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On Some of the Properties of Water and of Steam

William Ramsay and Sydney Young

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III. *On some of the Properties of Water and of Steam.*

By William Ramsay, *Ph.D.*, *F.R.S.*, *and* Sydney Young, *D.Sc.*

Received November 5,—Read December 10, 1891.

[Plate 7.]

The work of which an account is given in the following pages was carried out in the winter of 1887–88, and forms a sequel to much of a similar character already published by the authors, on methyl, ethyl, and isopropyl alcohols, on ethyl oxide, on acetic acid, and on a mixture of alcohol and ether ('Phil. Trans.,' 1886, Part I., p. 123; 1887, A., p. 57; 1887, A., p. 313; 1889, A., p. 137; 'Chem. Soc. Trans.,' 1886, p. 790; 1887, p. 755).

The apparatus with which it was carried out has been fully described in the memoir on ether (*loc. cit.*). The only important change was in the nature of the glass tubes used to contain the liquid under experiment. While, in the case of the alcohols, ether, &c., lead glass proved the best material for tubes, it is too easily attacked by water. At comparatively low temperatures it becomes etched, and it is impossible to take readings. Moreover, the water dissolves a not inconsiderable quantity of potassium silicate; tubes of green boiler-gauge glass were, therefore, substituted for tubes of lead glass. This glass consists of a silicate of calcium and potassium, containing a trace of ferrous iron ($SiO_2 = 71{\cdot}20$; $CaO = 14{\cdot}99$; $K_2O = 13{\cdot}19$; Total, 99·38.) They withstand a higher pressure than lead-glass tubes, and they are attacked with difficulty. Even after an exposure of several days to liquid water at 280° C., only 0·7 per cent. of residue remained on evaporating the water. Inasmuch as *some* of the material of the glass is dissolved, however, the water cannot be considered to be absolutely pure, but the results may be given as the best attainable with water in contact with glass.

It may be advisable to state here again, that the *pressures* were read from gauges containing dry air, kept at a known temperature by jackets of running water; and that they are corrected for deviation from Boyle's law by help of experiments made by Amagat ('Compt. Rend.,' vol. 99, p. 1153); that the *temperatures* are those of an air-thermometer, and that they were secured by jacketing the tube containing the water with the vapours of pure chlorobenzene, bromobenzene, aniline, methyl-salicylate, or bromonaphthalene, of which the vapour-pressures corresponding to known tempera-

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tures have been determined by us ('Chem. Soc. Trans.,' vol. 47, p. 640). By causing one or other of these liquids to boil under definite known pressures, any desired temperature, within certain limits, was attainable; and, as a small alteration of temperature corresponds to a considerable alteration of pressure, it may be taken for certain that the temperatures are practically correct. The expansion of the glass made use of for the volume tube was carefully determined, and a correction was in all cases applied, so that the apparent volumes are reduced to real volumes. No correction, however, was applied for the alteration in the volume tube due to internal pressure, because an estimation of its amount showed it to be much within the error of reading volume.

The results may be classified under three heads :—

I. Expansion of liquid water.
II. Vapour-pressures.
III. Density of unsaturated and saturated steam.

I. *Expansion of Liquid Water.*

For these experiments, the tube was two-thirds filled with water freed from air by boiling *in vacuo*. That no air was present was often proved during the experiments by condensing a bubble of steam; condensation always took place without appreciable rise of pressure. The weight of water taken was deduced from observations of its volume at the ordinary temperature, both before and after experiment. The results are as follows :—

Temperature.	Divisions of tube.	Volume at 4 and weight.
°		c.c. or grm.
12·25	246·75	1·1054
12·40	246·90	1·1060
15·7	246·20	1·1031
17·9	246·25	1·1035

The first pair of readings was taken before the commencement of the experiments; the second pair after the expansions had been measured. The small difference is probably due to adherence of liquid to the lower portions of the tube, which had become etched during the experiments.

The mean result, from which the following Table is calculated, is 1·1045 c.c. at 4°, or 1·1045 grm :—

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Temperature.	Volume of 1 grm. in c.cs.		Temperature.	Volume of 1 grm. in c.cs.	
	Observed.	Smoothed.		Observed.	Smoothed.
c			°		
100	1·0432	1·0432	190	1·1412	1·1407
110	1·0510	1·0513	200	1·1567	1·1566
120	1·0594	1·0592	210	1·1734	1·1733
130	1·0678	1·0678	220	1·1915	1·1914
140	1·0791	1·0772	230	1·2122	1·2112
150	1·0880	1·0878	240	1·2319	1·2320
160	1·0996	1·0995	250	1·2516	1·2533
170	1·1124	1·1124	260	1·2750	1·2755
180	1·1260	1·1260	270	1·3000	1·2985

NOTE.—The pressures are here nearly those of the vapour at the respective temperatures.

The volumes of 1 grm. of water have been measured by MENDELÉEFF ('LIEBIG'S Annalen,' vol. 119, 1861, p. 10), and by HIRN ('Annales de Chimie' [4], vol. 10, 1866, p. 32). The following short Table shows that HIRN's results agree very closely with those given by us :—

Temperature.	Volume of 1 grm.		
	MENDELÉEFF.	HIRN.	R. and Y.
°			
100	1·0428	1·04315	1·0432
120	..	1·05992	1·0594
131	1·0722	..	..
140	..	1·07949	1·0791
156·8	1·1016	..	..
160	..	1·10149	1·0996
180	..	1·12678	1·1260
200	..	1·15900	1·1567

The compressibility of water was measured at 190° and at higher temperatures. The results are as follows :—

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Temperature.	Volume of 1 grm.	Pressures of mercury.	Temperature.	Volume of 1 grm.	Pressures of mercury.
	cub. centims.	millims.		cub. centims.	millims.
190°	1·1412	9,837	230°	1·2122	21,085
	1·1408	12,813		1·2101	31,745
	1·1386	30,029		1·2079	42,249
	1·1365	39,904			
			240	1·2319	25,276
200	1·1567	15,014		1·2300	32,452
	1·1559	18,695		1·2282	41,614
	1·1538	30,513			
	1·1516	43,901	250	1·2516	30,059
				1·2508	36,040
210	1·1734	14,404		1·2490	43,925
	1·1732	17,488			
	1·1710	31,467	260	1·2750	35,028
	1·1689	43,405		1·2735	40,210
220	1·1915	17,622			
	1·1905	27,251			
	1·1884	39,432			

II. *Vapour-pressures.*

The pressures of the vapour were read from experiments with a larger quantity of water in the tube, as well as when the quantity was small; but uniform results were not obtained. The vapour-pressure of water, unlike that of other liquids, depends to some extent on the amount of substance present.* This is to be attributed to the fact, that with only a small amount of liquid present, a relatively large surface of the tube is exposed to the vapour, and, as there can be no doubt that the vapour adheres to the surface, the pressure is lowered to a certain extent. The results, with the larger quantity, are therefore given as probably more correct. Each pressure is the mean of some seven or eight readings in which the relative volumes of water and steam were altered within the greatest limits which the tube allowed.

The pressures are, as before stated, corrected for deviations from BOYLE'S law.

To facilitate comparison, the results obtained by REGNAULT and others are placed in juxtaposition with ours; and also columns showing the differences between our results and those obtained in other ways. The columns are distinguished as follows:—

"R. and Y." stands for RAMSAY and YOUNG.

"REG. curve" stands for REGNAULT'S copper-plate curves, given in the 'Mémoires de l'Académie,' vol. 26.

"REG. H." and "REG. F." signify REGNAULT'S results calculated by BIOT'S formula, $\log p = a + b\alpha^t + c\beta^t$, using the constants marked H and F respectively.

"REG K." signifies REGNAULT'S formula K, viz., $p = a\alpha^{\alpha/(1+mx)}$

* See Appendix, pp. 120 and 121.

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"UNWIN" ('Phil. Mag.,' 1886, p. 299). His formula is $\log p = 7{\cdot}5030^{-7{\cdot}579/t^{1{\cdot}25}}$.

"ANTOINE" refers to the last formula given by CH. ANTOINE ('Annales de Chimie,' 1891, vol. 22,' p. 283). It is $\log p = 7{\cdot}921^{-1638/t+225}$. It has the merit of allowing temperature to be calculated from pressure, as easily as the converse; the results, however, calculated in each way, are not absolutely the same, but do not differ to any important extent.

"BUFF" ('LIEBIG'S Annalen,' Suppl. 2, 1862–3, p. 137) uses the formula

$$\log p = \log \frac{760}{373} + \log (273 + t) + \frac{\log (273 + t) - \log 373}{\alpha}.$$

$$\alpha = 0{\cdot}06479 + 0{\cdot}0001722\, t - 0{\cdot}0000001\, t^2.$$

RANKINE" ('Steam Engine,' 9th Ed., p. 237) gives the formula

$$\log p = \mathrm{A} + \frac{\mathrm{B}}{\tau} + \frac{\mathrm{C}}{\tau^2}.$$

'BROCH" ('Travaux et Mémoires du Bureau Internat. des Poids et Mesures,' vol. 1, p. 19, *et seq.*). His formula is

$$p = a\,.\,10^{\frac{bt + ct^2 + dt^3 + et^4 + ft^5}{1 + \alpha t}}.$$

M. BROCH has undertaken a most laborious investigation of the formulæ employed for the calculation of the vapour-pressures of water, adopting finally the one given in the table. The utmost care was taken to obtain the best possible results from the data taken; but, unfortunately, M. BROCH has accepted REGNAULT'S conclusion that the curve representing the vapour-pressures of ice is continuous with that obtained from the vapour-pressures of water, and he has employed the whole of the data from $-32°$ to $100°$. By the method of calculation of the constants for the formula, this source of error has been to a certain extent eliminated, as is shown by the comparison (p. 31) of REGNAULT'S individual observations with the pressures calculated from the formula. In this table it is seen that below $-5°$, out of 31 comparisons, the calculated pressures are higher than those observed in every case but one. The error is, however, only partially eliminated, and this probably explains the fact that the formula, with the constants given, will not bear extrapolation above $100°$ even to $120°$, though it is supposed to hold good through a range of $132°$.

It is to be feared that the results between $0°$ and $100°$ may even be to some extent vitiated by this source of error—a most unfortunate circumstance, considering the enormous amount of labour bestowed on the work, and the fact that the pressures calculated from the formula have received the *imprimatur* of the Bureau International.

It is to be noticed that REGNAULT'S formula K gives results nearest the truth, but that fairly approximate results are also obtainable by the use of UNWIN'S and of ANTOINE'S formulæ. These formulæ, it need hardly be remarked, are all empirical.

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TABLE of Vapour-pressures of Water.

T.	R. & Y.*	Reg. Curve.	Δ_1	Reg. H.	Δ_2	Reg. F.	Δ_3	Reg. K.	Δ_4	Unwin.	Δ_5	An-toine.	Δ_6	Buff.	Δ_7	Ran-kine.	Δ_8	Broch.	Δ_9
°																			
120	1,484	1,489	+ 5	1,491	+ 7	1,491	+ 7	1,487	+ 3	1,486	+ 2	1,491	+ 7	1,491	+ 7	1,491	+ 7	1,545	+ 61
130	2,019	2,029	10	2,030	11	2,030	11	2,023	4	2,020	1	2,030	11	2,029	10	2,030	11		
140	2,694	2,713	19	2,718	24	2,718	24	2,706	12	2,710	16	2,718	24	2,716	22	2,716	22		
150	3,568	3,572	4	3,581	13	3,582	14	3,564	− 4	3,564	− 4	3,581	13	3,578	10	3,578	10	4,244	+ 676
160	4,652	4,647	− 5	4,652	0	4,652	0	4,629	−23	4,633	− 19	4,652	0	4,646	− 6	4,647	− 5		
170	5,937	5,960	+21	5,962	25	5,959	22	5,933	− 4	5,942	+ 5	5,962	25	5,953	+ 16	5,955	+ 18		
180	7,487	7,545	67	7,546	68	7,537	59	7,513	+35	7,525	47	7,546	68	7,535	57	7,539	61		
190	9,403	9,428	25	9,443	40	9,425	22	9,407	4	9,423	20	9,443	40	9,429	26	9,432	29		
200	11,625	11,660	35	11,689	64	11,663	38	11,656	31	11,665	40	11,689	64	11,672	47	11,679	54	31,861	+20,237
210	14,240	14,308	68	14,325	85	14,297	57	14,302	62	14,316	76	14,325	85	14,310	70	14,319	79		
220	17,365	17,390	25	17,390	25	17,381	16	17,390	25	17,398	33	17,390	25	17,386	21	17,390	25		
230	20,936	20,915	−21	20,926	− 10	20,981	45	20,965	29	20,952	16	20,926	− 10	20,937	1	20,936	0		
240	25,019	..	..	24,973	− 46	25,176	157	25,074	55	25,046	27	25,027	+ 8	24,966	− 53	25,009	− 10		
250	29,734	..	..	29,571	−163	30,072	338	29,765	31	29,694	− 40	29,689	− 45	29,687	− 47	29,648	86		
260	35,059	..	..	34,757	−302	35,798	739	35,086	27	34,965	− 94	34,970	− 89	34,978	− 81	34,898	161		
270	41,101	..	..	40,570	−531	42,545	1444	41,088	−13	40,887	−214	40,926	−175	40,948	−153	40,794	307		

* Observed. The details of the observations are to be found in the Appendix, pp. 120 and 121.

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III. *The Densities of the Saturated and Unsaturated Vapour of Water at Different Temperatures and Pressures.*

The method pursued was (1) to find the weight of the small quantity of water in the tube by ascertaining the values of the products of pressure and volume at large volumes and at high temperatures. If these products, for slight decrease of volume, and at any one temperature, were sensibly constant, and if the products at different temperatures bore to one another the same ratio as that between the absolute temperatures, it was assumed that the vapour-density of the steam was normal; if hydrogen be taken as unity, the density is nine. The weight could then be calculated by the equation given in the Appendix, p. 122. (2) The volume of the gas was then diminished by regular decrements at temperatures rising by 10° at a time, and the pressure corresponding to each volume was read. From these data the volume of 1 grm. in cubic centimetres could be calculated. When the volume was sufficiently diminished condensation ensued.

Two distinct sets of experiments were made: one with a large tube at low temperatures, and one with a strong pressure tube at high temperatures. The actual experimental data for high temperatures (120° to 270°) are given on pp. 124–127 of the Appendix; those at low temperatures on pp. 128–130. Reasons are there adduced to show that when the pressure approaches the vapour-pressure condensation on the glass occurs. This causes the pressure to be lower than it should be for a given volume, and renders the results very difficult to interpret. Such adhesion appears to be slight at large volumes where the vapour is unsaturated; but, as it occurs gradually, the effect is that on decreasing volume some water is left below the mercury, and as there is no clue to the amount thus trapped the weight is diminished by an unknown amount. But it is reckoned as undiminished, and hence in calculating the volume of 1 grm. from the actual measurements the volume ascribed is too small, and too small by an unknown quantity. At the same time the pressure is lowered by the adhesion to the glass, and so the curve is distorted as it approaches the pressure of the saturated vapour.

Under the circumstances it appeared best to follow the experimental results as closely as possible. However interesting from a theoretical point of view the absolute expansion of water-gas may be, in practice it is always in contact with a surface; and although it is probable that the material, as well as the extent of the surface, would influence the amount of adhesion, yet an indication of the behaviour of steam in contact with glass cannot fail to be of use in considering the practical case of steam in contact with iron. Moreover, the error is to a great extent eliminated by making use of the volumes of 1 grm. of saturated steam calculated from REGNAULT'S heats of vaporization.

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RANKINE ('Edinb. Trans.,' vol. 23, Part I., 1862, p. 147) discusses the want of concordance between the volumes of saturated steam observed by FAIRBAIRN and TATE, and those calculated from REGNAULT'S observations on the heats of vaporization; and suggests a difference in molecular condition between steam at rest, as in FAIRBAIRN and TATE'S experiments, and in motion, as in REGNAULT'S. It can scarcely be doubted that the true reason of the discrepancy is to be found in the adhesion of steam to glass. It is obvious that in REGNAULT'S experiments this source of error would be absent, inasmuch as the weight of water was simply that which entered the calorimeter.

Three sets of isothermal curves were drawn in which the experimental numbers were closely followed, the only adjustment being that of rendering the curves as smooth as possible, and of making use of the mutual relations between the curves, so as to smooth out the irregularities of each individual one. These curves were prolonged to the points calculated from REGNAULT'S observations by the formula

$$s_1 = \frac{\mathrm{LJ}}{\mathrm{T}\, dp/dt} + s_2,$$

where s_1 and s_2 are respectively the volumes of saturated vapour and liquid, L the heat of vaporization, J the mechanical equivalent of heat, T absolute temperature, and dp/dt the differential of pressure in degrees with respect to temperature.

By help of this formula the following table was calculated :—

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VAPOUR-Densities (Saturated) of Water from REGNAULT'S Heats of Vaporization.

$t.°$ C.	T.°abs.	p.	dp/dt.	L (total).	Q.	Ht. of Vap. L.	$s_1 - s_2$.	s_1.	V.D.
0	273	4·600	0·329	606·5	0	606·5	211,130	211,131	8·74
10	283	9·165	0·609	609·5	10	599·5	108,730	108,731	8·83
20	293	17·39	1·074	612·6	20	592·6	58,867	58,868	8·89
30	303	31·55	1·81	615·7	30	585·7	33,384	33,385	8·94
40	313	54·91	2·93	618·7	40·1	578·6	19,722	19,723	8·98
50	323	91·98	4·58	621·7	50·1	571·6	12,078	12,079	9·04
60	333	148·8	6·91	624·8	60·1	564·7	7,671	7,672	9·06
70	343	233·1	10·11	627·8	70·2	557·6	5,026	5,027	9·10
80	353	354·6	14·40	630·9	80·3	550·6	3,386	3,387	9·13
90	363	525·4	20·01	633·9	90·4	543·5	2,339	2,340	9·18
100	373	760·0	27·14	637·0	100·5	536·5	1,657	1,658	9·20
110	383	1,075	36·27	640·0	110·6	529·4	1,191	1,192	9·29
120	393	1,491	47·35	643·1	120·8	522·3	877·4	878·5	9·32
130	403	2,030	60·90	646·1	131·0	515·1	656·1	657·2	9·39
140	413	2,718	77·06	649·2	141·2	508·0	499·0	500·1	9·44
150	423	3,581	96·17	652·2	151·5	500·7	384·7	385·8	9·52
160	433	4,652	118·5	655·3	161·7	493·6	300·7	301·8	9·58
170	443	5,962	144·1	658·3	172·1	486·2	238·1	239·2	9·65
180	453	7,546	173·4	661·4	182·4	479·0	190·6	191·7	9·73
190	463	9,443	206·5	664·4	192·8	471·6	154·2	155·3	9·81
200	473	11,689	243·4	667·5	203·2	464·3	126·1	127·3	9·88
210	483	14,325	284·4	670·5	213·7	456·8	104·0	105·2	9·96
220	493	17,390	329·4	673·6	224·2	449·4	86·50	87·70	10·05
230	503	20,926	378·5	676·6	234·7	441·9	72·54	73·76	10·13

p, REGNAULT'S formula H; dp/dt from same formula; L (total), Q and L from REGNAULT.

As REGNAULT'S measurements do not extend beyond 230° the higher isothermals were smoothed as well as possible and made to cut the vapour-pressure lines at certain points, to which we were guided to some extent by their own regularity, and to some extent by extending the curve drawn to pass through the points representing the volumes of 1 grm. of saturated vapour. The results cannot be far from the truth.

The next table shown was constructed by reading the pressures and temperatures corresponding to equal volumes.

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Vol. c.c. per gramme.	T=140°.	150°.	160°.	170°.	180°.	190°.	200°.	210°.	220°.	230°.	240°.	250°.	260°.	270°.
650	2,128	2,190	2,250	2,310	2,370	2,425	2,485	2,540	2,600	2,660	2,720	2,780	2,840	2,900
600	2,285	2,365	2,425	2,490	2,552	2,615	2,685	2,745	2,810	2,880	2,965	3,015	3,070	3,135
550	2,480	2,560	2,640	2,710	2,775	2,850	2,925	2,995	3,070	3,145	3,215	3,290	3,350	3,415
500	2,720	2,810	2,895	2,975	3,045	3,125	3,210	3,295	3,375	3,455	3,535	3,615	3,685	3,760
450	..	3,110	3,205	3,300	3,390	3,475	3,565	3,650	3,740	3,830	3,920	4,010	4,095	4,175
400	..	3,465	3,600	3,705	3,800	3,905	4,000	4,095	4,205	4,305	4,400	4,505	4,600	4,690
350	..	..	4,085	4,215	4,325	4,450	4,560	4,660	4,780	4,905	5,020	5,140	5,260	5,375
300	..	..	..	4,920	5,040	5,170	5,315	5,460	5,595	5,725	5,865	5,995	6,125	6,255
250	..	..	..	5,760	6,020	6,190	6,360	6,530	6,700	6,870	7,030	7,200	7,360	7,510
200	..	..	..	..	7,300	7,660	7,875	8,080	8,300	8,505	8,710	8,930	9,140	9,360
175	..	..	..	..	..	8,580	8,990	9,175	9,430	9,675	9,900	10,120	10,375	10,600
150	..	..	..	..	..	..	10,230	10,570	10,850	11,100	11,370	11,650	11,930	12,185
125	..	..	..	..	..	..	..	12,490	12,860	13,180	13,490	13,840	14,150	14,480
100	..	..	..	..	..	..	..	..	15,660	16,160	16,545	16,920	17,300	17,700
90	..	..	..	..	..	..	..	..	17,010	17,740	18,180	18,590	19,000	19,400
80	..	..	..	..	..	..	..	..	..	19,550	20,150	20,650	21,060	21,520
70	..	..	..	..	..	..	..	..	..	..	22,470	23,340	23,750	24,200
60	..	..	..	..	..	..	..	..	..	..	..	26,350	27,060	27,650
50	..	..	..	..	..	..	..	..	..	..	..	..	31,120	32,000
45	..	..	..	..	..	..	..	..	..	..	..	..	33,650	34,780

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The vapour-densities and volumes of a gramme of saturated vapour can be given at temperatures above 230°. They are as follows :—

Temperature.	Pressure.	Vol. of 1 grm.	Vapour-density (H = 1).		Vol. of 1 grm.
°	millims.	c.c.	read.	smoothed.	recalculated.
230	20936	73·00	10·23	10·22	73·06
240	25019	60·65	10·51	10·40	61·28
250	29734	50·30	10·87	10·63	51·43
260	35059	42·40	11·14	10·94	43·19
270	41100	37·20	11·04	11·36	36·15

There is very great difficulty in reconciling the results given by REGNAULT at the highest temperatures with our own direct measurements. REGNAULT'S results interpreted as vapour-density obviously increase at too slow a rate above 210°, while ours appear to increase too rapidly at 240°, 250°, and 260°. We therefore constructed a curve showing the relationship of vapour-densities from all sources to temperature ; the numbers given as "smoothed" are read from the curve, and the volumes of 1 grm. were again calculated.

In a series of papers published in the 'Philosophical Magazine' (1887, vol. 27, pp. 196 and 435), we showed that for ether, ethyl alcohol, and carbon dioxide, the pressures of the vapours of these substances for constant volumes are, within limits of experimental error, a rectilinear function of the temperature, or $p = bt - a$, where a and b are two constants, depending on the volume, and t is the absolute temperature. CARL BARUS, as the result of experiments with other substances, has confirmed the statement, both for liquid and gas. He states ('Phil. Mag.,' 1890, vol. 30, p. 358) that "below 1000 atmospheres, the curves for ether, alcohol, thymol, diphenylamine, and toluidine, are so nearly linear that they may be accepted as such with an error no larger than 2 or 3 degrees at 1000 atmospheres." He also found that in the case of water the rectilinear relation does not hold.

If an isochoric diagram be constructed from the results given on p. 116, it will be seen that, except at small volumes, the isochoric lines are approximately straight, but curve considerably on approaching the condensation points. The lines should probably, as BARUS found, be curved throughout, but no considerable error is introduced in considering them as straight during the major part of their course. Indeed, accepting REGNAULT'S determinations as correct, it would appear that at temperatures above 140°, the curvature cannot be due to premature condensation, since the isothermal curves given in the diagram have been drawn, as already stated, to coincide with the results of REGNAULT'S work on the heats of vaporization, and yet coincide with our experimental results, except at volumes very close to those at which liquefaction takes place ; and at such small volumes, surface condensation is unmistakeable.

On reference to the Appendix, p. 128, an account of experiments at much lower

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temperatures will be found. These show that the relative effect of surface condensation is much more marked at low than at high temperatures. Thus, at about 30 millims. pressure the vapour-density calculated at 75° is 9·01; at 50°, 9·46; at 40°, 9·90; and at 30°, 10·70. An increase of pressure does not appear to raise the apparent vapour-density to the same extent as a fall of temperature. This may explain why an increase of pressure, at high temperatures, does not influence surface condensation appreciably, except very close to the point of condensation.

In addition to the work of REGNAULT, that of FAIRBAIRN and TATE on the densities of unsaturated and saturated steam may be mentioned. As their results were given in English units, we think it well to reproduce them here in the same form as has been adopted in this paper. It will be seen that the densities of the saturated vapour show a gradual rise with increase of temperature, although the results of individual experiments are far from regular.

FAIRBAIRN and TATE, 'Phil. Trans.,' 1860, pp. 218, 219. Quoted by RANKINE in Fahr. degrees and cubic feet per lb.

T. ° C.	T. ° Abs.	Volume of 1 grm.	Pressure.	Vapour-density.
		c.cs.	millims.	
58·20	331·20	8275·3	135·9	9·15
68·51	341·51	5333·5	218·9	9·09
70·75	343·75	4920·2	240·0	9·05
77·18	350·18	3722·6	316·7	9·23
77·49	350·49	3715·1	320·3	9·15
79·40	352·40	3438·1	346·0	9·21
83·50	356·50	3051·0	406·7	8·93
86·83	359·83	2623·4	466·4	9·14
92·65	365·65	2149·5	581·1	9·10
117·16	390·16	943·12	1361·7	9·44
118·23	391·23	908·03	1410·1	9·49
118·45	391·45	892·54	1419·6	9·60
124·16	397·16	759·44	1697·7	9·57
128·41	401·41	649·24	1935·4	9·93
130·67	403·67	635·30	2070·8	9·54
131·77	404·77	605·65	2138·9	9·71
134·86	407·86	584·44	2342·6	9·26
134·05	407·05	543·17	2287·9	10·18
137·45	410·45	514·98	2529·8	9·79
139·21	412·21	497·25	2655·2	9·70
141·80	414·80	458·30	2864·6	9·82
144·74	417·74	433·12	3105·1	9·65
142·36	415·36	449·62	2901·9	9·89

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FAIRBAIRN and TATE. Superheated Steam. 'Edinb. Trans.,' vol. 23, 1862, p. 147. Results arranged in isotherms, and Pressures and V.D.'s corrected for vapour pressure of mercury, using (1) Pressures used by RANKINE, (2) Pressures by RAMSAY and YOUNG.

Temperature.	Temperature.	Weight.	Volume.	P_1.	P_2.	V. D. (1.)	V. D. (2.)
° F.	° C.	grms.	c.cs.	millims.	millims.		
302·88	150·5	0·01845	197·3	132·3	134·0	9·31	9·19
,,	,,	0·02625	197·3	184·6	186·3	9·48	9·39
,,	,,	0·03530	197·3	250·4	252·1	9·41	9·34
,,	,,	0·03435	197·3	242·0	243·7	9·46	9·40
,,	,,	0·05670	197·3	408·6	410·3	9·25	9·22
251·64	122·0	0·01845	197·2	123·8	124·7	9·29	9·22
,,	,,	0·02625	197·2	171·5	172·4	9·53	9 48
,,	,,	0·03530	197·2	234·0	234·9	9·39	9·36
,,	,,	0·03435	197·2	226·1	227·0	9·46	9·42
,,	,,	0·05670	197·2	381·6	382·5	9·25	9·23
200·74	93·75	0·01845	197·1	114·7	115·1	9·31	9·28
,,	,,	0·02625	197·1	159·9	160·3	9·49	9·47
,,	,,	0·03530	197·1	217·1	217·5	9·41	9·39
,,	,,	0·03435	197·1	210·0	210·4	9·46	9·44
,,	,,	0·05670	197·1	353·2	353·6	9·28	9·27
180·72	82·6	0·04670	197·0	340·2	340·5	9·35	9·34
165·45	74·15	0·03435	197·0	197·3	197·5	9·53	9·52
,,	,,	0·05670	197·0	259·3	259·5	11·98	11·97
150·18	65·65	0·01845	196·9	105·7	105·9	9·34	9·32
,,	,,	0·02625	196·9	147·6	147·8	9·50	9·49
,,	,,	0·03530	196·9	176·1	176·3	10·72	10·71
,,	,,	0·03435	196·9	177·1	177·3	10·37	10·35
100·0	37·75	0·01845	196·8	44·6	44·7	20·3	20·3

HIRN, in his 'Théorie Mécanique de la Chaleur,' vol. 1, 3rd Ed., p. 468, gives a table of the densities of saturated vapour at various temperatures, ranging from 98° to 196°. As these agree absolutely with the results calculated from REGNAULT'S measurements, and as neither the method adopted by HIRN, nor his individual observations would appear to lead one to anticipate such concordance, we would suggest that it may be attributed to the "tracé de sentiment" with which he credits the assistant who interpreted his results.

In conclusion, it may be noted that REGNAULT made experiments on the densities of saturated steam at low temperatures for hygrometric purposes, and has shown that it is practically normal at temperatures between 0° and 27° ('Annales de Chimie' [3], vol. 15, 1845, p. 129, *et seq.*).

NOTE.—In Plate 7 the curves representing the relations of temperature, pressure, and volume of unsaturated and saturated steam are given on a scale large enough, we hope, to prove of practical use. For this purpose they have been divided into three sets, a different scale, however, being applied to each set. The pressures are given in metres of mercury; the volumes, in cubic centimetres per gramme. The heavy line shows the volumes of saturated vapour, and may be termed the orthobaric line.

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Appendix.

Volumes (Vapour pressures) and Compressibility of Liquid Water at various Temperatures.

Temperature.	Divisions of tube.	Pressure.	Actual volumes.	Temperature.	Divisions of tube.	Pressure.	Actual volumes.
°		millims.	cub. centims.	°		millims.	cub. centims.
100	256·85	760	1·1503	210	288·00	17,488	1·2937
,,	256·50	19,651	1·1488	,,	287·50	31,467	1·2912
110	258·80	1,073	1·1546	,,	287·00	43,405	1·2888
120	260·95	1,484	1·1682	220	292·30	17,622	1·3138
130	263·10	2,019	1·1775	,,	292·00	27,251	1·3128
140	265·70	2,694	1·1900	,,	291·50	39,432	1·3105
150	268·25	3,568	1·1998	230	297·00	21,085	1·3367
160	271·05	4,652	1·2126	,,	296·50	31,745	1·3343
170	274·00	5,937	1·2267	,,	296·00	42,249	1·3319
180	277·10	7,478	1·2416	240	302·00	25,276	1·3584
190	280·60	9,837	1·2583	,,	301·50	32,452	1·3563
,,	280·50	12,813	1·2579	,,	301·00	41,614	1·3543
,,	280·00	30,029	1·2555	250	307·20	30,059	1·3801
,,	279·50	39,904	1·2532	,,	307·00	36,040	1·3793
200	284·20	15,014	1·2755	,,	306·50	43,925	1·3773
,,	284·00	18,695	1·2746	260	313·40	35,028	1·4059
,,	283·50	30,513	1·2723	,,	313·00	40,210	1·4043
,,	283·00	43,901	1·2698	270	319·50	43,433	1·4334
210	288·05	14,404	1·2942				

Vapour-pressures of Water.—Individual Observations.

Temperature.	Pressure.	Mean corrected.*	Pressure.†	Temperature.	Pressure.	Mean corrected.*	Pressure.†
°	millims.	millims.	millims.	°	millims.	millims.	millims.
120	1,482			140	2,691		
	1,484				2,701		
	1,483	1,484	1,445		2,703	2,694	2,658
	1,493				2,695		
	1,483				2,700		
130	2,024			150	3,555		
	2,022			(Jacket	3,552		
	2,021	2,019	1,950	C_6H_5 Br)	3,559	3,553	3,475
	2,018				3,558		
	2,022				3,569		

* For deviation from Boyle's law, and for vapour-pressure of mercury. In previous work the measurements of pressure were made rapidly; after the volume had been increased to its maximum, it was diminished by stages, and pressure was read at each stage. The correction for vapour-pressure of mercury is in such a case not admissible. But in this research the temperature was allowed to remain constant for at least an hour before taking the first reading.

† Observed with a much smaller quantity of liquid present—nearly all vapour.

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VAPOUR-PRESSURES of Water.—Individual Observations—(continued).

Temperature.	Pressure.	Mean corrected.	Pressure.	Temperature.	Pressure.	Mean corrected.	Pressure.
°	millims.	millims.	millims.	°	millims.	millims.	millims.
150	3,580			210	14,338		
(Jacket	3,580				14,329		
$C_6H_5NH_2$)	3,588	3,581			14,320	14,241	14,197
	3,590				14,343		
	3,594				14,383		
160	4,656			210	14,337		
	4,648				14,346		
	4,660	4,652	4,609		14,342	14,255	
	4,668				14,382		
	4,671				14,377		
170	5,958			210	14,324		
	5,958				14,321	14,223	
	5,939	5,937	5,889		14,326		
	5,966						
	5,966			220	17,484		
					17,468	17,329	17,472*
180	7,549				17,490		17,426
(Aniline)	7,559			220	17,498		
	7,547			(End of work)	17,519		
	7,552				17,541	17,401	
	7,581	7,518	7,493		17,582		
	7,536				17,632		
	7,519						
	7,480			230	21,059		
	7,539				21,175		
	7,578				21,163	20,936	20,879
					21,158		
180	7,423				21,152		
(Methyl Sali-	7,453			240	25,296		
cylate)	7,446				25,294		
	7,449				25,340	25,019	24,803*
	7,467	7,437			25,399		25,040
	7,457				25,393		
	7,457						
	7,452			250	30,150		
	7,474				30,130		
					30,142	29,734	29,527*
190	9,425				30,214		29,687
	9,418				30,272		
	9,431			260	35,644		
	9,425				35,630		
	9,456	9,403	9,374		35,649	35,059	35,036
	9,469				35,654		
	9,484				35,650		
	9,462						
				270	41,913		
200	11,679				41,890		
	11,685				41,869	41,101	40,956*
	11,674	11,625	11,564		41,864		41,149
	11,708				41,861		
	11,705				41,821		

* Determinations with two separate quantities, one of which was larger than the other.

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Volumes of 1 *grm. of Steam, at Various Temperatures and Pressures.*

I. *High Temperatures.*

Two series of experiments were made. The weight of the water in the tube was ascertained by determining the products of pressure and volume, altering the volumes; and this was repeated at different temperatures. Assuming that if these products for any one temperature were constant, the density of the steam was constant, viz., the theoretical density, 9, the weight could be ascertained by the equation

$$W = \frac{\text{V.D.} \times p.v \times 273}{11{\cdot}1636 \times 1000 \times 760 \times (273 + t)}.$$

This expression simplifies to

$$\log W = \log p.v. + \bar{4}{\cdot}46179 - \log (273 + t).$$

During the progress of the experiments it happened that a trace of water passed up the tube, adding itself to that already present. This, of course, increased the weight, hence new measurements were made to determine the amount of the increase.

These weights were obtained from the following readings:—

DETERMINATION of the Weight of the Smallest Quantity of Water. (A.)

Temperature.	Volume.	Pressure.	p. v.	Weight.	Mean weight.
°	cub. centims.	millims.		grm.	grm.
220	1·7147	2528	4335	0·002546	
	1·5565	2770	4311	0·002533	
	1·4080	3060	4308	0·002531	
	1·2592	3435	4325	0·002541	
	1·1072	3893	4310	0·002532	0·002536
230	1·7151	2585	4434	0·002553	
	1·5569	2820	4391	0·002529	
	1·4084	3119	4393	0·002529	
	1·1579	3815	4417	0·002543	0·002538
	General mean, 0·002537.				
	Here some water rose in the tube and increased the weight.				
230	1·7151	2633	4516	0·002600	
	1·5569	2879	4482	0·002581	
	1·4084	3153	4441	0·002587	0·002579
240	1·7156	2697	4627	0·002612	
	1·5573	2948	4591	0·002598	
	1·4087	3253	4583	0·002587	
	1·1582	3964	4591	0 002592	0·002597
250	1·5064	3097	4665	0·002582	
	1·4091	3310	4664	0·002581	
	1·1585	4026	4664	0·002581	0·002581
	General mean, 0·002587.				

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DETERMINATION of the Weight of the Smallest Quantity of Water. (A.)—(continued).

Temperature.	Volume.	Pressure.	p. v.	Weight.	Mean weight.
Here more water rose in the tube and increased the weight.					
°	cub. centims.	millims.		grms.	grm.
250	1·7160	2819	4837	0·002679	
	1·5577	3114	4851	0·002686	
	1·4091	3403	4795	0·002655	
	1·1585	4155	4813	0·002665	0·002671
260	1·7165	2872	4930	0·002678	
	1·5580	3144	4899	0·002662	
	1·4094	3478	4902	0·002663	
	1·1588	4220	4890	0·002657	0·002665
270	1·7169	2918	5010	0·002672	
	1·5585	3196	4981	0·002657	
	1·4099	3529	4975	0·002654	
	1·1591	4283	4964	0·002648	0·002656
General mean, 0·002664.					

These results can be verified by taking the weight at 270° as a standard, and calculating the smaller weights by the equation

$$\frac{p.v.}{273+t} : \frac{p'v'}{273+t'} :: W : W'$$

identical numbers with those found are obtained.

Hence the largest weight at 250°, 260°, and 270° is 0·002664 grm.;
the second weight at 250°, 240°, and 230° is 0·002588 grm.;
the first weight at 220° and 230° is 0·002547 grm.

The first weight holds also for lower temperatures.

These data are adduced as a proof of the relative accuracy of the determinations which follow.

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VOLUMES of 1 grm. of Steam and Vapour-densities.

Temperature.	Pressure.	Volume of 1 grm.	p. v.	Vapour-density H = 1.	Remarks.
	millims.	c.c.			
120°	1,448	602·0	..	..	Condensed
	1,450	545·2	..	..	Condensed
130	1,930	622·7	..	..	Condensed
	1,953	563·7	..	..	Condensed
140	2,093	661·7	1,384,900	9·268	
	2,245	609·9	1,369,200	9·374	
	2,449	551·7	1,351,100	9·500	
	2,620	453·6	1,188,400	10·800	
	2,645	338·3	894,810	..	Condensed
	2,650	107·1	..	..	Condensed
150	2,147	661·8	1,420,900	9·251	
	2,309	610·0	1,408,500	9·333	
	2,550	551·8	1,407,100	9·343	
	3,068	453·7	1,392,000	9·445	
	3,280	415·2	1,361,900	9·654	
	3,442	353·9	..	..	Condensed
	3,475	241·5	..	..	Condensed
150	2,149	661·8	1,422,200	9·243	
	2,310	610·0	1,409,100	9·329	
	2,547	551·8	1,405,400	9·354	
160	2,211	662·0	1,463,700	9·193	
	2,382	610·2	1,453,500	9·258	
	2,633	552·0	1,453,400	9·259 ?	
	3,182	453·8	1,444,000	9·319	
	3,997	354·1	1,415,300	9·509	
	4,571	241·6	..	..	Condensed
170	2,267	662·2	1,501,200	9·171	
	2,447	610·3	1,493,400	9·219	
	2,705	552·1	1,493,500	9·219	
	3,271	453·9	1,484,700	9·273	
	4,172	354·1	1,477,300	9·364	
	5,603	252·7	1,415,900	9·722	
180	2,330	662·4	1,543,400	9·122	
	2,509	610·5	1,531,800	9·193	
	2,771	552·2	1,530,100	9·200	
	3,356	454·0	1,523,600	9·240	
	4,271	354·2	1,512,800	9·306	
	5,854	252·8	1,479,900	9·512	
	7,296	192·5	1,404,500	10·025	
	7,444	152·3	..	..	Condensed
	7,471	112·1	..	..	Condensed
190	2,387	662·6	1,581,600	9·098	
	2,576	610·7	1,573,200	9·147	
	2,842	552·4	1,569,900	9·172	
	3,441	454·2	1,562,900	9·208	
	4,385	354·3	1,553,600	9·261	

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VOLUMES of 1 grm. of Steam and Vapour-densities—(continued).

Temperature.	Pressure.	Volume of 1 grm.	p. v.	Vapour density H = 1.	Remarks.
	millims.	c.c.			
190°	6,057	252·9	1,531,800	9·393	
(continued)	7,839	192·5	1,509,000	9·534	
	9,254	152·3	1,409,400	10·207	
	9,337	112·2	..	..	Condensed
200	2,458	662·7	1,628,900	9·024	
	2,655	610·8	1,621,700	9·065	
	2,930	552·5	1,618,800	9·080	
	3,546	454·2	1,610,600	9·126	
	4,516	354·4	1,600,400	9·185	
	6,276	253·0	1,587,800	9·260	
	8,107	192·6	1,561,400	9·738	
	10,004	152·4	1,524,600	10·246	
	11,505	112·2	..	..	Condensed
210	2,525	662·9	1,673,300	8·989	
	2,723	611·0	1,663,800	9·023	
	3,000	552·7	1,658,100	9·053	
	3,652	454·4	1,659,500	9·048	
	4,646	354·5	1,647,000	9·114	
	6,437	253·1	1,629,200	9·214	
	8,371	192·6	1,612,300	9·309	
	10,331	152·4	1,574,400	9·533	
	13,538	112·2	1,519,000	9·880	
	14,102	92·2	1,300,200	11·548	
220	2,585	663·0	1,713,800	8·939	
	2,782	611·1	1,700,100	9·012	
	3,072	552·8	1,698,200	9·022	
	3,734	454·5	1,697,100	9·029	
	4,758	354·6	1,687,300	9·082	
	6,601	253·1	1,670,700	9·171	
	8,580	192·7	1,653,400	9·268	
	10,649	152·4	1,622,900	9·438	
	14,073	112·2	1,579,000	9·699	
	16,458	92·2	1,517,400	10·098	
	17,165	72·2	..	..	Condensed
220	2,529	675·9	1,709,400	8·964	Weight altered
	2,770	613·5	1,699,400	9·016	
	3,060	555·0	1,698,300	9·022	
	3,435	496·3	1,704,800	8·986	
	3,894	436·4	1,699,400	9·016	
	4,493	376·2	1,690,300	9·064	
	5,685	294·3	1,673,100	9·136	
	7,114	235·8	1,677,500	9·134	
	8,575	193·4	1,658,400	9·237	
	10,638	153·0	1,627,600	9·411	
	14,032	112·7	1,581,400	9·690	
	16,641	92·6	1,541,000	9·948	
	17,476	72·5	1,267,000	10·059	
230	2,585	676·1	1,747,700	8·945	
	2,820	613·7	1,730,700	9·033	

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VOLUMES of 1 grm. of Steam and Vapour-densities—(continued).

Temperature.	Pressure.	Volume of 1 grm.	p. v.	Vapour-density H = 1.	Remarks.
	millims.	c.c.			
230° (continued)	3,119	555·1	1,731,400	9·028	
	3,615	477·9	1,727,600	8·978	
	4,840	356·1	1,723,500	9·070	
	6,725	254·1	1,708,800	9·146	
	8,815	193·5	1,705,700	9·165	
	10,887	153·1	1,666,800	9·380	
	14,430	115·1	1,660,900	9·633	
	17,148	92·6	1,587,900	9·847	
	20,662	72·5	1,498,000	10·433	
	20,884	52·5	..	..	Condensed
230 (repeated)	2,633	664·5	1,749,600	8·934	Taken as normal; weight altered
	2,879	603·2	1,736,600	9·002	
	3,153	545·7	1,720,600	9·086	
240	2,697	664·7	1,792,700	8·691	Doubtful
	2,948	603·4	1,778,900	8·973	
	3,253	545·8	1,775,500	8·980	
	3,964	448·7	1,778,600	8·963	
	5,053	350·1	1,769,000	9·012	
	7,002	249·9	1,749,800	9·112	
	9,158	190·2	1,741,900	9·170	
	11,395	150·5	1,715,000	9·151	
	15,084	110·8	1,671,300	9·296	
	17,998	91·0	1,637,800	9·559	
	21,336	71·3	1,524,100	9·732	
	22,162	61·4	1,360,700	10·480	
	25,049	41·7	..	..	Condensed
250	3,097	583·6	1,807,400	8·992	
	3,310	545·9	1,806,900	8·995	
	4,027	448·8	1,807,300	8·993	
250 (repeated)	2,819	644·2	1,816,000	8·951	
	3,114	584·7	1,820,800	8·927	
	3,403	528·9	1,799,800	9·030	
	4,155	434·9	1,807,000	8·996	
	5,290	339·3	1,794,900	9·056	
	7,367	242·2	1,784,300	9·110	
	9,560	184·4	1,762,900	9·222	
	11,907	145·9	1,737,300	9·359	
	15,852	107·4	1,702,500	9·547	
	18,897	88·2	1,666,700	9·751	
	23,594	69·1	1,630,400	9·970	
	26,395	59·5	1,570,500	10·343	
	29,473	50·0	1,473,600	11·034	
	29,696	31·0	..	..	Condensed
260	2,872	644·3	1,850,400	8·952	
	3,144	584·9	1,838,900	9·008	
	3,479	529·1	1,840,800	9·000	
	4,225	435·0	1,837,900	9·013	
	5,409	339·4	1,835,800	9·045	
	7,521	242·2	1,821,600	9·093	

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VOLUMES of 1 grm. of Steam and Vapour-densities—(continued).

Temperature.	Pressure.	Volume of 1 grm.	p. v.	Vapour density H = 1.	Remarks.
	millims.	c.c.			
260°	9,811	184·4	1,809,100	9·177	
(continued)	12,164	145·9	1,774,800	9·334	
	16,228	107 4	1,741,800	9·501	
	19,326	88·2	1,704,600	9·714	
	23,886	69·1	1,650,500	10·034	
	27,193	59·6	1,620,700	10·229	
	31,142	50·0	1,571,000	10·640	
	35,040	31·0	..	..	Condensed
270	2,918	644·5	1,880,700	8·973	
	3,196	585·0	1,869,700	9·025	
	3,529	529·2	1,867,600	9·036	
	4,288	435·1	1,865,700	9·045	
	5,486	339·5	1,862,600	9·062	
	7,664	242·3	1,857,000	9·088	
	9,974	184·4	1,839,200	9·173	
	12,392	145·9	1,808,000	9·331	
	16,519	107·5	1,775,800	9·507	
	19,729	88·3	1,742,100	9·691	
	24,427	69·1	1,687,900	9·993	
	27,813	59·6	1,657,700	10·185	
	31,958	50·0	1,597,900	10·560	
	37,862	40·5	1,533,400	11·010	
	40,854	29·1	..	..	Condensed

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II. *Low Temperatures.*

(*a.*) Weight of water in the modified HOFMANN'S apparatus (described with a wood-cut in 'Phil. Trans.,' 1887 A., p. 59).

0·20087 grm.

Readings commenced at largest volume, and vapour then compressed.

Temperature.	Pressure.	Volume.	Vapour Density (H = 1).	Temperature.	Pressure.	Volume.	Vapour Density (H = 1).
°	millims.	c.c.		°	millims.	c.c.	
75	23·35	150·5	8·83	40	19·15	149·1	9·78
	23·40	148·5	8·93		21·2	135·7	9·71
	23·65	146·3	8·97		23·15	122·3	9·86
	25·80	134·9	8·92		26·0	109·0	9·85
	27·4	125·9	8·99		29·2	96·54	9·90
	29·6	116·4	9·01		33·75	83·07	9·96
	32·2	106·2	9·08		39·3	71·10	9·99
	35·3	96·36	9·13		48·45	55·90	10·31
	39·95	86·52	8·98		52·2	49·66	10·77
	45·7	74·78	9·08		54·1	42·05	12·27
				30	18·05	154·9	9·66
75	23·6	146·9	8·96		18·9	145·2	9·85
(repeated)	24·1	141·2	9·12		20·1	134·5	10·00
	30·3	111·9	9·16		22·1	122·0	10·03
	47·65	72·17	9·03		24·45	109·0	10·14
	57·7	58·12	9·26		26·7	96·72	10·46
	79·2	42·76	9·17		29·9	84·50	10·70
					31·05	68·61	(12·69)
					31·35	55·0	Condensed
					31·45	43·0	„
50	20·35	153·0	9·25				
	21·8	140·5	9·40	25	17·25	154·2	9·99
	23·4	130·5	9·43		18·0	144·8	10·20
	26·95	113·2	9·45		19·25	134·4	10·27
	33·25	91·35	9·49		20·35	123·1	10·62
	42·1	71·82	9·53		21·8	111·6	10·93
	54·75	54·49	9·66		22·4	99·32	11·95
	70·75	42·52	9·58		23·35	86·5	(13·16)

It is to be noticed that four readings are required for each pressure, so that at the lowest pressure an error of 1 per cent., or say 0·2 millim., is not excessive.

In considering these results it is seen that, as a rule, the density increases on diminishing volume. This, however, cannot be ascribed to real increase of density, but to diminution of the actual weight of the water present in the state of vapour through adhesion of water to the surface of the tube. That this explanation is the correct one is seen from the following considerations.

At 75° very little rise of vapour-density is to be observed, although there is a slight tendency towards a higher value at the smallest volumes. The pressure was never near the vapour-pressure, which at this temperature is 288·5 millims.

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At 50°, at which the vapour-pressure is 92 millims., the vapour-densities are all high, but do not rise rapidly after the first one. The highest pressure registered (70·75) approached the vapour-pressure.

At 40° the vapour-pressure is 54·9 ; the highest pressure read was 54·1. The rise of vapour-density is slow at first, and afterwards more rapid.

At 30° the vapour-pressure is 31·55 millims., while the highest pressure read was 31·05 millims. The vapour-densities are very high, and rise rapidly with decrease of volume ; and at 25° the vapour-pressure is 23·55 millims., the highest pressure read being 23·35. Again, there is a rapid increase of density with diminishing volume.

These pressures are all somewhat lower than the values given by REGNAULT.

(*b*). Weight = 0·00295 grm.

The tube was heated to 100°.

Temperature.	Pressure.	Volume.	Vapour-density.
°	millims.	c.c.	
100	25·1	152·4	8·94
	28·7	131·3	9·08
	34·1	110·4	9·08
	41·45	91·13	9·05
	52·4	72·34	9·02

The tube was then cooled with the mercury at the same height as at the last reading, and then, without drawing down the mercury, the tube was heated to 40°. In this case there was no possibility of condensation of vapour on the lower part of the tube, while previously, when readings were begun at the largest volume, condensation might have taken place on the lower part of the tube. If, therefore, the high vapour-densities are due to adhesion and condensation, the value of this reading at 40° should be lower than it was found in the first series. This is in fact the case, as is shown by the following determinations :—

Temperature.	Pressure.	Volume.	Vapour-density.
°	millims.	c.c.	
40	42·05	71·7	9·52
	45·75	64·63	9·70
	51·6	55·41	10·04
	53·95	49·83	10·67
	54·8	42·0	Condensed.

In the first series, at volume 71·1 cub. centims., the vapour density was 9·99, as against 9·52 in the second at volume 71·7 cub. centims. The largest volume in the

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first series, 149·1, is a little more than twice as great as the largest volume in the second; therefore, as the tube was cylindrical, the surface on which condensation could take place was about twice as great. If the condensation is not much affected by the rise of pressure from 19·15 millims. at the largest volume of the first series to 42·05 millims. at the largest volume of the second, and if the high vapour-density is entirely due to condensation, we should expect the error to be about half as great in the second as in the first series, and this is approximately the case. It will be noticed that the weight of the water in both sets is nearly the same.

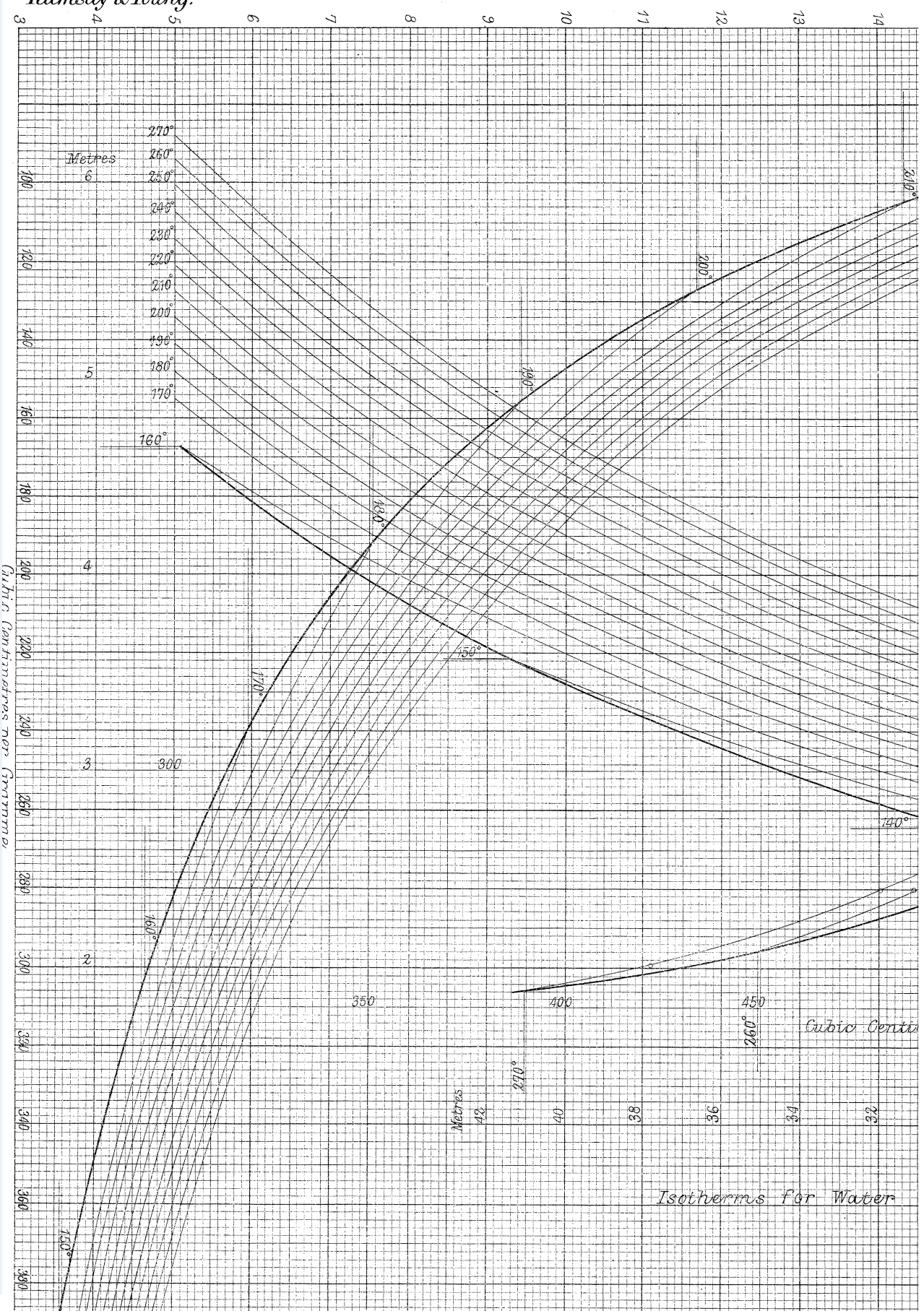
The tube was again heated to 100°, and the external pressure so arranged that the volume of vapour remained about 56 cub. centims. After cooling, the tube was again heated to 40°, and a reading was taken with the following results:—

Temperature.	Pressure.	Volume.	Vapour-density.
° 40	millims. 52·3	c.c. 54·87	10·00

The result is not much lower than at the corresponding volume in the last experiment, but the gain of surface was not very great, and the pressure, 52·3 millims., was very near the condensing pressure, 54·9 millims.; and it is to be noticed that the vapour-density rises rapidly as this pressure is approached. At the same pressure in the first series, the vapour-density observed was 10·77—a much higher value.

The experiments show that the high vapour-densities are due to condensation on the walls of the tube, and that the error due to this cause may vary considerably, especially at pressures near the true vapour pressures.

Similar experiments were not made at high pressures, but on constructing isothermal curves, it is seen that as the volume diminishes, and as the vapour-pressure is approached, the curves instead of cutting the vapour-pressure line so as to form an angle, as is the case with the other liquids which we have examined, gradually turn and run nearly parallel to the vapour-pressure line at a somewhat lower pressure. When a considerable amount of liquid has condensed, the true vapour-pressure is reached. This behaviour is analogous to that of a mixture of a condensible vapour with a gas like air; but it cannot be attributed to such admixture, for the last bubble of steam left on raising pressure was easily and quickly absorbed, and without any perceptible rise of pressure. Its cause must, as already explained, lie in the adhesion of the vapour to the glass, causing condensation before the true vapour-pressure is reached.



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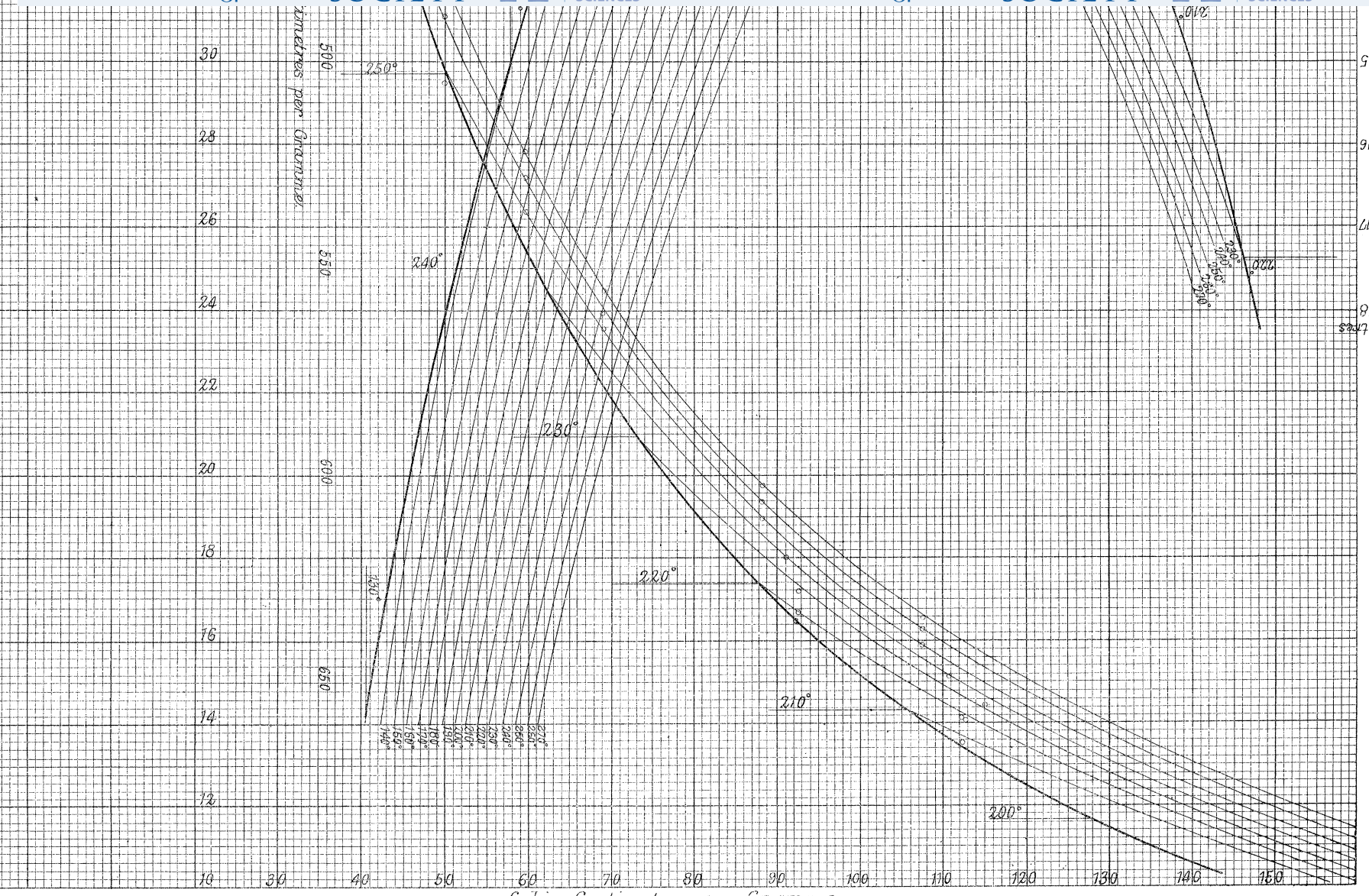

Phil. Trans. 1892. A. *Plate* 7.

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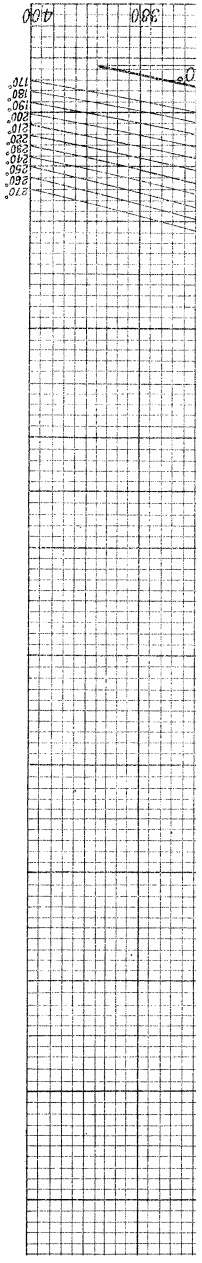

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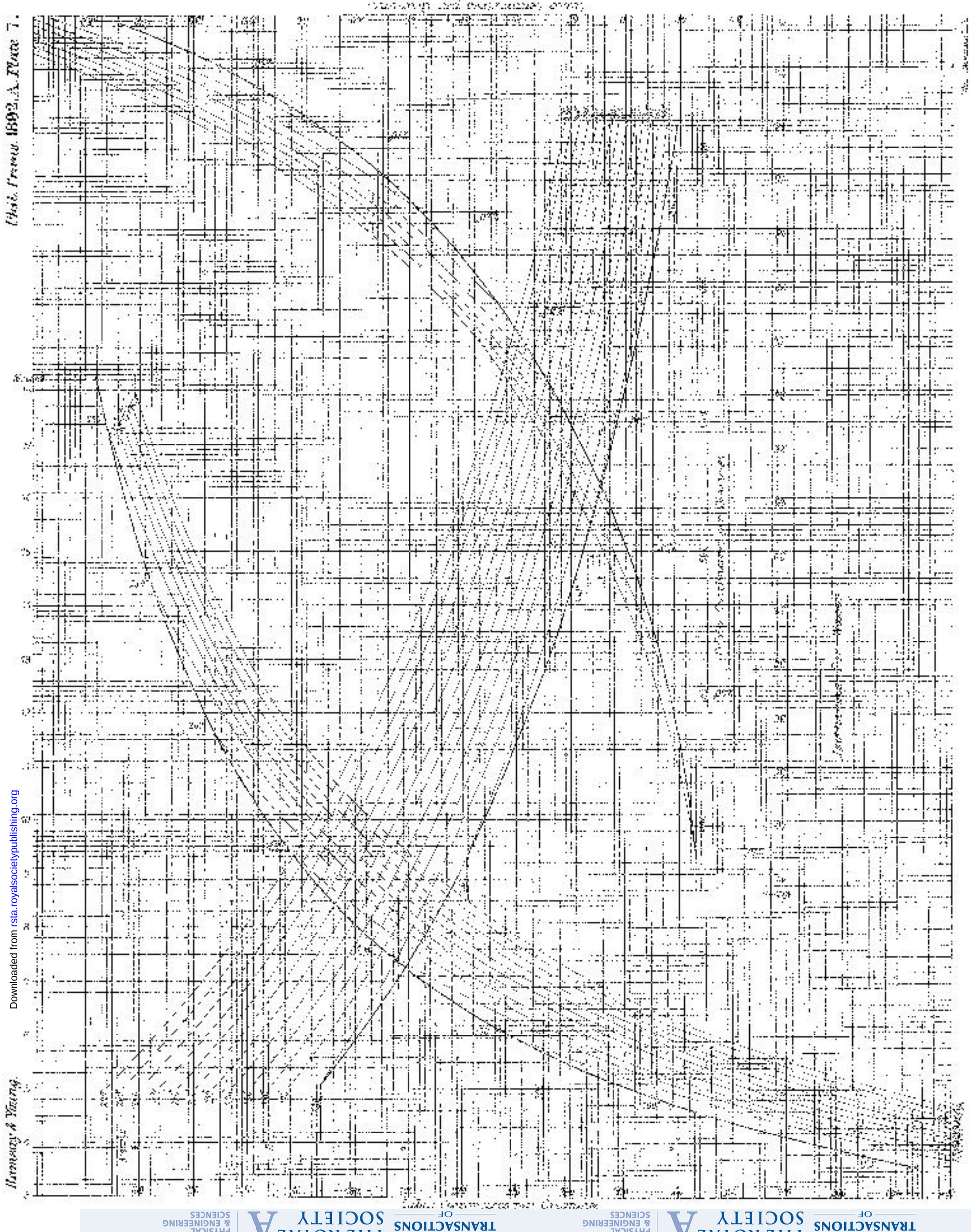

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