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William Ramsay and Sydney Young

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IV. *On Evaporation and Dissociation.*—Part VIII. *A Study of the Thermal Properties of Propyl Alcohol.*

By Professor WILLIAM RAMSAY, *Ph.D., F.R.S., and Professor* SYDNEY YOUNG, *D.Sc.*

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[PLATES 3–7.]

IN continuation of our investigations of the thermal properties of pure liquids, we have now determined the vapour-pressures, vapour-densities, and expansion in the liquid and gaseous states, of Propyl Alcohol, and from these results we have calculated the heats of vaporization at definite temperatures. The range of temperature is from 5° to 280°, and the range of pressure from 5 mms. to 56,000 mms.

Preparation of pure Propyl Alcohol.—A sample of propyl alcohol was procured from KAHLBAUM, of Berlin. It was dried with barium oxide, and then with small quantities of sodium; but in this case the results were not nearly so satisfactory as with methyl and ethyl alcohol, for propyl alcohol is soluble in water, forming a mixture or "hydrate," which boils constantly at a lower temperature than the pure alcohol. It is not completely decomposed by sodium, and can be separated only by repeated fractional distillation. This hydrate was first described by CHANCEL ('Comptes Rendus,' vol. 68, 1867, p. 659), who, observing that it boiled with perfect constancy, assumed that it possessed a definite composition, and gave it the formula C_3H_8O, H_2O. It has more recently been examined by KONOWALOW (WIEDEMANN'S 'Annalen,' vol. 14, 1881, p. 34), who has determined the vapour-pressures of varying mixtures of propyl alcohol and water at definite temperatures. KONOWALOW finds that the composition of the mixture, the vapour of which exerts the greatest pressure, is not the same at different temperatures, but that the mixture contains more alcohol at high temperatures than at low. From this it has been concluded that the composition of the "hydrate" must depend on the pressure under which the liquid is distilled. We have proved experimentally that this is the case (but we reserve a discussion of this interesting substance for a future paper), and we give the results of our experiments in an Addendum to this paper.

After repeated fractionation we succeeded in obtaining a quantity of propyl alcohol

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which boiled almost constantly at 97°·6 (the rise of temperature during distillation being less than 0°·1) under a pressure of 763·8 mms. This sample was employed for the determination of vapour-pressures at low temperatures, and for the constants at high temperatures with quantities A, B, and D (see p. 140).

The specific gravity of the alcohol was determined several months later, and a fresh quantity of the alcohol was prepared from the hydrate into which the greater part of the alcohol had been converted. The hydrate was treated with dry potassium carbonate, when, as described by CHANCEL (*loc. cit.*), two layers were formed, the lower one being an aqueous solution of potassium carbonate, the upper one consisting of the partially hydrated alcohol. The alcohol was fractionated several times, potassium carbonate being each time added to the most volatile distillate, until a quantity was obtained, boiling from 97°·1 to 97°·15 under a pressure of 752 mms.

For the determinations of vapour-density at high temperatures with quantity C, the alcohol was refractionated. The portion employed boiled constantly at 97°·1 under a pressure of 750·6 mms.

Reduced to 760 mms. these temperatures would be (1) 97°·45; (2) 97°·4; (3) 97°·4.

The boiling-point of propyl alcohol has been determined by numerous experimenters, and the results obtained by several are very concordant; the most reliable appear to be the following:—

Observer.	Reference.	Pressure.	Temperature.	Temperature reduced to 760 mms.
BRÜHL	'Annalen der Chemie,' vol. 200, p. 173	752·2	97–97·2	97·35
ZANDER	,, ,, ,, 214, p. 153	760·0	97·40	97·40
LINNEMANN	,, ,, ,, 161, p. 26	760·0	97·41	97·41
SCHIFF	,, ,, ,, 220, p. 101	752·4	97·10	97·35
KONOWALOW	*Loc. cit.*	749·2	97·00	97·37

PIERRE and PUCHOT ('Annales de Chimie,' vol. 22, 1871, p. 276) found 98°; and PERKIN ('Chem. Soc. Trans.,' vol. 45, p. 446) gives two determinations: 97°·5 to 98°·5 and 98°, but the boiling-point of the alcohol employed in the final determination of specific gravity is not stated.

Apparatus employed.—The apparatus employed was the same as that described in our memoir on Ethyl Oxide ('Phil. Trans.,' A, 1887, p. 57).

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Experimental Results.

Vapour-Pressures at Low Temperatures.—These were determined by our dynamical method. The thermometer had been standardized by determinations of the vapour-pressures of water; its zero point was redetermined.

Table I.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
mms.	°	mms.	°	mms.	°
5·25	5·5	34·5	33·7	235·35	69·5
5·10	4·9	42·05	36·95	240·1	70·0
5·25	5·5	50·05	40·0	273·7	72·85
6·10	7·5	57·55	42·3	312·85	75·85
7·25	9·7	67·6	45·2	355·8	78·8
8·70	12·8	79·7	48·2	404·9	81·9
9·20	13·4	94·6	51·4	455·5	84·6
10·55	15·6	110·95	54·5	505·6	87·0
13·30	18·7	130·8	57·6	561·9	89·6
16·40	21·75	151·85	60·5	615·1	92·0
20·30	25·1	175·3	63·4	672·7	94·3
24·55	28·2	201·1	66·2	760·7	97·5
29·35	31·1	204·8	66·7		

These results were plotted on sectional paper, curves drawn through them, and the pressures corresponding to equal intervals of temperature read off.

Specific Gravity of Propyl Alcohol.—A Sprengel's tube of the form recommended by Perkin was employed. The weighings were reduced to a vacuum :—

Weight of water at 16°·7	15·3169 grms.
Capacity of tube at 16°·7	15·3339 c.cs.
Weight of alcohol at 0°	12·5577 grms.
Capacity of tube at 0°	15·3275 c.cs.
Specific gravity at 0°	0·81929.
Volume of 1 grm. at 0°	1·22056 c.cs.

Weight of alcohol at 10°·72	12·4338 grms.
Capacity of tube at 10°·72	15·3316 c.cs.
Specific gravity at 10°·72	0·81099.
Volume of 1 grm. at 10°·72	1·23306 c.cs.

The results of other observers* are not very easy to compare with ours; some of them are given in terms of water at 0°, others at 4°, and others again at the same

* A tabulated statement of determinations of the boiling-point and specific gravity of propyl alcohol is given by Lossen, 'Annalen der Chemie u. Pharmacie,' vol. 214, p. 105.

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temperature as the alcohol. The best method of comparison appears to be to reduce the results of other observers to true densities, and to read from the curve constructed from our observations the densities at the corresponding temperatures. The most reliable results appear to be the following (the references are the same as before):—

Observer.	Specific gravity $\frac{t^\circ}{t'^\circ}$	Density or $\frac{t^\circ}{4^\circ}$	Result from our curve.
Brühl	·8044 20°/4°	·8044 at 20°	·8035
Zander	·8069 17°/0°	·8068 at 17°	·8059
Linnemann	·8066 15°/15°	·8059 at 15°	·8076
Perkin	·80883 15°/15°	·8082 at 15°	·8076
,,	·80247 25°/25°	·8002 at 25°	·7995
Schiff	·7366 97°·1/4°	·7366 at 97°·1	·7353

It will be seen that our results are in close agreement with those of other observers; they are very slightly lower than most of the others, but at 15° our result is rather higher than Linnemann's.

Constants at High Temperatures.—Four different amounts of propyl alcohol were employed for these determinations. The vapour-pressures and the orthobaric volumes and compressibilities of the liquid were determined with the largest quantity, A, the weight of which was calculated from its volume and specific gravity. The smaller quantities, B, C, D, were employed for the determinations of the volumes of a gram of vapour. The weight of B was ascertained by comparisons of its volume with that of A under similar conditions of temperature and pressure. The weight of C was obtained in a similar manner from that of B, and the weight of D similarly from that of C.

Weight of quantity A.—The actual volumes of this quantity at various temperatures were plotted on sectional paper, and a curve drawn through the points; the volumes at 0° and 10°·72 were read off, and the weight calculated from the densities at those temperatures.

Volume of A at 0°	0·32335.	Volume of 1 grm. at 0°	1·22056.
Volume of A at 10°·72	0·32675.	Volume of 1 grm. at 10°·72	1·23306.

	Grm.
Weight from volume at 0°	0·26492
Weight from volume at 10°·72	0·26499
Mean	0·26496

		Grm.
Weight of B.	Mean of numerous comparisons with A	0·03763.
Weight of C.	Mean of numerous comparisons with B	0·006015.
Weight of D.	Mean of numerous comparisons with C	0·005180.

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Constants with the largest quantity, A.—The vapour-pressures at each temperature were, as usual, determined at the widest possible limits of volume.

Volume of 1 grm. at 23°·7 = 1·2493. Specific gravity 0·8004.

The pure liquids employed for obtaining constant temperatures were carbon bisulphide, ethyl alcohol, chlorobenzene, bromobenzene, aniline, methyl salicylate, and bromonaphthalene ('Chem. Soc. Trans.,' 1885, p. 640). We think it unnecessary to state in each case the liquid employed and the pressure under which it boiled.

Temperature.	Volume of 1 grm.	Specific gravity. (Weight of 1 c.c.)	Pressure.
°	c.cs.		mms.
30	1·2569	0·7956	800
	1·2522	..	32,590
40	1·2712	0·7866	800
	1·2659	..	22,910
	1·2612	..	53,480
50	1·2850	0·7782	800
	1·2796	..	19,730
	1·2743	..	53,480
60	1·2992	0·7697	800
	1·2934	..	23,730
	1·2873	..	53,480
70	1·3137	0·7612	800
	1·3070	..	26,210
	1·3017	..	53,480
80	1·3298	0·7520	800
	1·3274	..	6,750
	1·3207	..	29,090
	1·3180	..	53,480
90	1·3742	0·7423	800
	1·3412	..	17,070
	1·3346	..	37,970
100	..	..	842
			843
			842
			843
		Mean vap.-press.	= 842·5
	1·3651	0·7326	800
	1·3618	..	11,510
	1·3550	..	31,910
	1·3483	..	53,480
110	..	..	1,204
			1,207
			1,205
			1,207
		Mean vap.-press.	= 1,206
	1·3863	0·7214	1,200
	1·3822	..	7,415
	1·3754	..	27,910
	1·3687	..	47,480

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Temperature.	Volume of 1 grm.	Specific gravity. (Weight of 1 c.c.)	Pressure.
°	c.cs.		mms.
120	..	..	1,681 } 1,683 } 1,684 } 1,684 }
		Mean vap.-press.	= 1,683
	1·4028	0·7129	1,684
	1·3961	..	18,540
	1·3894	..	35,000
	1·3833	..	53,490
130	..	..	2,292 } 2,293 } 2,291 } 2,302 }
		Mean vap.-press.	= 2,295
	1·4292	0·6997	2,300
	1·4231	..	12,300
	1·4163	..	26,100
	1·4097	..	40,290
	1·4031	..	54,680
140	..	..	3,077 } 3,071 } 3,076 } 3,072 }
		Mean vap.-press.	= 3,074
	1·4572	..	1,160
	1·4546	0·6875	3,074
	1·4505	..	7,305
	1·4439	..	20,190
	1·4371	..	33,430
	1·4303	..	48,270
150	..	..	4,053 } 4,062 } 4,067 } 4,054 }
		Mean vap.-press.	= 4,059
	1·4835	0·6741	4,022
	1·4775	..	11,250
	1·4708	..	23,010
	1·4642	..	35,230
	1·4576	..	44,690
160	..	..	5,270 } 5,257 } 5,272 } 5,259 }
		Mean vap.-press.	= 5,264
	1·5144	0·6603	5,294

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Temperature.	Volume of 1 grm.	Specific gravity. (Weight of 1 c.c.)	Pressure.
°	c.cs.		mms.
170	..	..	6,657
			6,720
			6,702
			6,702
		Mean vap.-press.	= 6,695
	1·5518	0·6444	6,750
	1·5458	..	14,012
	1·5391	..	22,689
	1·5323	..	29,197
	1·5256	..	38,919
	1·5189	..	45,898
	1·5122	..	55,431
180	..	..	8,374
			8,388
			8,387
			8,398
		Mean vap.-press.	= 8,387
	1·5913	0·6284	8,560
	1·5865	..	11,810
	1·5797	..	18,710
	1·5730	..	24,260
	1·5663	..	31,430
	1·5596	..	38,000
	1·5529	..	45,750
	1·5497	..	52,510
190	...	..	10,488
			10,467
			10,468
			10,441
		Mean vap.-press.	= 10,466
	1·6356	0·6114	10,410
	1·6343	..	12,020
	1·6274	..	16,680
	1·6206	..	22,040
	1·6138	..	26,650
	1·6070	..	32,250
	1·6004	..	38,020
	1·5938	..	43,800
	1·5869	..	49,500
200	..	..	12,807
			12,817
			12,831
			12,856
		Mean vap.-press.	= 12,828
	1·6888	0·5921	12,829
	1·6820	..	16,540
	1·6753	..	20,030
	1·6617	..	27,840
	1·6481	..	36,170
	1·6346	..	45,710
	1·6278	..	50,607

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Temperature.	Volume of 1 grm.	Specific gravity. (Weight of 1 c.c.)	Pressure.
°	c.cs.		mms.
210	..	..	15,525 15,562 15,614 15,599
		Mean vap.-press.	= 15,575
	1·7489	0·5718	15,576
	1·7435	..	17,910
	1·7299	..	23,680
	1·7164	..	29,580
	1·7028	..	36,050
	1·6892	..	43,240
	1·6757	..	51,690
220	..	..	18,626 18,653 18,692 18,712
		Mean vap.-press.	= 18,671
	1·8244	0·5481	18,695
	1·8121	..	21,690
	1·7985	..	25,710
	1·7849	..	29,860
	1·7713	..	34,680
	1·7576	..	39,970
	1·7440	..	45,540
	1·7304	..	51,710
230	..	..	22,108 22,158 22,144 22,234
		Mean vap.-press.	= 22,161
	1·9081	0·5241	22,223
	1·8944	..	24,870
	1·8808	..	27,520
	1·8672	..	30,490
	1·8536	..	33,900
	1·8399	..	37,290
	1·8262	..	41,090
	1·8126	..	45,170
	1·7990	..	49,810
	1·7854	..	54,770
240	..	..	26,204 26,224 26,201 26,204
		Mean vap.-press.	= 26,208
	2·0308	0·4924	26,202
	2·0182	..	27,160
	2·0044	..	28,640
	1·9907	..	30,140
	1·9632	..	33,860
	1·9360	..	38,050
	1·9085	..	43,430
	1·8812	..	49,340
	1·8677	..	53,170

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Temperature.	Volume of 1 grm.	Specific gravity. (Weight of 1 c.c.)	Pressure.
	c.cs.		mms.
250°	..	..	30,729
			30,725
			30,822
			30,840
		Mean vap.-press.	= 30,779
	2·2093	0·4526	30,831
	2·1989	..	31,160
	2·1703	..	32,470
	2·1426	..	33,950
	2·1150	..	35,640
	2·0875	..	37,940
	2·0600	..	40,390
	2·0327	..	43,470
	2·0049	..	47,050
	1·9774	..	51,300
260	..	..	36,137
			36,087
			36,101
			36,115
		Mean vap.-press.	= 36,110
	2·5601	0·3906	36,115
	2·5468	..	36,221
	2·4770	..	36,880
	2·4072	..	38,060
	2·3375	..	39,560
	2·2680	..	42,050
	2·1994	..	45,380
	2·1294	..	50,560
	2·1018	..	53,260
263·15	..	..	37,950
263·5	..	..	38,100
263·54	3·0102	0·3322	38,110
263·64	4·1697	..	38,130
(Critical	3·4696	..	38,110
Temperature)	3·0368	..	38,120
	2·7568	..	38,130
	2·6172	..	39,170
	2·4773	..	40,760
	2·3378	..	43,970
	2·2682	..	46,960
	2·1997	..	50,530
	2·1711	..	52,950
270	4·1702	..	41,540
	3·7496	..	41,940
	3·4701	..	42,150
	3·1770	..	42,620
	2·8973	..	43,340
	2·7571	..	44,000
	2·6172	..	45,480
	2·4776	..	47,760
	2·3381	..	52,130
	2·2686	..	55,630
280·1	4·1713	..	47,000
	3·7505	..	48,040
	3·4710	..	48,550
	3·1778	..	49,730
	2·8981	..	51,540
	2·7578	..	53,310
	2·6179	..	55,510

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Second Quantity, B. Weight = 0·03763.

Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
230	29·34	14,115	38·10
	26·38	15,254	39·14
	24·41	16,114	40·03
	22·35	17,120	41·16
	20·38	18,195	42·46
	19·40	18,793	43·20
	18·41	19,368	44·16
	17·43	20,037	45·09
	16·45	20,674	46·33
	15·48	21,373	47·61
	14·50	21,990	49·39
	Vapour-pressure	= 22,094	
240	29·35	14,602	37·48
	26·39	15,866	38·37
	23·34	17,356	39·65
	21·37	18,483	40·66
	19·40	19,742	41·93
	18·42	20,376	42·80
	17·43	21,073	43·72
	16·45	21,848	44·68
	15·48	22,606	45·89
	14·50	23,388	47·35
	13·54	24,229	48·97
	12·58	25,067	50·95
	11·62	25,869	53·44
	Vapour-pressure	= 26,102	
250	29·35	15,098	36·95
	26·39	16,414	37·80
	23·35	18,012	38·94
	21·38	19,209	39·87
	19·41	20,575	41·01
	17·44	22,126	42·44
	16·46	22,897	43·45
	15·49	23,811	44·41
	14·51	24,688	45·72
	13·54	25,657	47·13
	12·58	26,635	48·87
	11·62	27,658	50·94
	10·67	28,725	53·42
	9·72	29,649	56·81
	8·78	30,546	61·10
	Vapour-pressure	= 30,809	
260	29·36	15,647	36·32
	26·41	16,999	37·18
	23·35	18,710	38·20
	21·38	19,997	39·03
	19·41	21,424	40·13
	17·44	23,087	41·44
	15·49	24,939	43·20
	13·54	27,006	45·62
	12·58	28,178	47·07
	11·62	29,367	48·89
	10·67	30,586	51·12

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Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
260	9·72	31,867	53·85
	8·78	32,961	57·69
	7·83	34,138	62·45
	6·88	35,275	68·75
	6·41	35,646	73·06
	Vapour-pressure =	35,955	
263·64 (Critical Temperature)	9·73	32,467	53·21
	8·78	33,854	56·54
	7·83	35,224	60·92
	6·88	36,433	67·01
	5·94	37,309	75·85
	4·99	37,940	88·66
	4·05	37,969	109·20
	3·11	38,068	141·80
	2·64	39,037	162·70
270	29·37	16,098	35·96
	26·41	17,548	36·69
	23·36	19,379	37·56
	21·39	20,744	38·32
	19·42	22,266	39·32
	17·44	24,002	40·60
	15·49	26,076	42·08
	13·55	28,373	44·23
	11·63	30,953	47·24
	9·73	33,807	51·70
	7·83	36,917	58·81
	5·94	39,765	72·00
	5·00	40,908	85·13
	4·05	41,753	98·17
	3·11	42,824	127·50
	2·64	45,250	142·00
	2·36	51,749	139·00
280·15	29·38	16,572	35·58
	26·41	18,097	36·23
	23·36	19,982	37·10
	21·39	21,417	37·80
	19·42	23,005	38·76
	17·45	24,907	39·84
	15·50	27,073	41·28
	13·55	29,609	43·16
	11·63	32,469	45·86
	9·73	35,803	49·72
	7·83	39,485	56·00
	5·94	43,429	67·14
	5·00	45,290	76·53
	4·05	47,200	90·50
	3·59	48,304	100·00
	3·11	50,451	110·20
	2·83	52,312	116·90

Third Quantity, C. The experiments with this quantity were made with a new pressure apparatus, a new volume-tube, and new pressure-gauges. Fresh samples of methyl salicylate and bromonaphthalene were also employed for heating the tube.

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At each temperature the propyl alcohol vapour was made to occupy the largest possible volume, and was left for several hours until the vapour-pressure of mercury had attained its maximum. Readings were taken every half hour to ascertain when the pressure had become constant. The subsequent readings were taken at diminishing volumes.

Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
150	172·8	2,359	32·25
	162·4	2,497	32·41
	151·9	2,657	32·57
	141·4	2,838	32·77
	130·8	3,044	33·01
	120·2	3,281	33·33
	109·5	3,565	33·66
	98·5	3,891	34·21
	Vapour-pressure	= 4,053	
180	172·9	2,554	32·02
	152·0	2,884	32·25
	130·9	3,325	32·48
	115·0	3,745	32·84
	98·8	4,295	33·31
	82·6	5,043	33·95
	66·3	6,117	34·80
	55·4	7,091	36·02
	49·9	7,721	36·71
	Vapour-pressure	= 8,365	
200	173·0	2,683	31·67
	152·1	3,033	31·86
	131·0	3,492	32·14
	109·7	4,129	32·46
	93·5	4,786	32·85
	77·2	5,683	33·51
	60·9	7,013	34·43
	49·9	8,309	35·44
	44·5	9,136	36·20
	39·0	10,129	37·24
	33·5	11,362	38·63
	Vapour-pressure	= 12,691	
220	173·1	2,813	31·46
	152·2	3,182	31·64
	131·1	3,667	31·88
	109·7	4,335	32·20
	93·5	5,035	32·53
	77·2	5,995	33·09
	60·9	7,435	33·83
	49·9	8,850	34·66
	39·0	10,895	36·07
	33·5	12,318	37·12
	28·0	14,123	38·81
	22·4	16,454	41·56
	19·6	17,850	43·73
	Vapour-pressure	= 18,711	

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Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
230	173·2	2,881	31·34
	162·8	3,053	31·46
	147·0	3,367	31·60
	131·1	3,761	31·70
	115·1	4,252	31·93
	99·0	4,904	32·21
	82·7	5,783	32·69
	66·4	7,081	33·28
	55·4	8,317	33·90
	44·5	10,108	34·76
	33·5	12,784	36·48
	22·4	17,250	40·44
	16·8	20,587	45·09
	Vapour-pressure	= 22,183	
240	173·2	2,939	31·32
	152·3	3,327	31·47
	131·1	3,844	31·63
	109·8	4,552	31·90
	93·6	5,284	32·24
	77·3	6,304	32·73
	60·9	7,847	33·34
	50·0	9,380	34·02
	44·5	10,375	34·54
	39·0	11,606	35·21
	33·5	13,180	36·08
	28·0	15,215	37·46
	22·4	17,965	39·50
	19·6	19,674	41·26
	16·8	21,630	43·76
	14·1	23,894	47·43
	12·4	25,344	50·75
	Vapour-pressure	= 26,227	
260	173·3	3,061	31·23
	152·3	3,469	31·35
	131·2	4,006	31·52
	109·9	4,746	31·77
	93·6	5,521	32·04
	77·3	6,593	32·50
	61·0	8,228	33·02
	50·0	9,860	33·60
	44·5	10,929	34·05
	39·0	12,259	34·62
	33·5	13,977	35·34
	28·0	16,224	36·49
	22·4	19,320	38·23
	19·7	21,284	39·61
	16·9	23,612	41·63
	14·1	26,509	44·39
	12·4	28,499	46·87
	11·3	29,850	49·12
	Vapour-pressure	= 36,285	

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Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
279·9	173·4	3,184	31·13
	152·4	3,609	31·24
	131·3	4,168	31·41
	109·9	4,943	31·63
	93·7	5,754	31·87
	77·3	6,883	32·28
	61·0	8,596	32·77
	50·0	10,342	33·22
	39·0	12,904	34·10
	33·6	14,750	34·72
	28·0	17,196	35·69
	22·4	20,581	37·21
	19·7	22,810	38·32
	16·9	25,488	39·98
	14·1	28,886	42·25

Fourth Quantity, D. The experiments with this quantity were made with the old apparatus.

Temperature.	Volume of 1 grm.	Pressure.	Vapour-density.
°	c.cs.	mms.	
130	212·6	1,826	32·26
	191·1	2,014	32·54
	184·0	2,084	32·66
	176·9	2,158	32·80
	169·1	2,236	33·13
	Vapour-pressure =	2,288	
150	212·7	1,940	31·86
	191·2	2,147	32·02
	169·2	2,402	32·35
	154·9	2,607	32·56
	140·6	2,847	32·84
	126·4	3,134	33·20
	112·2	3,484	33·63
	98·1	3,905	34·31
	Vapour-pressure =	4,023	
180	212·9	2,097	31·68
	191·4	2,320	31·85
	169·3	2,612	31·98
	155·0	2,837	32·15
	140·7	3,102	32·39
	126·5	3,431	32·59
	112·3	3,821	32·96
	98·2	4,320	33·34
	84·3	4,953	33·88
	70·5	5,809	34·53

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Reduction and Arrangement of Results.

Vapour-Pressures.—The vapour-pressures experimentally determined, and also those calculated by the formula $\log p = a + b\alpha^t + c\beta^t$, are given in the following table:—

Temperature.	Pressure.							
	Still method.	A.	B.	C.	D.	Mean.	Calculated.	Δp.
0°	3·44	..	..	..	..	3·44	3·49	+ ·05
10	7·26	..	..	..	..	7·26	7·39	·13
20	14·50	..	..	..	..	14·5	14·78	·28
30	27·60	..	..	..	..	27·6	28·13	·53
40	50·20	..	..	..	..	50·2	51·12	·92
50	87·20	..	..	..	..	87·2	89·00	1·80
60	147·00	..	..	..	..	147·0	148·97	1·97
70	239·00	..	..	..	..	239·0	240·44	1·44
80	376·00	..	..	..	..	376·0	375·31	− 0·69
90	574·00	..	..	..	..	574·0	568·11	− 5·89
100	..	842·5	..	..	..	842·5	835·89	− 6·61
110	..	1206·0	..	..	..	1206	1198·2	− 7·8
120	..	1683·0	..	..	..	1683	1677·0	− 6·0
130	..	2295·0	..	..	2288	2293	2295·9	+ 2·9
140	..	3074·0	..	..	..	3074	3080·3	6·3
150	..	4059·0	..	4053	4023	4052	4057·1	5·1
160	..	5264·0	..	..	..	5264	5253·4	− 10·6
170	..	6695·0	..	..	..	6695	6697·8	+ 2·8
180	..	8387·0	..	8365	..	8383	8418·8	35·8
190	..	10466·0	..	..	..	10466	10445	− 21
200	..	12828·0	..	12691	..	12801	12809	+ 8
210	..	15575·0	..	..	..	15575	15539	− 36
220	..	18671·0	..	18711	..	18679	18667	− 12
230	..	22161·0	22094	22183	..	22154	22230	+ 76
240	..	26208·0	26102	26227	..	26194	26263	69
250	..	30779·0	30809	..	..	30785	30807	22
260	..	36110·0	35955	36285	..	36103	35908	− 195

In calculating the mean the greatest weight has always been given to the determinations with the largest quantity, A. The constants employed were calculated from pressures at 20°, 80°, 140°, 200°, and 260°. The constants for the formula are—

$$a = 4{\cdot}479370.$$

$$\log b = \bar{1}{\cdot}3915059. \qquad \log \alpha = 0{\cdot}001641423.$$

$$\log c = 0{\cdot}5509601. \qquad \log \beta = \bar{1}{\cdot}99657025.$$

$$c \text{ is negative.} \qquad t = t^\circ c - 20.$$

Determinations of the vapour-pressures of propyl alcohol by the statical method are given by Konowalow. They are reproduced in the following table, together with the pressures calculated from our constants for Biot's formula. It is to be noticed that our results at these temperatures were obtained by the dynamical method.

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Series I.

Temperature.	Pressure.		Temperature.	Pressure.	
	Konowalow observed.	R. and Y. calculated.		Konowalow observed.	R. and Y. calculated.
°			°		
11·50	8·1	8·2	59·40	143·25	144·6
16·80	10·0	11·9	59·90	146·90	148·3
21·80	17·2	17·1	70·40	245·80	245 0
28·35	24·7	25·4	74·90	304·20	300·3
30·60	29·5	29·2	80·50	384·10	383·5
33·75	35·7	35·4	81·75	405·20	404·7
39·10	48·3	48·5	81·90	406·40	407·2
49·20	85·3	85·3	89·60	561·70	559·3
52·35	101·0	100·9	98 60	794·90	793·4

Series II.

Temperature.	Pressure.	
	Konowalow observed.	R. and Y. calculated.
°		
16·5	10·9	11·65
52·4	101·1	101·10
59·9	148·5	148·30
70·5	247·7	246·10
82·1	411·4	410·60

It will be seen that, with the single exception of the observation at 16°·8 in Series I., the agreement is extremely satisfactory. The vapour-pressures have also been determined by Dr. A. Richardson by our method ('Chem. Soc. Trans.,' vol. 49, p. 763) with concordant results.

Orthobaric Volumes of 1 Gram of Liquid.

Temperature.	Volume.	Specific gravity.*	Temperature.	Volume.	Specific gravity.	Temperature.	Volume.	Specific gravity.
°	c.cs.		°	c.cs.		°	c.cs.	
0	1·221	0·8193	100	1·365	0·7325	200	1·689	0·5920
10	1·233	0·8110	110	1·385	0·7220	210	1·750	0·5715
20	1·245	0·8035	120	1·406	0·7110	220	1·823	0·5485
30	1·256	0·7960	130	1·430	0·6995	230	1·912	0·5230
40	1·270	0·7875	140	1·455	0·6875	240	2·032	0·4920
50	1·285	0·7785	150	1·484	0·6740	250	2·210	0·4525
60	1·299	0·7700	160	1·515	0·6600	260	2·561	0·3905
70	1·314	0·7610	170	1·550	0·6450	263·15	2·899	0·3450
80	1·330	0·7520	180	1·591	0·6285	263·50	2·959	0·3380
90	1·347	0·7425	190	1·637	0·6110	263·54	3·012	0·3320

* As in our former memoirs, the specific gravities are referred to water at 4°, and are therefore true masses of one cubic centimetre.

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Orthobaric Volumes of 1 Gram of Vapour.

Temperature.	Volume of 1 grm.	Specific gravity (mass of 1 c.c.).	Vapour-density.	Temperature.	Volume.	Specific gravity.	Vapour-density.
°	c.cs.			°	c.cs.		
80	958·0	0·00104	30·50	180	44·50	0·0225	37·6
90	643·0	0·00156	30·90	190	35·40	0·0282	38·9
100	443·0	0·00226	31·30	200	28·30	0·0353	40·5
110	312·0	0·00320	31·80	210	22·65	0·0442	42·7
120	225·0	0·00443	32·40	220	18·00	0·0556	45·6
130	165·0	0·00605	33·00	230	14·21	0·0704	49·5
140	124·0	0·00805	33·70	240	11·06	0·0904	54·9
150	93·9	0·01060	34·50	250	8·50	0·1180	62·1
160	72·3	0·01380	35·45	260	6·20	0·1610	74·4
170	56·4	0·01770	36·45				

The following table gives the densities of the unsaturated vapour at equal intervals of temperature and pressure.

Pressure.	Temperatures.											
	130°	150°	180°	200°	220°	230°	240°	250°	260°	263°·64	270°	280°
mms.												
2,000	32·49	31·95	31·59	31·33	31·11	30·99	30·93	..	30·80	..	..	30·70
4,000	..	34·41	33·06	32·46	32·04	31·86	31·71	..	31·50	..	..	31·32
6,000	..	..	34·80	33·75	33·02	32·76	32·52	..	32·16	..	..	31·89
8,000	..	..	37·02	35·19	34·17	33·73	33·39	..	32·90	..	..	32·50
10,000	..	..	..	37·11	35·43	34·86	34·38	..	33·66	..	..	33·12
12,000	..	..	..	39·42	36·93	36·16	35·50	..	34·51	..	..	33·78
14,000	..	..	..	..	38·85	37·74	36·84	..	35·48	..	..	34·47
16,000	..	..	..	..	41·26	39·63	38·41	37·44	36·51	..	35·86	35·23
18,000	..	..	..	..	44·40	41·97	40·23	38·89	37·72	..	36·84	36·06
20,000	..	..	..	..	..	45·00	42·30	40·47	39·00	..	37·89	36·97
22,000	..	..	..	..	..	48·99	44·94	42·33	40·51	..	39·10	38·02
24,000	..	..	..	..	..	..	48·42	44·70	42·25	..	40·48	39·15
26,000	..	..	..	..	..	..	53·76	47·70	44·28	..	42·03	40·41
28,000	..	..	..	..	..	..	..	51·66	46·62	..	43·83	41·82
30,000	..	..	..	..	..	..	..	57·90	49·80	..	46·02	43·38
32,000	..	..	..	..	..	..	..	..	54·66	51·90	48·72	45·24
34,000	..	..	..	..	..	..	..	..	61·80	56·97	52·11	47·43
36,000	..	..	..	..	..	..	..	..	..	64·32	56·40	50·01
38,000	..	..	..	..	..	..	..	..	..	..	62·64	53·16
40,000	..	..	..	..	..	..	..	..	..	..	..	57·12
42,000	..	..	..	..	..	..	..	..	..	..	..	62·40

Heats of Vaporization.

The heats of vaporization are calculated from the thermo-dynamical formula,

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

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The values of dp/dt were calculated in the same manner as with the other liquids. The pressures for one-tenth of a degree above and below the required temperature were calculated by means of the equation $\log p = a + b\alpha^t + c\beta^t$, and the difference was multiplied by 5 to obtain the value for 1°. The pressures were reduced to grams per square centimetre, and the value of J was taken as 42,500.

Temperature.		dp/dt		$s_1 - s_2$	L.
° C.	° Abs.	mms.	grms.	c.cs.	cals.
80	353	15·99	21·7	957·00	173·0
90	363	22·73	30·9	642·00	169·0
100	373	31·16	42·4	442·00	164·0
110	383	41·70	56·7	311·00	159·0
120	393	54·45	74·0	224·00	153·0
130	403	69·75	94·8	164·00	147·0
140	413	87·60	119·1	123·00	142·4
150	423	108·20	147·1	92·40	135·3
160	433	131·50	178·8	70·80	129·0
170	443	157·80	214·5	54·90	122·8
180	453	187·00	254·2	42·90	116·3
190	463	219·00	297·7	33·80	109·6
200	473	254·00	345·3	26·60	102·2
210	483	292·50	397·7	20·90	94·5
220	493	334·00	454·0	16·20	85·3
230	503	379·00	515·0	12·30	75·0
240	513	428·00	582·0	9·03	63·4
250	523	481·00	654·0	6·29	50·6
260	533	540·00	734·0	3·64	33·5

The heat of vaporization of propyl alcohol at the boiling-point 97°·4 would be 165·2 calories.

Pressures and Temperatures of Propyl Alcohol at Definite Volumes.

In our previous papers we have given tables of the volumes of a gram of substance at definite temperatures and pressures.

We have recently shown, however, in two papers read before the Physical Society of London and published in the 'Philosophical Magazine' (May and August, 1887), that, when the volume of a stable liquid or gas is kept constant, a very simple relation exists between the pressure and the absolute temperature, which is expressed by the equation

$$p = bt - a,$$

where p is the pressure, t the absolute temperature, and b and a are constants depending on the substance and on the volume occupied by a gram of it.

We have, therefore, considered it better to construct lines of equal volume or "isochors," and to read temperatures and pressures from the isochors, rather than to read the volumes of a gram from isobars constructed from the isotherms.

Owing to the directions assumed by the isochors, it is most convenient to give

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temperatures (Centigrade) at definite pressures for volumes below the critical volume, and pressures at definite temperatures for larger volumes.

Volumes Smaller than Critical Volume.

Volume.	Pressure in metres of mercury.										
	5	10	15	20	25	30	35	40	45	50	55
1·26	32·40	33·05	33·70	34·35	35·00	35·70	36·35	37·00	37·65	38·30	39·00
1·28	48·10	48·80	49·50	50·20	50·90	51·60	52·30	53·00	53·70	54·40	55·10
1·30	62·80	63·55	64·30	65·05	65·80	66·30	67·05	67·80	68·55	69·30	70·00
1·32	75·40	76·20	77·00	77·75	78·55	79·30	80·10	80·90	81·65	82·45	83·20
1·34	87·55	88·35	89·15	90·00	90·80	91·65	92·45	93·25	94·10	94·90	95·75
1·36	98·85	99·70	100·55	101·40	102·30	103·15	104·00	104·85	105·60	106·50	107·35
1·38	109·00	109·90	110·80	111·70	112·60	113·50	114·40	115·30	116·20	117·10	118·00
1·40	118·40	119·35	120·30	121·25	122·20	123·15	124·10	125·05	126·00	126·95	127·90
1·42	127·05	128·05	129·05	130·05	131·05	132·05	133·05	134·05	135·05	136·05	137·05
1·44	134·75	135·80	136·85	137·90	138·90	139·95	141·00	142·05	143·10	144·10	145·15
1·46	142·00	143·10	144·20	145·25	146·35	147·40	148·50	149·60	150·65	151·75	152·80
1·48	148·55	149·70	150·85	151·95	153·10	154·20	155·35	156·50	157·60	158·75	159·85
1·50	..	155·85	157·05	158·20	159·40	160·55	161·75	162·95	164·10	165·30	166·45
1·52	..	161·85	163·10	164·30	165·55	166·75	168·00	169·25	170·45	171·70	172·90
1·54	..	167·35	168·60	169·90	171·15	172·45	172·70	174·95	176·25	177·50	178·80
1·56	..	172·40	173·70	175·05	176·35	177·70	179·00	180·30	181·65	182·95	184·30
1·58	..	177·30	178·70	180·05	181·40	182·80	184·20	185·55	186·95	188·30	189·70
1·60	..	..	183·15	184·55	186·00	187·40	188·85	190·30	191·70	193·15	194·55
1·62	..	..	187·65	189·10	190·60	192·05	193·55	195·05	196·50	198·00	199·55
1·64	..	..	191·95	193·45	195·00	196·50	198·05	199·60	201·10	202·65	204·15
1·66	..	..	195·50	197·05	198·65	200·20	201·80	203·40	204·95	206·55	208·10
1·70	..	..	202·40	204·10	205·80	207·50	209·20	210·90	212·60	214·30	216·00
1·75	..	..	209·80	211·65	213·45	215·30	217·15	219·00	220·85	222·65	224·50
1·80	..	..	..	218·05	220·00	222·00	224·00	226·00	228·00	229·95	231·95
1·85	..	..	..	..	225·75	227·85	230·00	232·15	234·30	236·45	238·55
1·90	..	..	..	..	230·60	232·90	235·20	237·50	239·80	242·10	244·40
1·95	..	..	..	..	..	237·00	239·50	241·95	244·40	246·90	249·35
2·00	..	..	..	..	..	240·60	243·25	245·90	248·55	251·20	253·80
2·10	..	..	..	..	..	..	248·80	251·80	254·80	257·80	260·80
2·20	..	..	..	..	..	..	..	256·10	259·50	262·90	266·30
2·30	..	..	..	..	..	..	..	259·40	263·25	267·05	270·90
2·40	..	..	..	..	..	..	..	261·70	266·00	270·25	274·55
2·50	..	..	..	..	..	..	..	263·20	267·95	272·75	277·50
2·60	..	..	..	..	..	..	..	264·30	269·40	274·50	279·60
2·70	..	..	..	..	..	..	..	265·25	270·45	275·60	
2·80	..	..	..	..	..	..	..	265·90	271·40	277·00	
2·90	..	..	..	..	..	..	..	266·00	272·00	278·10	
3·00	..	..	..	..	..	..	..	266·10	272·60	279·15	

It is, however, possible to give a few pressures at even volumes and temperatures, and these, and also the pressures in the following table for volumes up to 30 c.cs. are represented by crosses in the plates (Plate 3 and 6).

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Volumes Larger than Critical Volume.

Volume.	Temperature.											
	130°	150°	180°	200°	220°	230°	240°	250°	260°	263°·64	270°	280°
c.cs.												
3	..	..	..	..	..	..	..	..	..	38,120	43,000	50,660
4	..	..	..	..	..	..	..	..	..	38,120	41,680	47,280
5	..	..	..	..	..	..	..	..	..	37,960	40,850	45,380
6	..	..	..	..	..	..	..	..	..	37,280	39,610	43,280
7	..	..	..	..	..	..	..	..	35,190	36,280	38,190	41,200
8	..	..	..	..	..	..	..	..	34,000	34,940	36,580	39,150
9	..	..	..	..	..	..	..	30,390	32,650	33,480	34,920	37,180
10	..	..	..	..	..	..	..	29,430	31,360	..	33,300	35,230
12	..	..	..	..	..	..	25,710	27,270	28,820	..	30,380	31,940
14	..	..	..	..	..	..	23,910	25,190	26,470	..	27,776	29,040
16	..	..	..	..	..	21,130	22,220	23,310	24,390	..	25,480	26,570
18	..	..	..	..	..	19,800	20,730	21,660	22,580	..	23,510	24,440
20	..	..	..	..	17,660	18,480	19,310	20,130	20,950	..	21,780	22,600
25	..	..	..	..	15,340	15,940	16,540	17,150	17,750	..	18,350	18,950
30	..	..	..	12,474	13,430	13,910	14,390	14,860	15,340	..	15,820	16,300
40	..	..	..	9,998	10,656	10,985	11,314	..	11,972	..	..	12,630
50	..	..	7,780	8,299	8,818	9,078	9,337	..	9,856	..	..	10,375
60	..	..	6,695	7,109	7,523	7,730	7,937	..	8,351	..	..	8,765
80	..	..	5,210	5,504	5,798	5,945	6,092	..	6,386	..	..	6,680
100	..	3,898	4,252	4,488	4,724	4,842	4,960	..	5,196	..	..	5,432
120	..	3,321	3,606	3,796	3,985	4,080	4,175	..	4,365	..	..	4,555
140	..	2,876	3,120	3,283	3,447	3,528	3,610	..	3,772	..	..	3,935
170	2,258	2,391	2,590	2,724	2,857	2,923	2,990	..	3,122	..	..	3,255
200	1,955	2,063	2,224	2,332	2,439	2,493	2,547	..	2,654	..	..	2,762

These pressures agree very well with those read directly from the isotherms, except near the condensing point at low temperatures, and to a much smaller extent at high temperatures. The greatest error is at the lowest pressure at 150°, and amounts to 1·45 per cent.

The approximate critical temperature of propyl alcohol is 263°·7, the approximate critical pressure 38,120 mms., and the approximate volume of 1 grm. 3·6 c.cs. The first two of these constants must be very nearly correct; the third cannot be determined with nearly the same accuracy.

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Addendum.

(Added February 11, 1889.)

The conclusions of Konowalow (*loc. cit.*) regarding the nature of the so-called hydrate of propyl alcohol have been fully confirmed. It was found that the composition of the mixture, which boiled constantly under a pressure of 198·7 mms., differed from that obtained under the ordinary atmospheric pressure; the lower the pressure, the higher is the percentage of water in the distillate.

The boiling-points of four different samples of the mixture were determined under pressures varying from 746 to 762 mms.; corrected to 760 mms., the temperatures observed were 87°·65, 87°·85, 87°·9, and 87°·6—mean 87°·75.

The vapour-pressures were determined by both the dynamical and statical methods, with the following results:—

Dynamical Method.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
mms.	°	mms.	°	mms.	°
5·75	− 0·9	38·9	27·4	269·8	63·5
6·75	+ 1·25	46·0	30·2	304·3	66·1
8·15	4·1	57·1	33·6	347·9	69·1
9·0	5·5	66·8	36·3	358·7	69·8
9·2	5·85	78·9	39·2	405·7	72·6
10·1	7·2	92·55	42·2	466·4	75·9
12·55	9·8	109·5	45·3	526·6	78·9
15·8	13·3	123·5	47·65	590·9	81·9
19·05	16·1	143·7	50·5	658·8	84·5
22·75	18·7	167·4	53·6	760·6	87·9
27·55	21·7	200·6	57·4		
32·75	24·6	232·0	60·3		

Statical Method.

Temperature.	Pressure.	Pressure read from curve constructed from results by dynamical method.
°	mms.	mms.
13·3	16·6	15·7
15·1	18·2	17·7
15·7	19·2	18·45
25	35·5	33·8
30	47·9	45·4
40 *	83·8 and 83·95	81·1
50	142·1	138·9
60	231·7	226·5
70	365·4	361·5
75	452·7	450·0

* The following pressures were also observed at 40° in the vapour-density tube:—83·5, 82·35, 82·55, 82·25.

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It will be seen that the results by the statical method are uniformly a very little higher than by the dynamical method. The behaviour of the substance resembles that of an imperfectly purified stable substance more closely than that of a dissociating body.

A considerable number of determinations of vapour-density were made under varying conditions of temperature and pressure. It was proved, however, that condensation—probably of water—took place on the sides of the tube, and the results at the same temperature and pressure could be made to vary considerably by altering the conditions in such a manner as to increase or diminish the chance of such condensation taking place. The rise of vapour-density at low temperatures or high pressures was in no case greater than could be accounted for by premature condensation of liquid, and the only conclusion to be drawn from the results is that combination of propyl alcohol and water does not take place in the gaseous state.

The contraction on mixing propyl alcohol and water at 0°, in the ratio of 71·46 per cent. of alcohol to 28·54 of water, was ascertained by determining the specific gravities of the alcohol and of the mixture, that of water being known. For 1 grm. of the mixture the contraction was 0·0215 c.c., or 1·857 per cent. With ethyl alcohol and methyl alcohol the contraction is considerably greater.

It may be stated, in conclusion, that we have obtained no experimental evidence of chemical combination between propyl alcohol and water.

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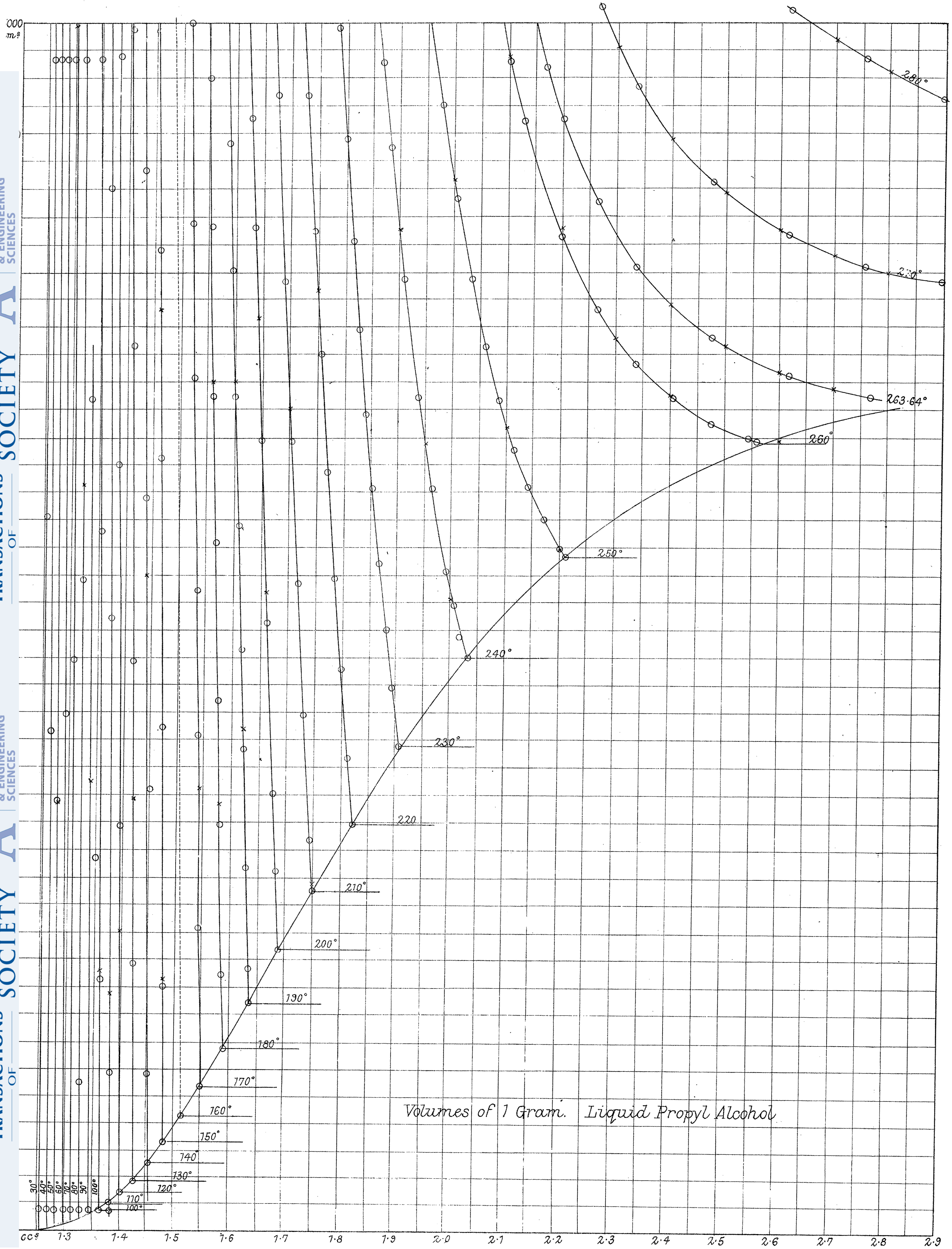

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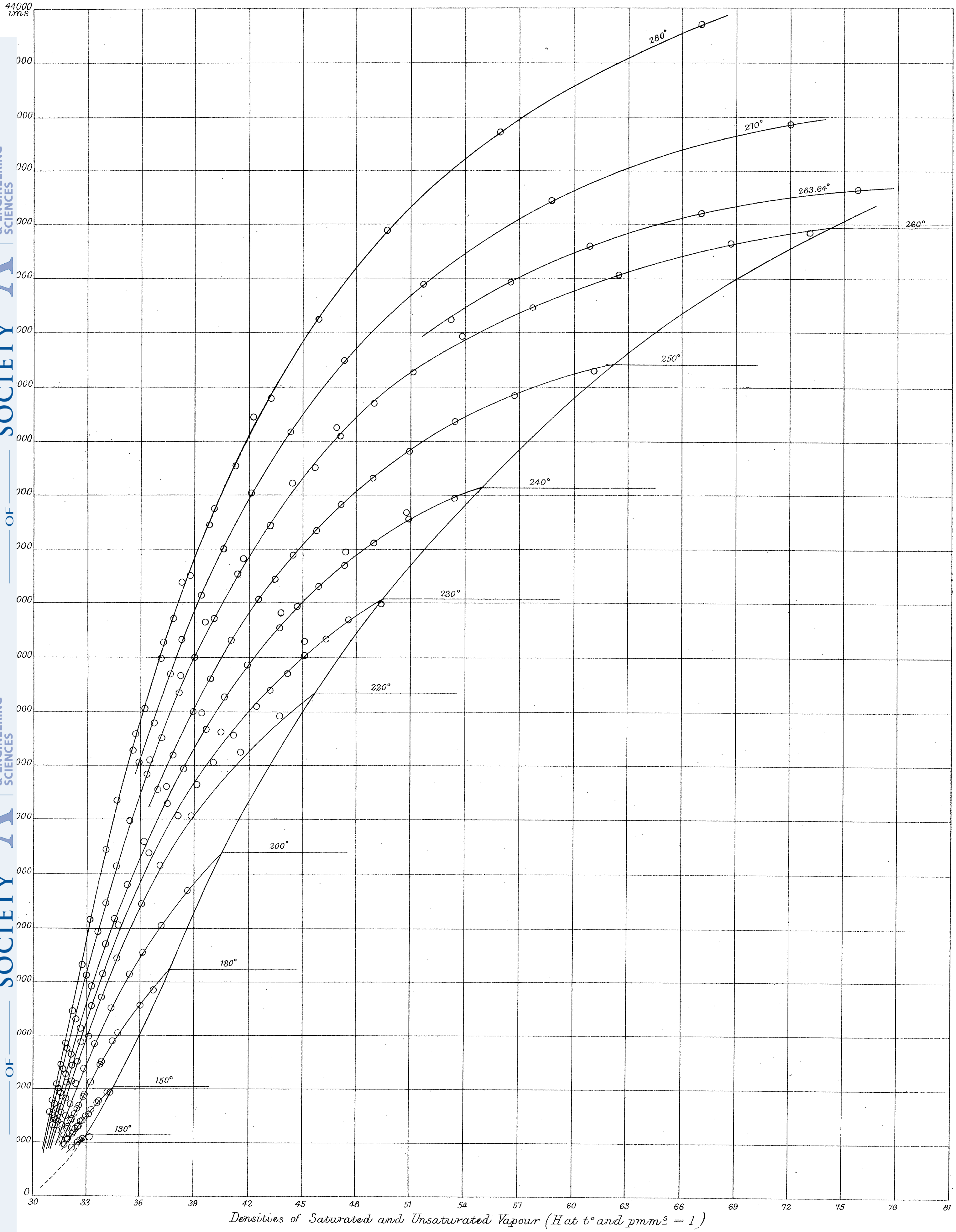

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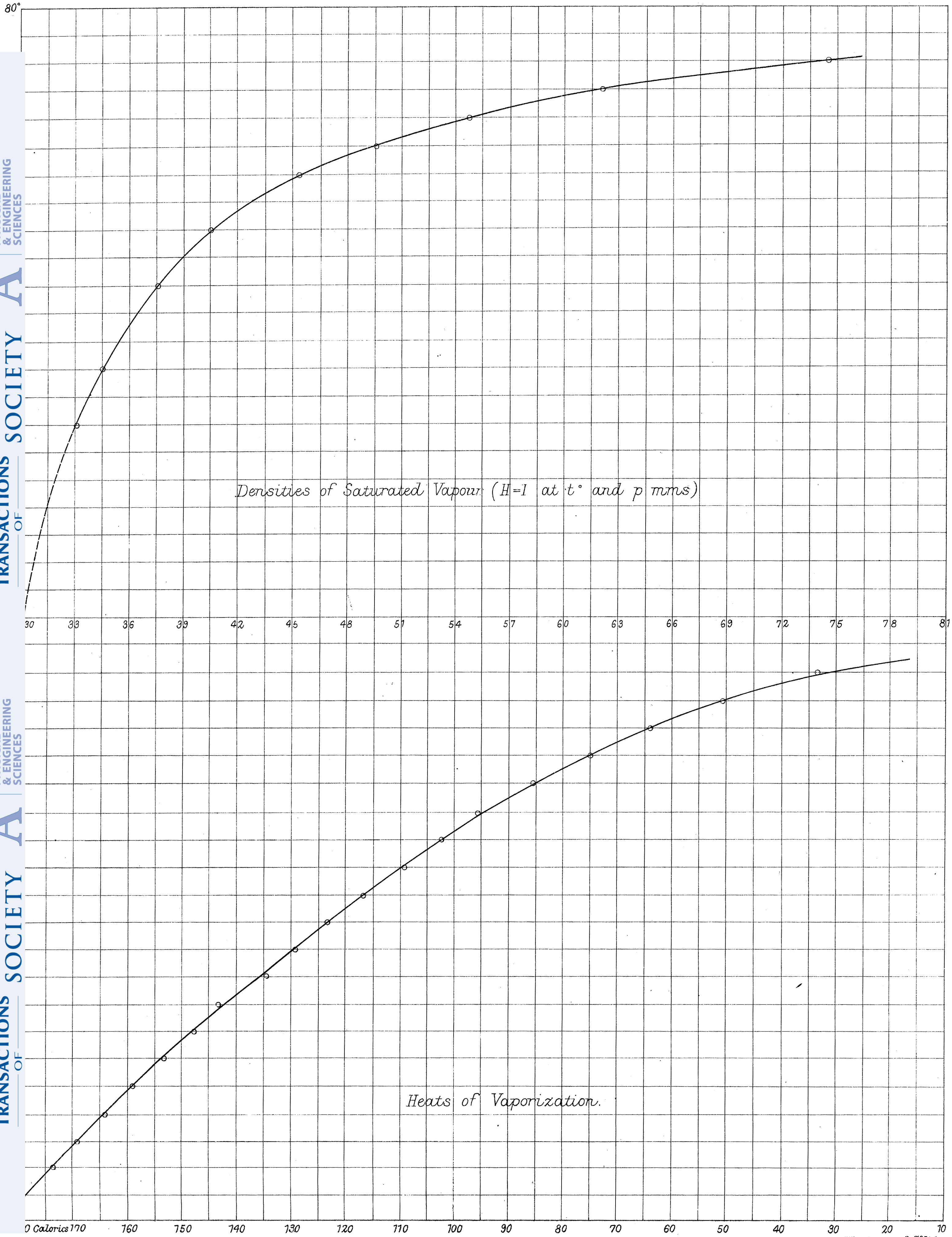

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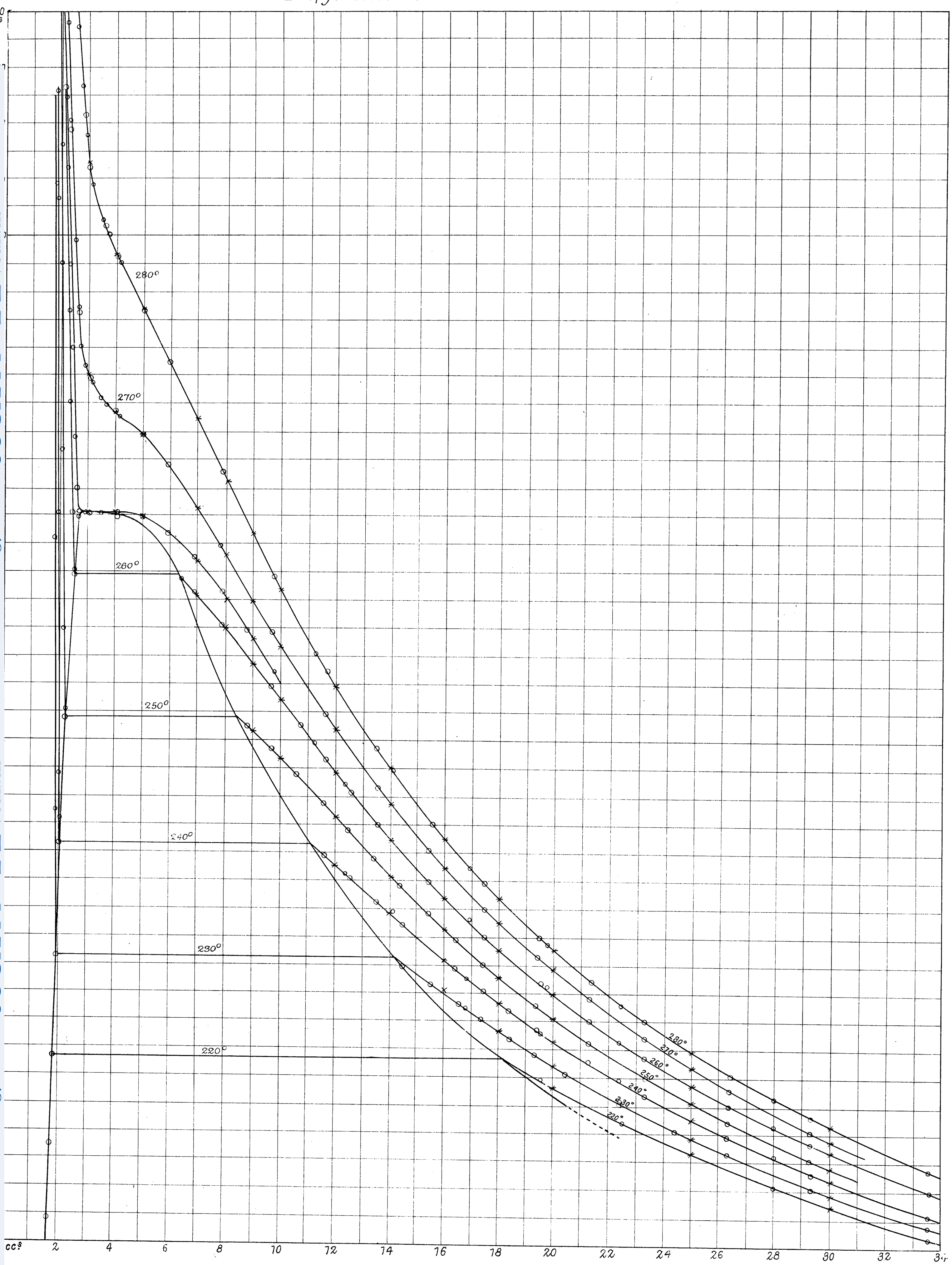
Propyl Alcohol. Volumes of 1 Gram.



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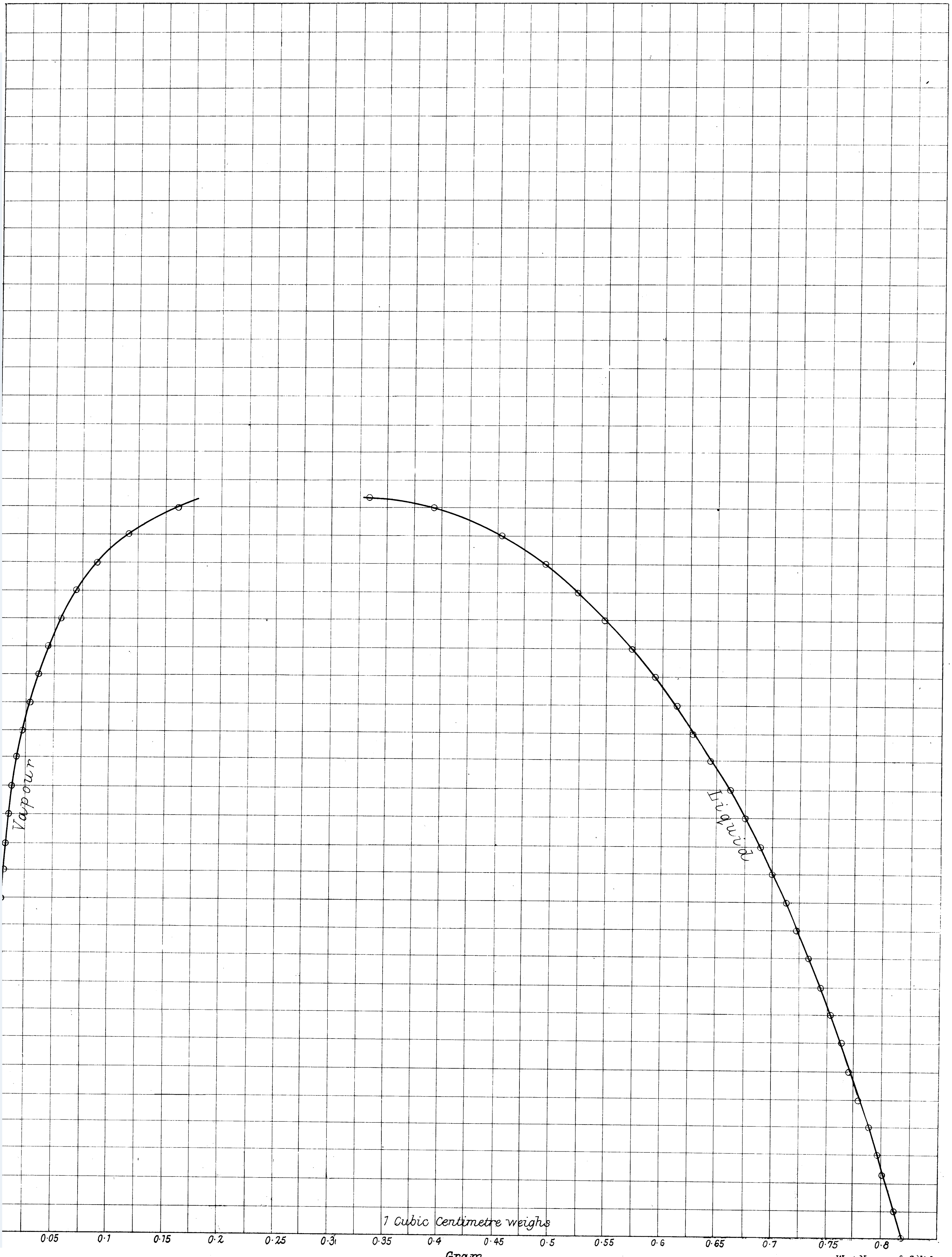

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