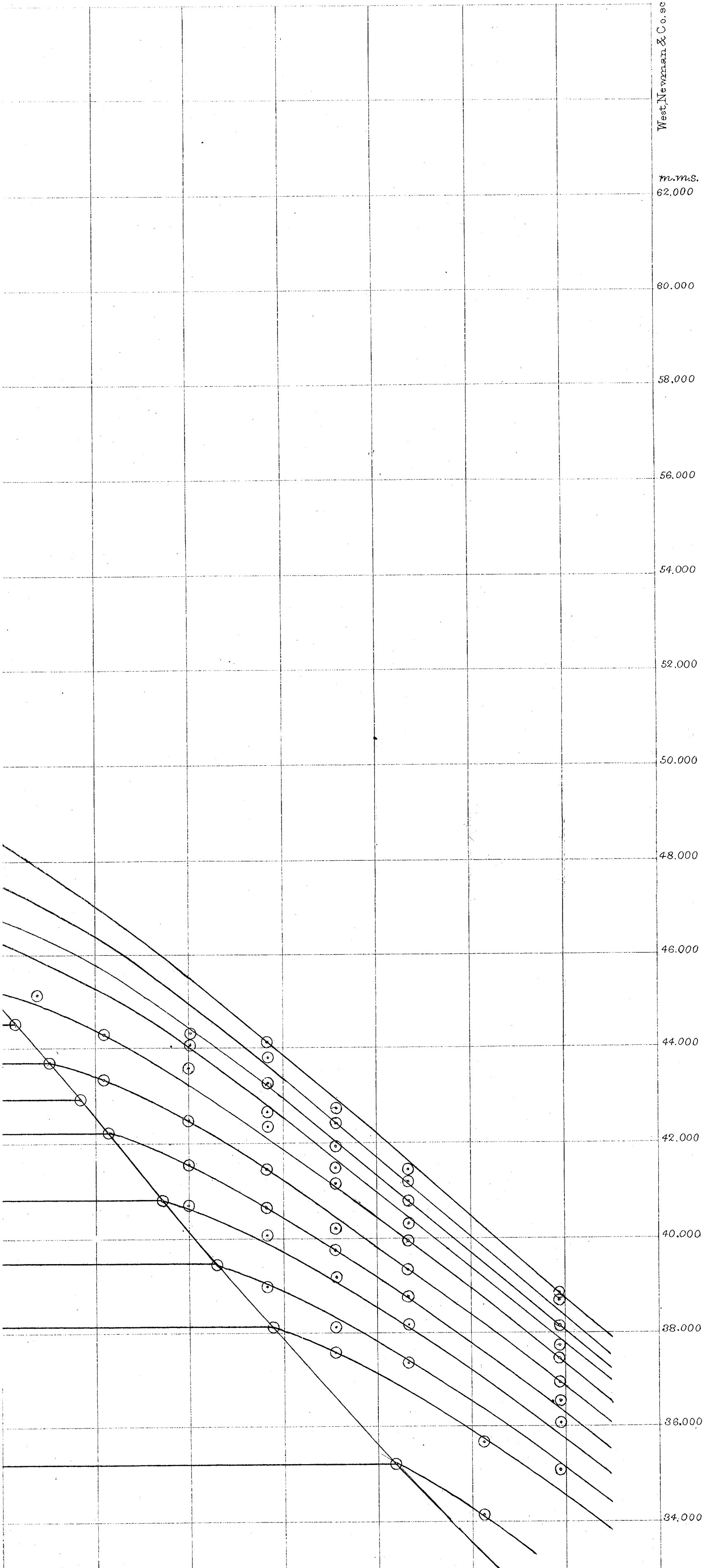
West, Newman & Co. lith.


140°
120°
100°
80°
60°
40°
20°
0°
20
30
40
50
60
70
Ramsay & Young
Regnault
Andrews
Favre & Silbermann
Herwig

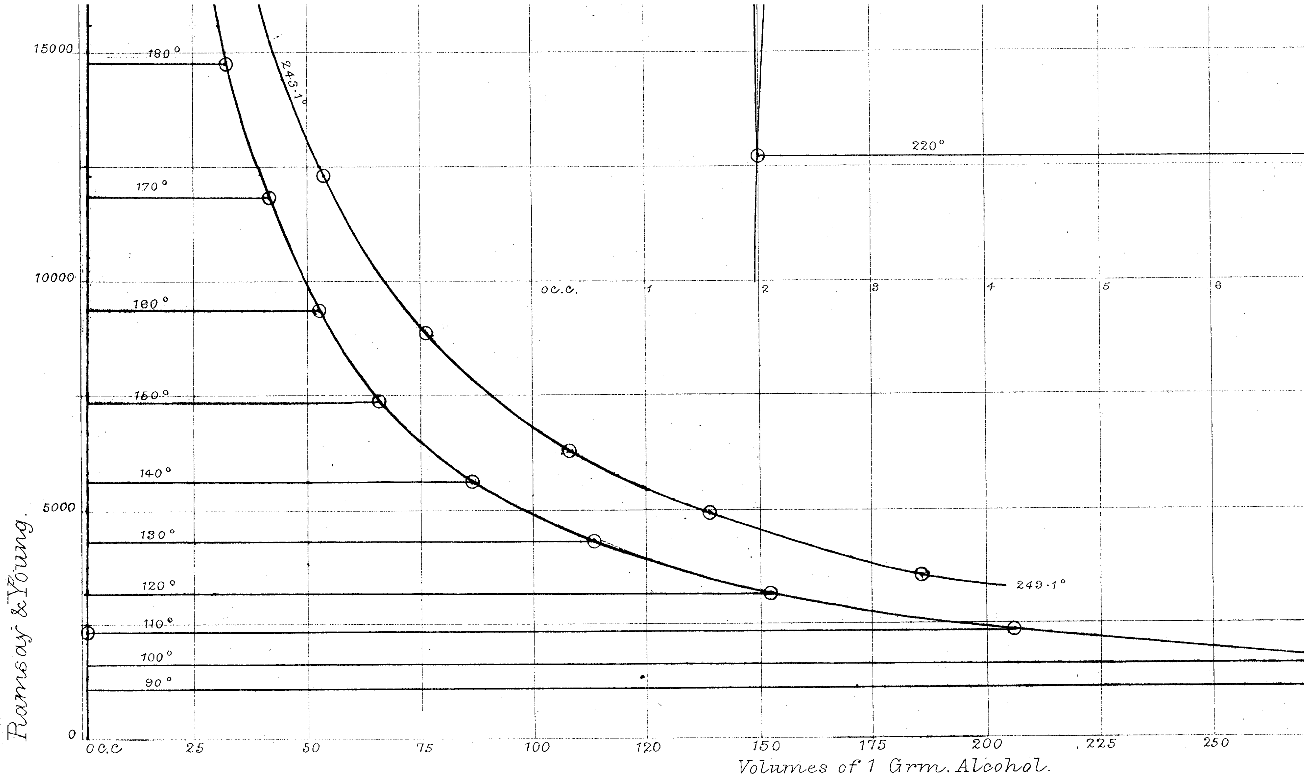

70
80

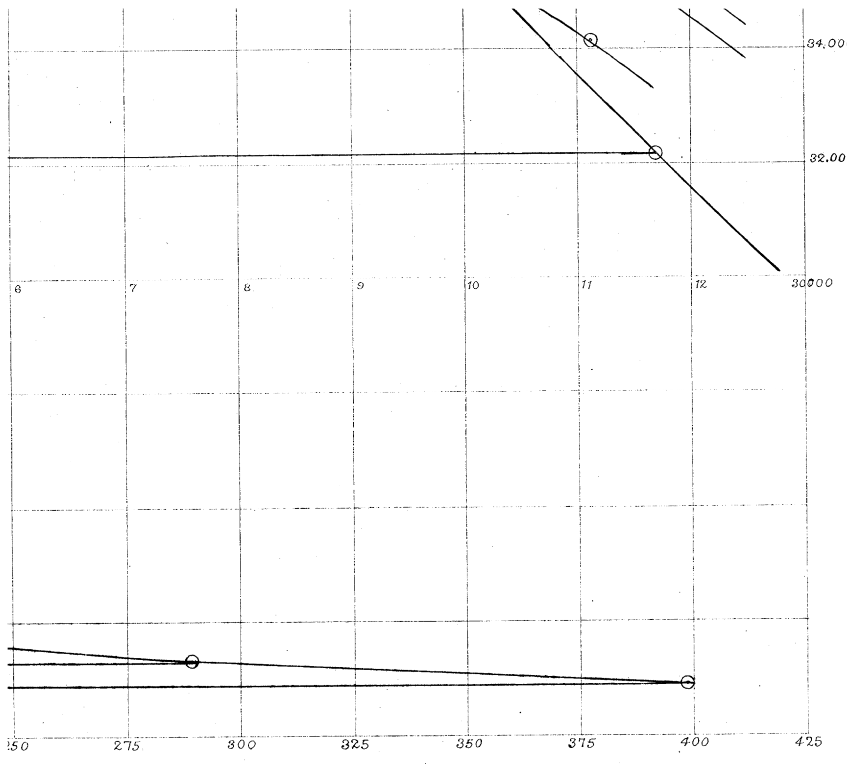
Phil. Trans. 1886. Plate 6.



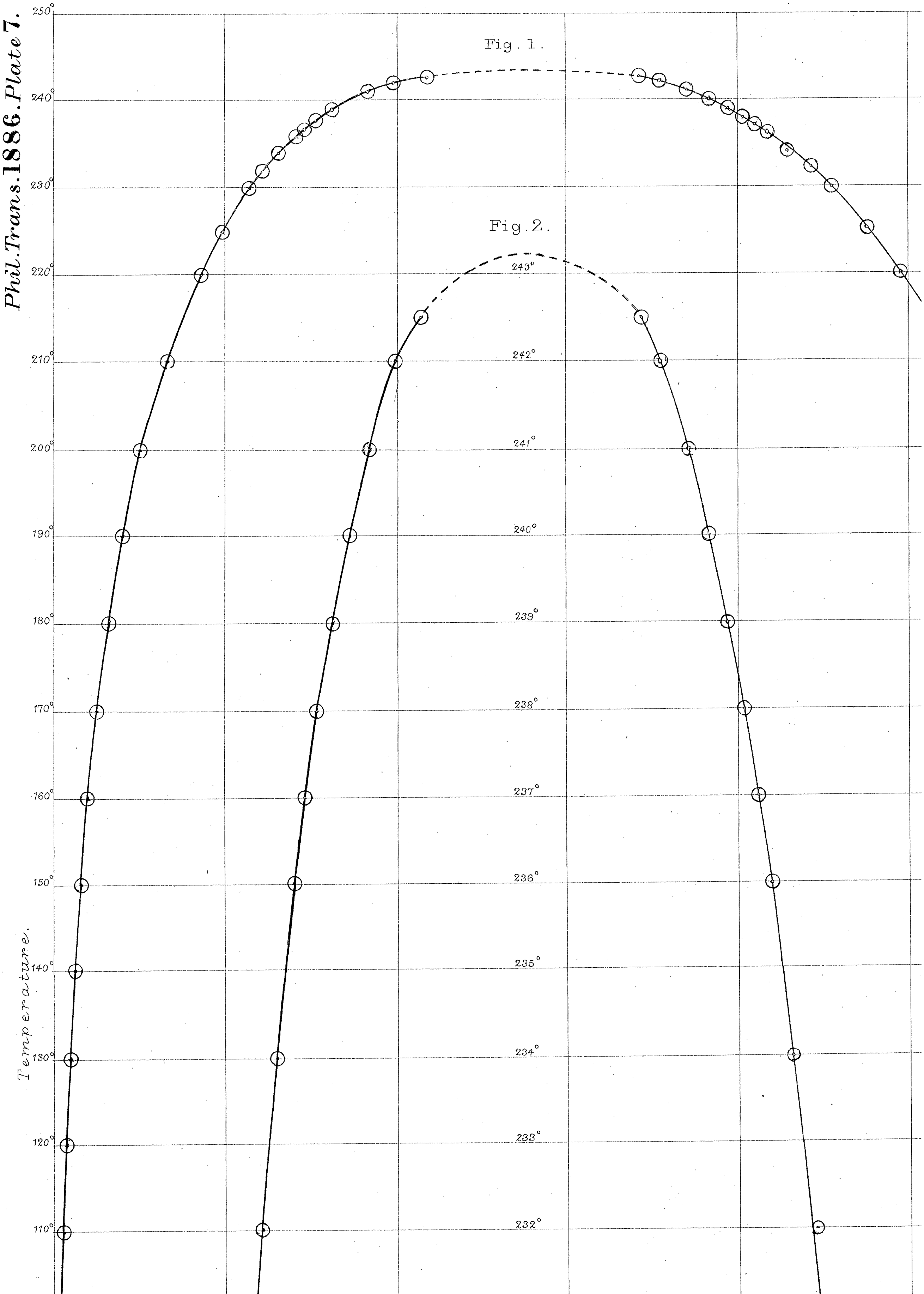


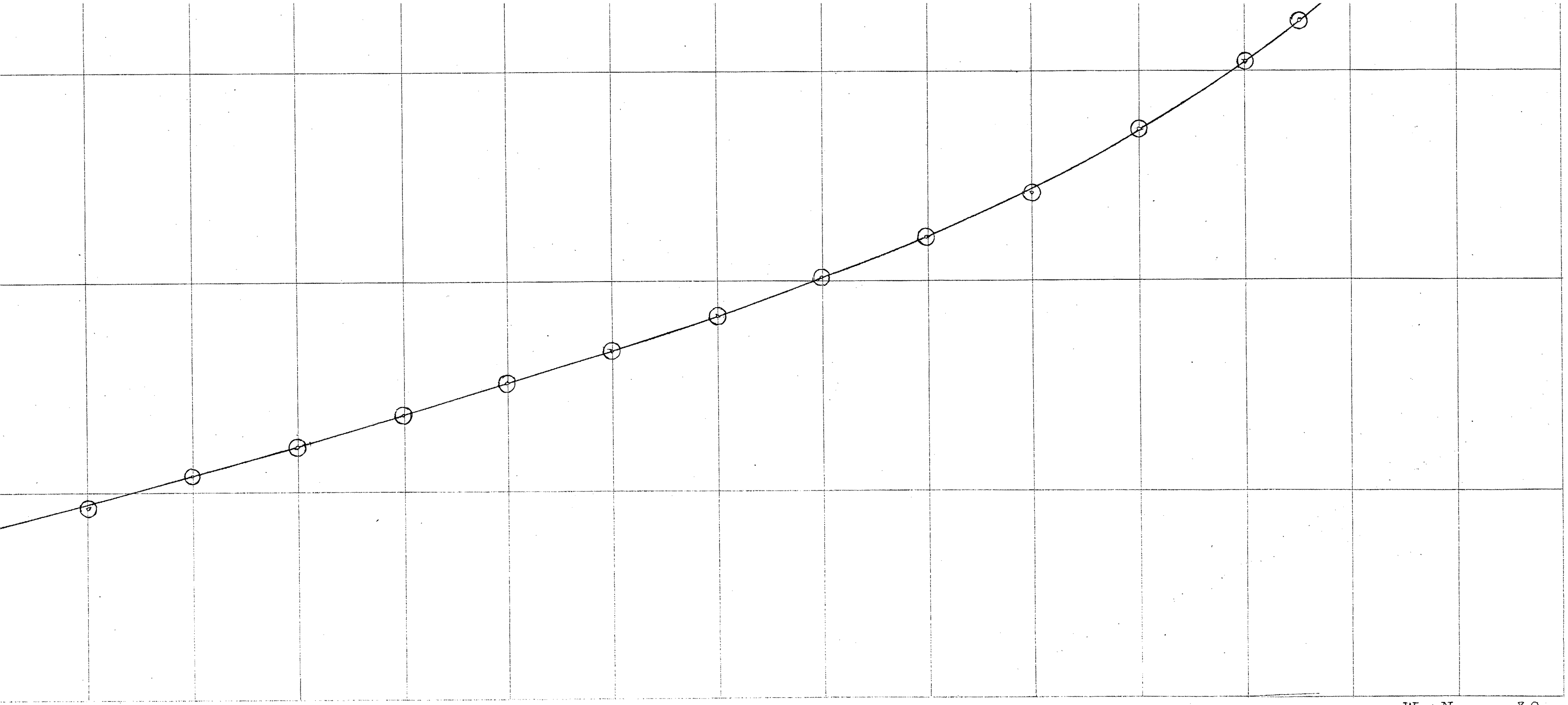
West, Newman & Co. sc.


15000
10000
5000
0
180°
170°
160°
150°
140°
130°
120°
110°
100°
90°
220°
243.1°
243·1°
0 C.C.
1
2
3
4
5
6
0 C.C
25
50
75
100
120
150
175
200
225
250
Volumes of 1 Grm. Alcohol.
Ramsay & Young.

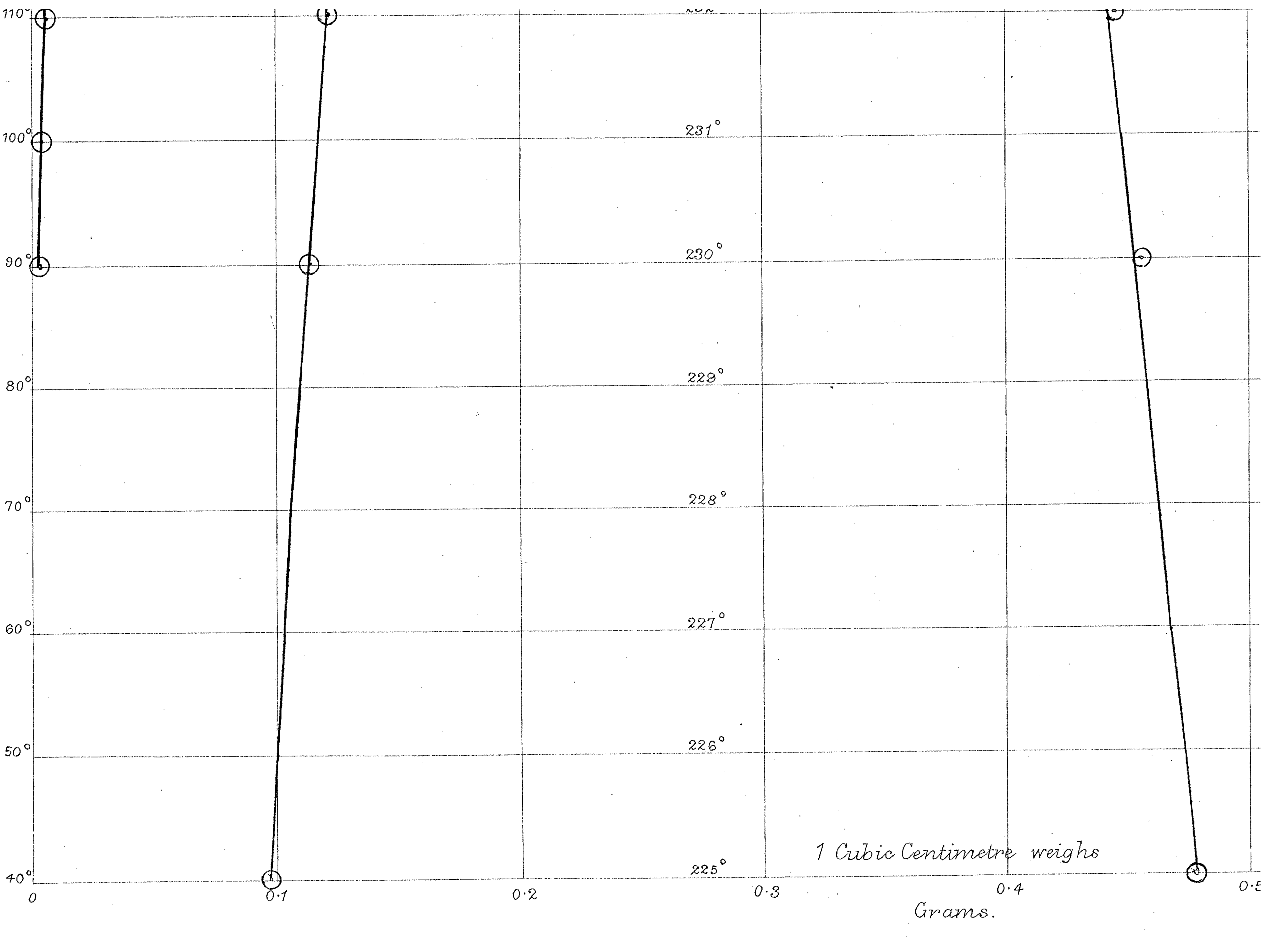

34.000
32.000
30000
6
7
8
9
10
11
12
250
275
300
325
350
375
400
425

Phil. Trans. 1886. Plate 7.

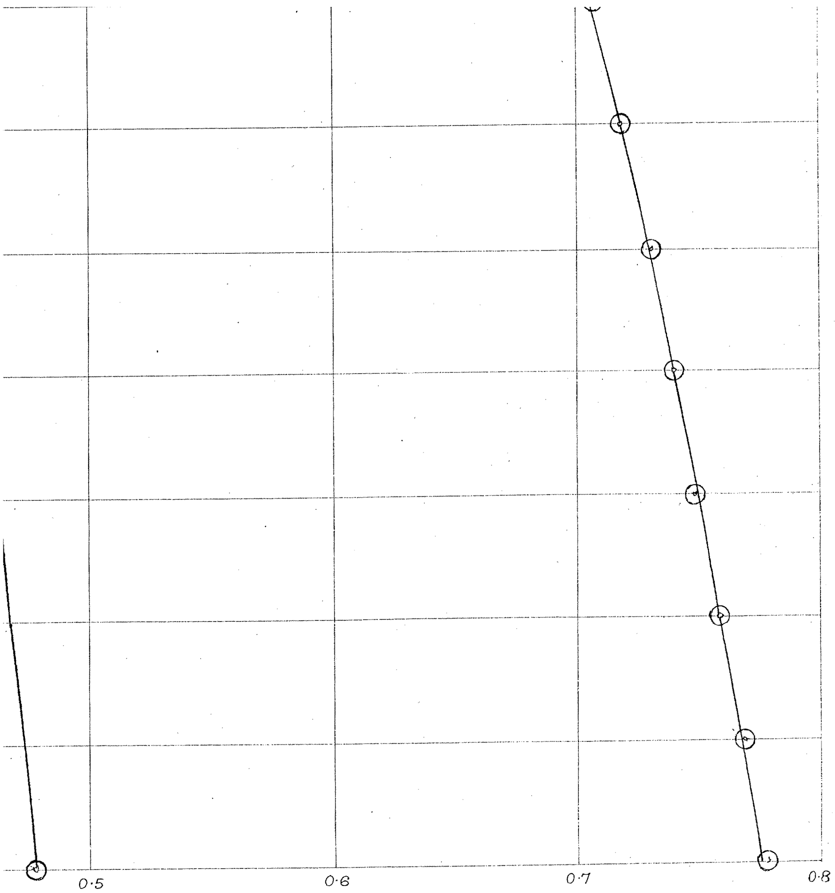


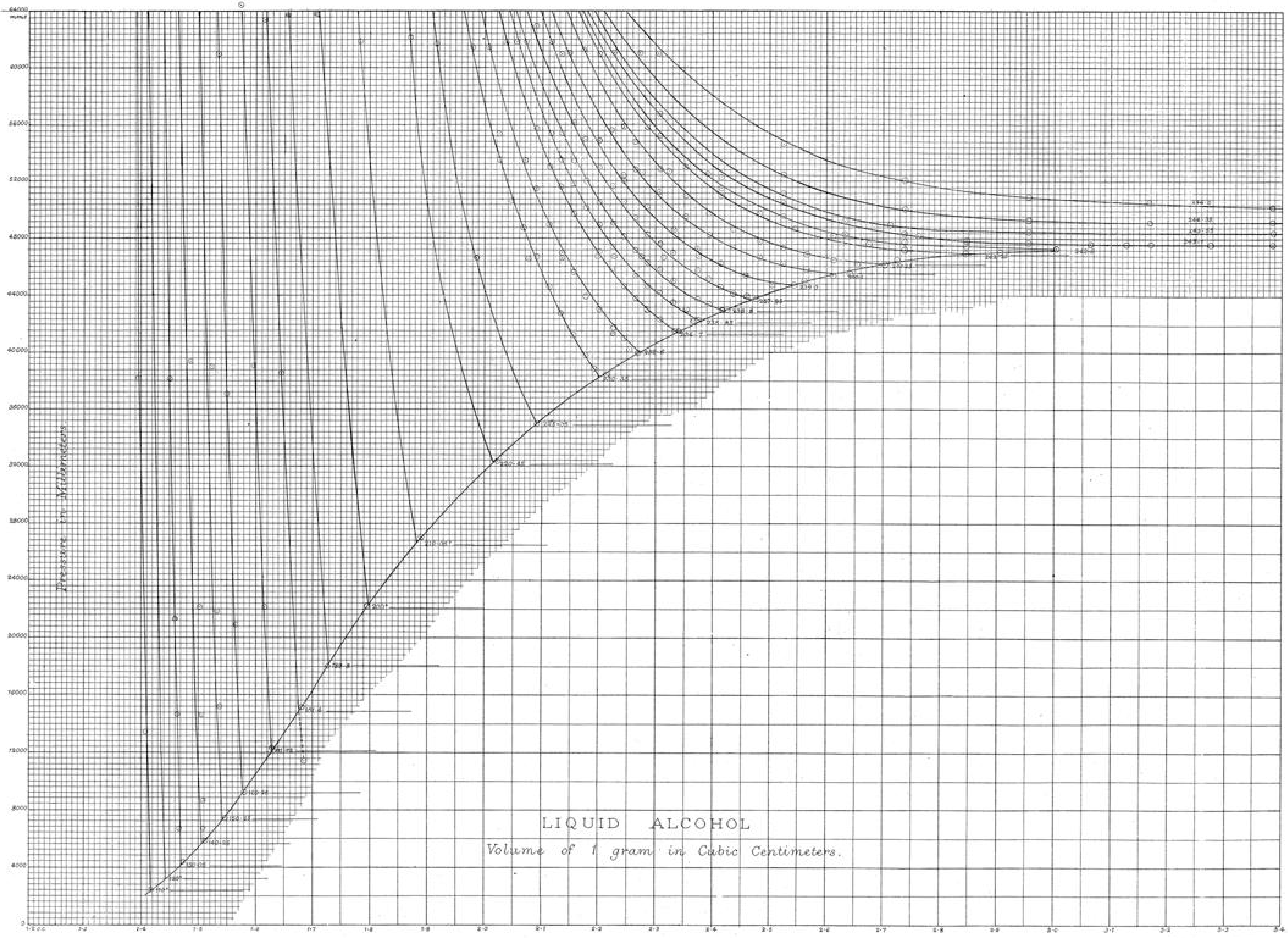


West, Newman & Co. sc.



Ramsay & Young.


0·5
0·6
0·7
0·8

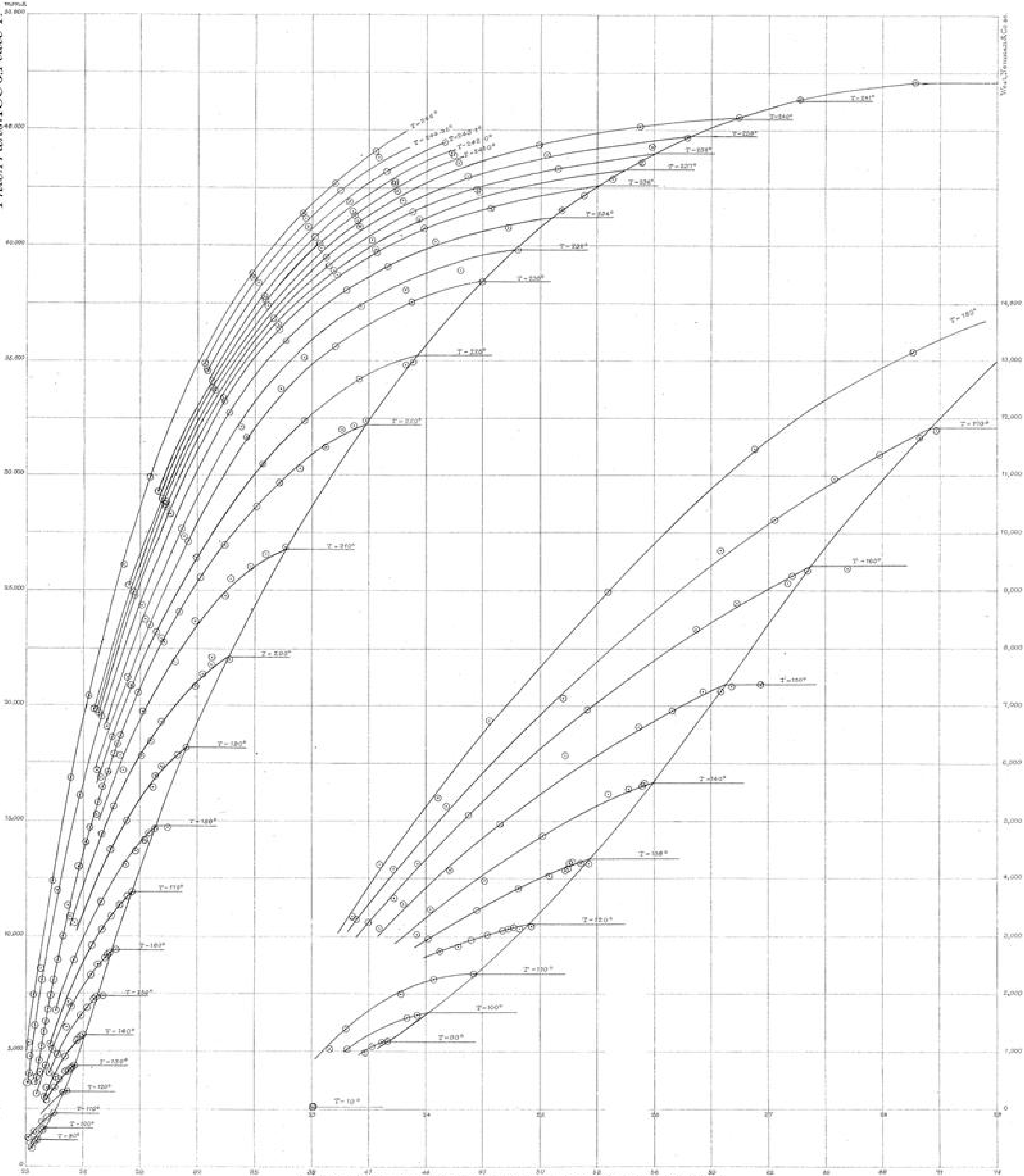


LIQUID ALCOHOL

Volume of 1 gram in Cubic Centimeters.

West Newman & Co lith.

Phil. Trans. 1886, Plate 4.



Ramsay & Young.

West, Newman & Co. sc.

Phil. Trans. **1886.** *Plate* **5.**

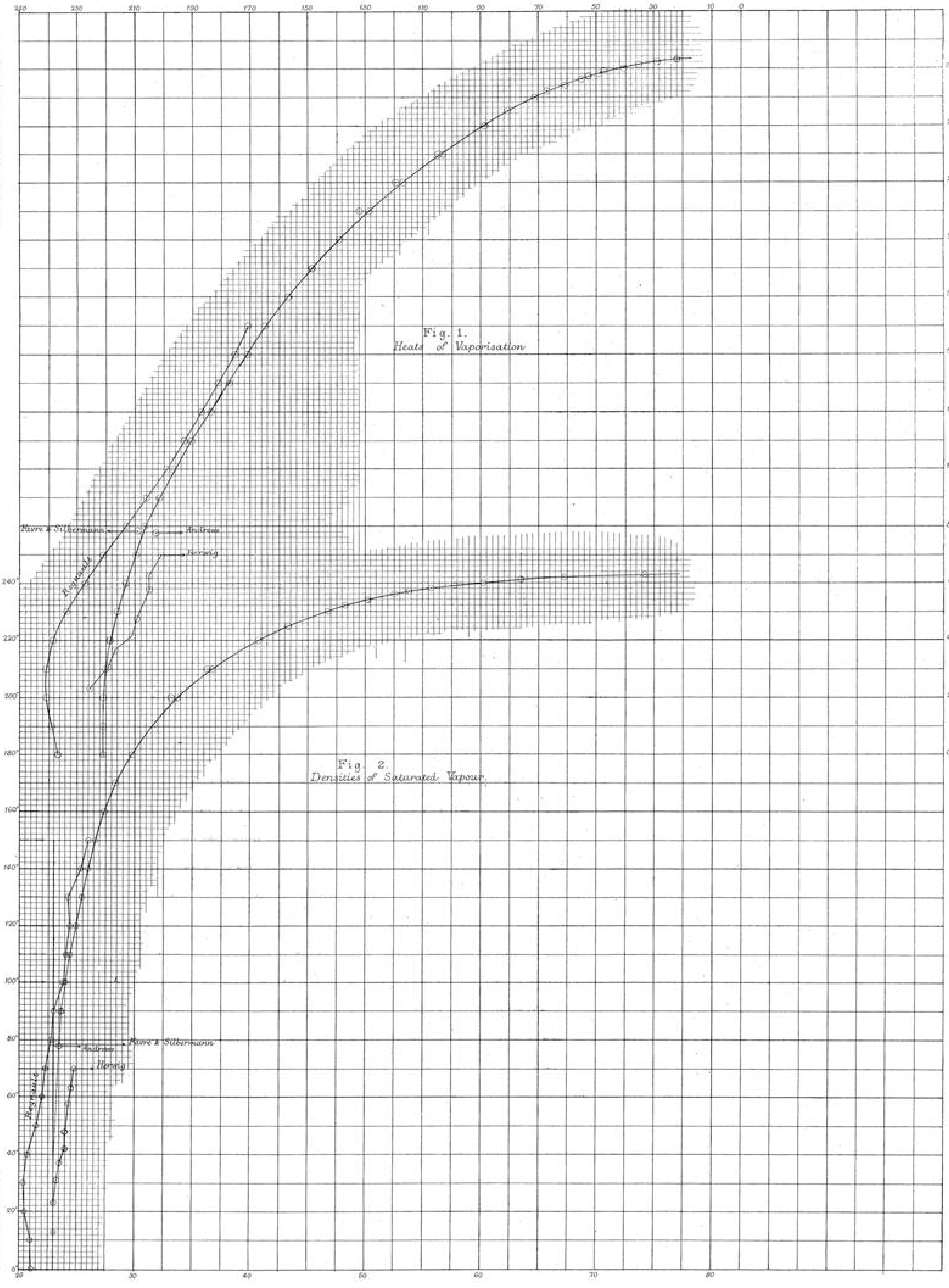
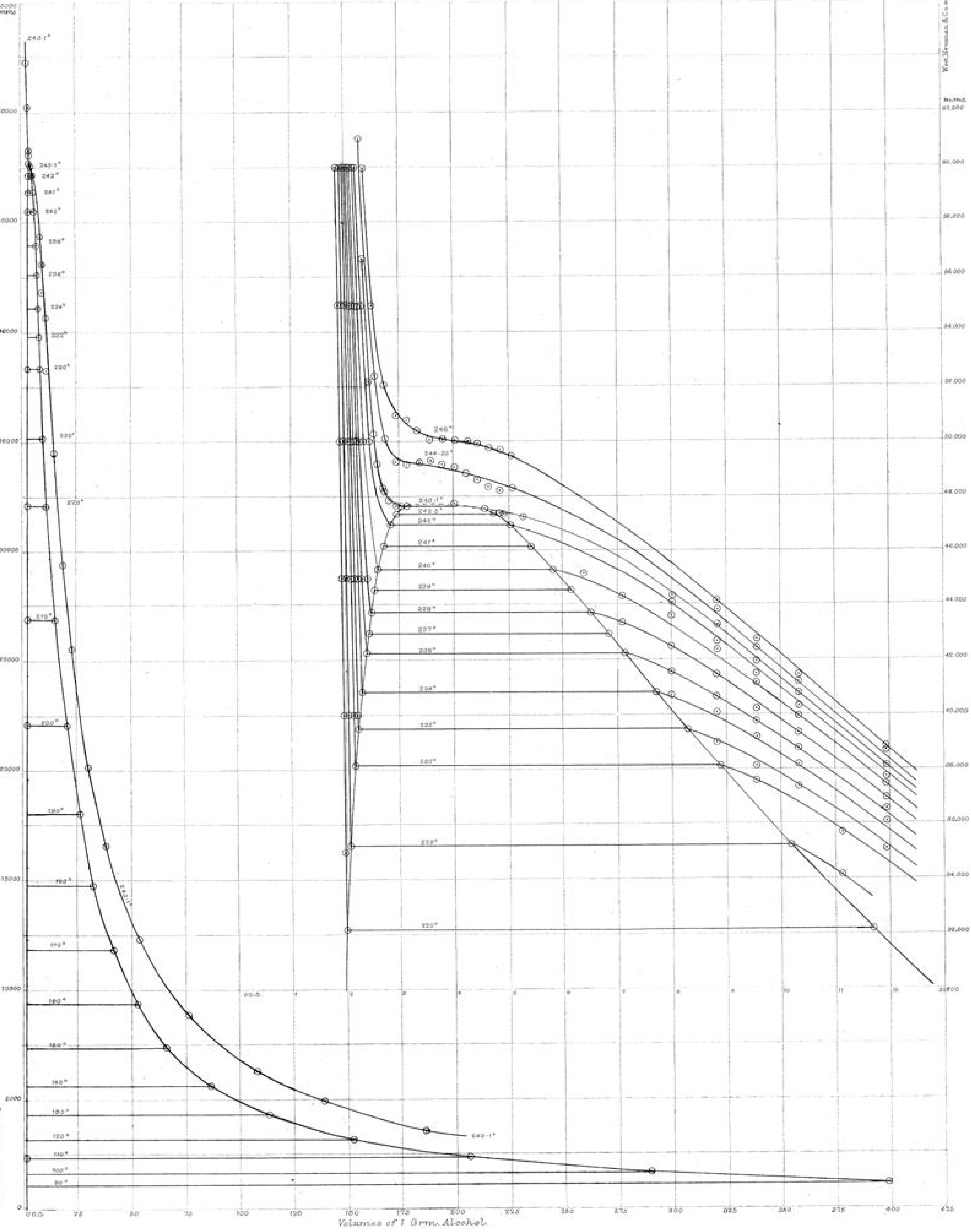


Fig. 1.
Heats of Vaporisation

Fig. 2.
Densities of Saturated Vapour.

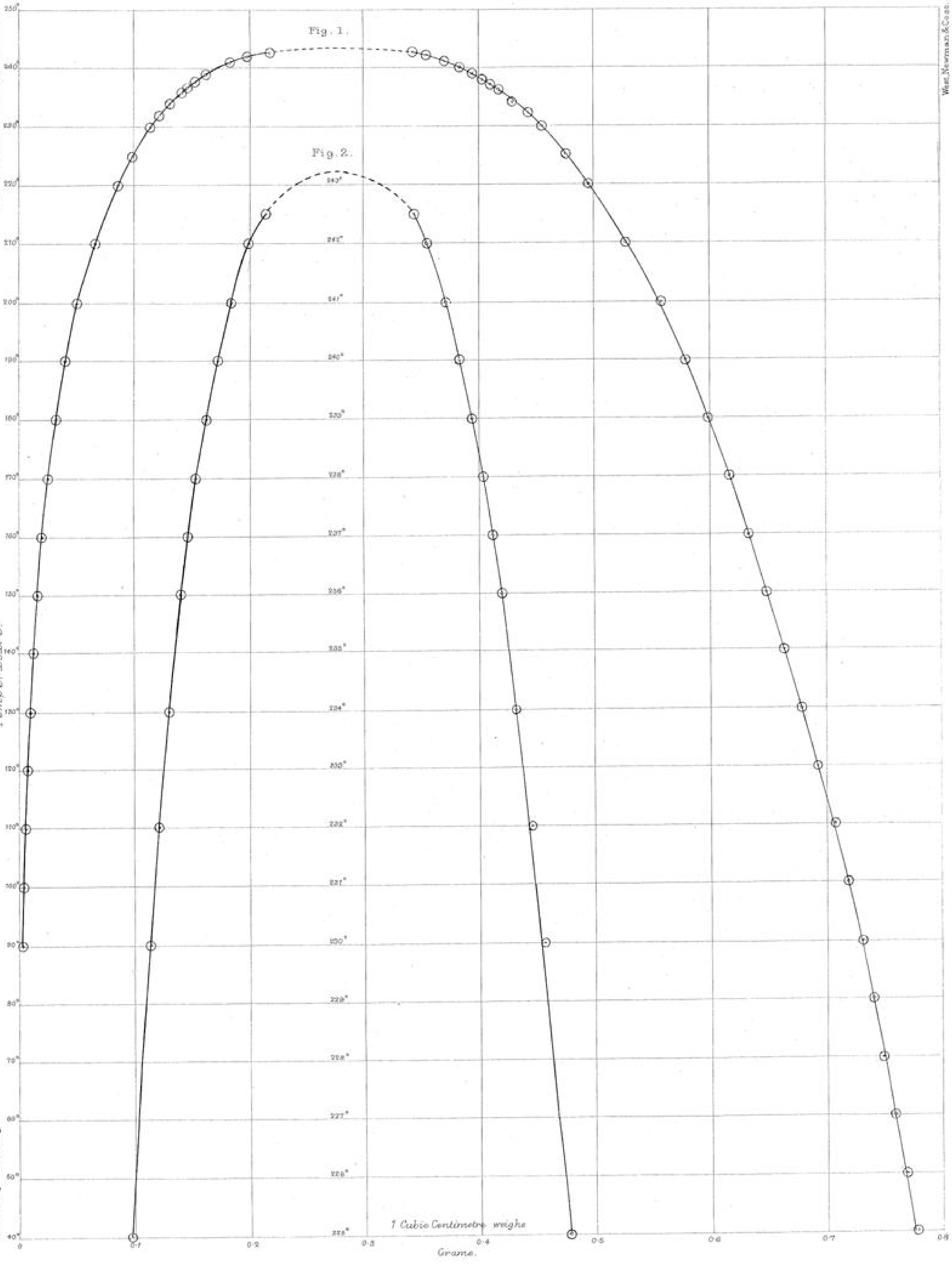
Ramsay & Young



Ramsay & Young.

West, Newman & Co. sc.

Phil. Trans. 1886. Plate 7.



Ramsay & Young.

Wm. Newman & Co. sc.