On Evaporation and Dissociation. - Part VI. On the Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1886 Proc. Phys. Soc. London 8 194

(<http://iopscience.iop.org/1478-7814/8/1/330>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 192.236.36.29

This content was downloaded on 03/10/2015 at 07:33

Please note that [terms and conditions apply](#).

XXIX. *On Evaporation and Dissociation.*—Part VI.* *On the Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures.* By WILLIAM RAMSAY, *Ph.D.*, and SYDNEY YOUNG, *D.Sc.*†

[Plates IV., V., VI., & VII.]

It was proved by Boyle, in 1662, that the volume of a gas, provided temperature be kept constant, varies inversely as the pressure to which it is subjected; this relation may be expressed by the equation $p = \frac{c}{v}$, or $pv = \text{constant}$, where p and v respectively stand for pressure and volume. But subsequent experiments by Van Marum, Oersted, Despretz, and others showed that certain gases do not obey this law; and it is now well known that Boyle's statement is only approximate; for it has been proved by experiment by Regnault, Natterer, and more recently by Amagat, that no gas, under high pressures, is diminished in volume in inverse ratio to the rise of pressure. Indeed Boyle's law could hold only on the assumption that the actual molecules of matter possess no extension in space and exert no attraction on each other. A gas, such as hydrogen, at low pressures, and consequently at large volumes, fills a space very great when compared with the space occupied by the actual molecules; and these molecules are comparatively so distant from one another, that the attraction which they mutually exercise is inappreciable. But, on compression, the actual space occupied by the molecules bears an increased ratio to the space which they inhabit; and, by their approach, the attraction which they exert is also increased. The gas, then, deviates appreciably from Boyle's law.

Gay-Lussac, in 1808, enunciated the law that the volumes of all gases increase by a constant fraction of their volume at

* Parts I. and II., *Philosophical Transactions*, part i. 1886, pp. 71 and 123; Part III., *ibid.* part ii., 1886, p. 1; Part IV., *Trans. Chem. Soc.* 1886, p. 790; Part V., in the hands of the Royal Society.

† Read February 26. 1887.

0° for each rise of 1° in temperature. It was subsequently ascertained by Magnus, and confirmed by Regnault, that certain gases deviate from this law, expanding more rapidly than others. Such gases, as a rule, are at temperatures not far removed from those at which they condense to liquids; that is, their volumes are comparatively small, and the actual size of the molecules and their mutual cohesion begin to manifest themselves within the range of experimental observation. Again, it is evident that no gas can perfectly follow Gay-Lussac's law; but the larger the volume it occupies the smaller is the influence of the disturbing factors. The usual expression for Gay-Lussac's law is $v = c(1 + \alpha t)$, or, if the absolute temperature-scale be employed, $v = cT$.

As a deduction from these laws, it follows that if the volume of unit mass of a gas, supposed to follow them rigorously, be kept constant, the pressure varies directly as the absolute temperature; or $p = cT$.

Now, so long as the volume of unit mass of a gas is kept constant, the average distance of its molecules from one another will remain constant; and it is a fair assumption that the attraction of the molecules for each other will not vary. It may, of course, be the case that the effect of a rise of temperature on any individual molecule is to alter its actual volume; but of this we know nothing; and, in default of knowledge, it has been assumed by us that no such alteration takes place. If these assumptions are correct, it follows that the temperature and pressure of gases—and indeed the same assumptions may be extended to liquids—should then bear a simple relation to each other. We have obtained experimental proof of a convincing nature that this is the case; and in a preliminary note to the Royal Society, read on January 6, we promised such a proof. This proof is the subject of the present paper; and we must ask for indulgence in quoting a large array of figures, some of which have already been published, on the ground that such an important generalization requires as much experimental evidence as can be brought to bear on it.

The relation between the pressures and temperatures of a

liquid or a gas at constant volume is expressed by the equation

$$p = bT - a ;$$

where p is the pressure in millimetres, T the absolute temperature, and b and a constants. The values of these constants depend on the nature of the substance and on the volume. It follows from this, that if a diagram be constructed to express the relations of pressure, temperature, and volume of liquids and gases, where pressure and temperature form the ordinates and abscissæ, the lines of equal volume are straight*.

We have proved this to be the case for ethyl oxide (ether) between the temperatures 100° and 280° , and for volumes varying from 1.85 cubic centim. per gram to 300 cubic centim. per gram. This proof we now proceed to give.

The data for the calculations are at present in the press, and will shortly appear in the *Philosophical Transactions* for 1886, p. 10. A diagram (which will accompany that memoir) was constructed with the greatest care, showing isothermal lines, the ordinates and abscissæ being respectively pressures and volumes. It was possible to read pressure accurately to within 20 millim.; and volume, up to a volume of 3.1, to within 0.001 cubic centim. per gram; and, at volumes greater than 3.1 cubic centim. per gram, to 0.01 cubic centim. per gram. Pressures corresponding to each isothermal were then read off on the equal volume-lines, from curves constructed to fit the experimental points as accurately as could be drawn with the help of engineers' curves. These pressures and temperatures were then mapped as ordinates and abscissæ; and it was found that points corresponding to each volume lay in a straight line. Again, two points were chosen on these equal volume-lines, as far apart as the scale of the diagram would permit, and the values of the change of pressure per unit change of temperature, $\frac{dp}{dt}$, were ascertained for each

* Amagat (*Comptes Rendus*, xciv. p. 847) has stated a similar relation for gases; his data are, however, imperfect, and he expressly states that the law does not apply to liquids.

separate volume chosen. To eliminate irregularities, these values were smoothed graphically ; but it was difficult to find any very satisfactory method. The method employed for ether, which we found to give the best results, was to map as ordinates the ratios between these values, and similar values calculated on the supposition that the gas or liquid followed the usual gaseous laws, against the reciprocals of the volumes as abscissæ. A curve was then drawn, taking a mean course among the actual points, and the values of $\frac{dp}{dt}$ were calculated from readings at definite volumes. This expression, $\frac{dp}{dt}$, is the b of our formula. Having thus obtained the most probable value of b for each volume, the value of a at each volume was ascertained by calculation from each individual point read from the original curves, and at each volume the mean of all was chosen.

Isothermals were then calculated by means of the equation $p=bT-a$, T being kept constant ; and those values of a and b corresponding to the volumes required being selected. These calculated isothermals are shown on Plate IV. ; and the lines of equal volume, or isochors*, on Plate V. It is evident, from inspection of the former, that the calculated lines correspond as closely as possible with the actual observations.

It is necessary now to give the data on which these deductions are based. The following Table gives those points corresponding to lines of equal volume read from the diagram constructed from experimental observations.

* From *ἴσος*, *equal*, and *ἔχειν*, *to contain*. Another suitable word would be "*isoplethe*," but we have Professor Jowett's preference for the one selected. Either of these terms seems preferable to that (*isometrics*) already proposed.

4	{ P.... T....	27600 195°	27690 195°	28440 197°	29900 200°	31840 205°	34050 210°	37830 220°	38900 223°	50260 250°
5	{ P.... T....	27000 192°-8	27460 195°	27460 195°	28150 197°	29250 200°	30800 205°	32400 210°	35440 220°	44620 250°
6	{ P.... T....	26100 192°	26400 193°	26640 193°-8	27000 195°	28970 195°	27560 197°	28400 200°	29700 203°	30950 210°
7	{ P.... T....	25130 190°	25500 192°	25750 193°	25950 193°-8	26210 195°	26150 195°	26670 197°	27350 200°	28400 205°
8	{ P.... T....	23250 185°	23380 185°	24300 190°	24660 192°	24850 193°	25060 193°-8	25250 195°	25190 195°	25640 197°
9	{ P.... T....	22540 185°	22600 185°	23400 190°	23650 192°	23830 193°	23950 193°-8	24130 195°	24050 195°	24450 197°
10	{ P.... T....	21650 185°	21790 185°	22350 190°	22650 192°	22770 193°	22870 193°-8	23030 195°	23350 197°	24400 205°
11	{ P.... T....	19550 175°	19550 175°	20800 185°	20860 185°	21450 190°	21700 192°	21800 193°-8	21870 195°	22020 195°
12	{ P.... T....	18780 175°	18800 175°	19950 185°	19990 185°	20530 190°	20740 192°	20850 193°	20930 193°-8	21060 195°
13	{ P.... T....	18050 175°	18070 175°	19130 185°	19090 185°	19650 190°	19840 192°	19960 193°	20030 193°-8	20130 195°
14	{ P.... T....	17330 175°	17400 175°	18300 185°	18300 185°	18740 190°	18960 192°	19100 193°	19200 193°-8	19250 195°
15	{ P.... T....	16670 175°	16750 175°	17570 185°	17570 185°	17970 190°	18280 193°-8	18500 195°	18380 195°	20250 220°
16	{ P.... T....	16000 175°	16100 175°	16830 185°	16850 185°	17180 190°	17500 193°-8	17740 195°	17610 195°	19380 220°
17	{ P.... T....	15440 175°	15520 175°	16180 185°	16200 185°	16530 190°	16840 193°-8	17030 195°	16890 195°	18540 220°

Table I. (continued).

[illegible]

Lines of equal volume, or isochors, were then mapped from these results, pressures and temperatures being ordinates and abscissæ. The values of $\frac{dp}{dt}$, or b , were then read for each separate volume and smoothed, as before described. The following Table shows the read values, and the values after smoothing. The values of a are also given, calculated by the equation $a=bt-p$, from the results shown on the previous table; the means of all the individual results for each volume are stated.

TABLE II.

Volume.	b found.	b calcu- lated.	$\log b$.	a .
1.85		2034	3.30826	826860
1.90	1746	1861	3.26986	767670
1.95		1716	3.23452	715860
2.0		1597	3.20335	672820
2.05	1561	1492	3.17372	633070
2.1	1500	1405	3.14777	600110
2.15	1342	1320	3.12061	566170
2.2	1211	1243	3.09462	535100
2.25	1155	1175	3.07022	507170
2.3	1117	1115	3.04744	482160
2.4	1020	1010	3.00423	437240
2.5	920.8	919.7	2.69363	397970
2.75	732.0	732.0	2.86451	313605
3.0	623.5	621.7	2.79357	262917
3.3	535.7	532.8	2.72659	221630
3.7	453.1	454.6	2.65762	185109
4.0	413.7	413.7	2.61669	165996
5.0	321.5	319.1	2.50392	121895
6.0	257.15	254.2	2.40511	91906
7	213.6	208.7	2.31959	71464
8	178.0	176.1	2.24584	57203
9	150.95	151.4	2.18022	46742
10	130.8	132.7	2.12280	39079
11	116.25	117.6	2.07027	33037
12	104.45	105.5	2.02336	28401
13	94.29	95.54	1.98017	24659
14	85.00	87.09	1.93998	21567
15	78.82	80.06	1.90339	19125
16	72.29	73.95	1.86893	17049
17	67.53	68.76	1.83733	15313
18	62.53	64.24	1.80780	13854
19	59.23	60.11	1.77893	12533
20	55.70	56.43	1.75151	11386
25	43.75	43.26	1.63612	7529
30	35.60	34.99	1.54393	5412
40	26.23	25.09	1.39945	3159
50	20.38	19.46	1.28925	2077
75	12.82	12.50	1.09674	994
100	9.32	9.119	0.95997	571
150	5.87	5.923	0.77254	270
200	4.38	4.396	0.64306	160.5
250	3.46	3.483	0.54198	105
300	2.93	2.858	0.45605	59

TABLE III.

V.	0°	100°	150°	160°	175°	185°	190°	192°	193°·8	195°	197°	200°	205°	210°	220°	223°	250°	280°
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
1·85	-271700	-68330	+33340	+53680														
1·9	-259490	-73330	19740	38360														
1·95	-247390	-75790	10110	27180														
2·0	-236800	-77070	2780	18760	42720													
2·05	-225800	-76710	-2020	12900	35270													
2·1	-216460	-75930	-5670	8390	29470	43530												
2·15	-205780	-73770	-7660	5440	25240	38450	45040	47680	50060									
2·2	-195650	-71300	-9130	3310	21960	34400	40610	43090	45330									
2·25	-186260	-68710	-9940	2880	19450	31210	37080	39430	41550	42970								
2·3	-177650	-66110	-10340	820	17550	28710	34280	36510	38520	39860	42090							
2·4	-161750	-60590	-10100	0	15150	25250	30290	32310	34130	35340	37360	40390						
2·5	-146900	-54930	-8950	250	14040	23240	27830	29670	31330	32440	34280	37030	41630	46230				
2·75	-113700	-40490	-3900	3429	14410	21730	25380	26850	28170	29050	30510	32710	36370	40030	47350	49540		
3·0	-93135	-30965	+115	6335	15665	21875	24985	26225	27345	28095	29335	31205	34315	37425	43635	45495		
3·3	-76170	-22880	3760	9080	17080	22410	25070	26130	27100	27740	28800	30400	33070	35730	41060	42650		
3·7	-61110	-15550	7180	11730	18550	23090	25360	26270	27090	27640	28550	29910	32190	34460	39060	40370	52640	

4	-53056	-11686	9004	13144	19344	23484	25544	26374	27124	27624	28444	29684	31754	33824	37964	39204	50374	
5	-34783	-2875	13085	16275	21065	24255	25845	26485	27055	27445	28085	29035	30635	32225	35425	36375	44955	54565
6	-22520	+2897	15604	18144	21954	24504	25774	26274	26734	27044	27554	28314	29584	30854	33394	34164	41024	48644
7	-14480	6393	16830	18918	22049	24136	25179	25596	25972	26224	26636	27266	28311	29356	31446	32061	37706	43966
8	-9119	8495	17301	19063	21705	23467	24346	24698	25016	25228	25580	26108	26989	27870	29641	30158	34914	40200
9	-5481	9743	17314	18829	21100	22615	23371	23674	23947	24129	24432	24886	25643	26401	27915	28369	32457	37001
10	-2858	10410	17044	18371	20361	21683	22351	22816	22855	23015	23280	23678	24342	25005	26332	26729	30311	34293
11	-943	10814	16692	17868	19631	20807	21394	21629	21841	21983					24922	25274	28448	31976
12	+407	10960	16237	17292	18875	19930	20457	20668	20859	20986					23624	23940	26789	29956
13	1422	10976	15753	16709	18142	19037	19574	19765	19937	20053					22441	22727	25307	28173
14	2209	10929	15273	16144	17451	18322	18757	18931	19088	19193					21370	21631	23982	26596
15	2730	10736	14738	15539	16740	17541	17941	18100	18245	18341					20343	20582	22744	25146
16	3139	10534	14231	14971	16080	16820	17189	17337	17470	17559					19408	19629	21626	23845
17	3458	10334	13772	14460	15491	16179	16522	16660	16784	16867					18586	18791	20648	22711
18	3683	10107	13319	13962	14925	15568	15889	16017	16133	16210					17816	18009	18743	21671
19	3876	9887	12903	13494	14395	14997	15297	15417	15525	15598					17100	17280	18903	20707
20	4019	9662	12478	13048	13895	14459	14741	14854	14955	15023					16434	16606	18127	19820
25	4282	9608	10771	11204	11853	12286	12502	12588	12666	12718					13800	13930	15098	16396
30	4140	7639	9388	9738	10263	10613	10788	10858	10921	10963					11838	11942	12887	13937
40	3690	6199	7453	7704	8080	8331	8456	8506	8552	8582						9284		
50	3237	5183	6227	6351	6643	6838	6935	6974	7009	7033						7578		
75	2417	3667	4291	4416	4604	4729	4791	4816	4839	4854						5244		
100	1919	2831	3287	3378	3515	3606	3651	3670	3686	3697						3952		

The lines of equal volume calculated from these values of a and b are reproduced graphically in Plates V. and VI. We propose to discuss the form of the diagram later.

We have calculated the values of p for various isothermals, at the above volumes. These are shown in Plate IV.; the actual experimental observations, of which a detailed account is given in the 'Philosophical Transactions,' 1886, p. 10 *et seq.*, are represented by circles. It is evident that the curves through the calculated points represent the actual measurements very closely, indeed as nearly as unavoidable error of experiment allows. It is to be noticed that the greatest divergence is at the temperatures 250° and 280° , but the deviations are in opposite directions, and must therefore be ascribed to experimental error.

Table III. (pp. 202, 203) gives the data from which the calculated isothermals were constructed.

As volumes above 30 cubic centim. per gram are not given in the diagram, we have thought it advisable to show the correspondence of calculated and observed results by a table; the calculated numbers were read from curves specially constructed from the formula $p=bt-a$, and the observed results are those actually furnished by our experiments. It will be seen that the correspondence is very close.

Table III. (*continued*).

Temperature 100° .

Volume.	Pressure found.	Pres. calculated.	Volume.	Pressure found.	Pres. calculated.
c. c.	millim.	millim.	c. c.	millim.	millim.
54.06	4817	4875	74.42	3668	3685
55.50	4720	4760	77.34	3546	3550
56.95	4627	4670	83.14	3334	3320
59.84	4434	4470	86.02	3243	3215
62.73	4265	4290	88.89	3150	3120
65.63	4102	4100	94.63	2978	2970
68.56	3946	3970	97.51	2893	2900
71.48	3818	3815			

Temperature 150° .					
31.09	9066	9110	68.64	4651	4675
33.94	8497	8520	74.51	4304	4310
39.66	7484	7505	80.35	4027	4010
45.43	6674	6745	86.13	3783	3760
51.23	6024	6100	91.87	3564	3530
57.02	5480	5560	97.63	3375	3345
62.81	5034	5090			

Table III. (continued).

Temperature 175°.					
Volume.	Pressure found.	Pres. cal- culated.	Volume.	Pressure found.	Pres. cal- culated.
c. c.	millim.	millim.	c. c.	millim.	millim.
31·11	9906	9975	68·69	4987	5000
33·96	9248	9290	74·56	4626	4630
39·68	8065	8130	80·40	4307	4310
45·46	7208	7205	86·18	4035	4030
51·26	6485	6510	91·93	3803	3800
57·06	5903	5940	97·69	3589	3600
62·85	5396	5450			
Temp. 185°.			Temp. 190°.		
31·12	10284	10300	31·12	10455	10460
45·47	7434	7460	45·47	7549	7545
59·97	5811	5865	59·97	5902	5940
74·58	4755	4770	74·59	4828	4810
86·21	4159	4140	86·21	4210	4190
91·95	3915	3900			
97·72	3692	3690			
Temp. 192°.			Temp. 193°·8.		
31·12	10544	10520	31·12	10587	10590
45·48	7590	7600	45·48	7627	7630
59·98	5930	5970	59·98	5951	6000
74·60	4847	4850	74·60	4867	4875
86·42	4230	4200	86·42	4252	4220
Temp. 195°.			Temp. 197°.		
31·12	10631	10620	33·17	10108	10055
45·48	7651	7675	38·07	8972	8965
59·98	5969	6020	47·84	7312	7320
74·60	4884	4895	57·59	6166	6130
86·42	4260	4230	67·33	5356	5340
91·97	4007	4000	77·05	4718	4735
97·74	3797	3775	86·75	4219	4220
			96·44	3820	3820
Temperature 223°·25.					
31·15	11567	11550	80·50	4870	4880
45·51	8260	8240	86·29	4556	4550
60·02	6412	6420	92·04	4289	4270
74·65	5232	5225	97·81	4044	4020

These complete the data for ether. It appeared necessary

to examine the relations between volume, temperature, and pressure for carbon dioxide, because it is chemically entirely different from ether, and also because the data are furnished by Dr. Andrews, whose experimental skill was very great; and we shall prove that his results entirely corroborate our views.

It was first necessary to correct the pressures given by him in atmospheres by means of Amagat's results, so far as that is possible. As Amagat's experiments on the compressibility of dry air do not extend beyond 65,000 millim., no correction was possible above that pressure; and extrapolation is inadmissible, inasmuch as the minimum value of pv for air is at 60,000 millim.

Data for obtaining the actual volume of carbon dioxide used are given by Andrews. The weight was calculated in the following manner:—Andrews gives the volume of carbon dioxide filling his tubes at 0° and 0.76 millim., and from Regnault's data the weight was calculated. This refers to Andrews's first paper (Phil. Trans. 1869, ii. p. 575). In his second paper (Phil. Trans. 1876, p. 421) no direct data are given from which the weight can be determined; but we succeeded, by combining the results given in his various tables, in arriving at the weight without any serious error. His results are reproduced in an available form in the following Tables.

TABLE IV. (The first quantity weighed 0.000612 gram.)

Temp. $13^{\circ}1$.		Temp. $21^{\circ}5$.		Temp. $31^{\circ}1$.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.
68726 *	1.038	46600	1.232	63462	1.389
56333	1.059	46383	1.241	61416	1.425
40725	1.104	45490	1.484	59540	1.470
37631	1.124	45155	2.270	57847	1.495
37459	1.145	44962	3.124	56178	1.812
37074	1.377	44787	4.760	55010	2.234
36942	1.547	34907	8.118	54588	2.338
36816	1.972			53089	3.814
36719	2.758			51709	4.192
36668	3.733			50390	4.534
36610	5.004			49118	4.855
36528	6.554			47910	5.147
36433	6.595			46725	5.471
35497	6.964			45622	5.750
				44577	6.009
				43611	6.265
				43182	6.515
				41761	6.765
				40895	7.003

* The pressures to which an asterisk is affixed are not corrected.

Table IV. (*continued*).

Temp. 32°·5.		Temp. 35°·5.		Temp. 48°·1.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.
63246	1·461	81775 *	1·330	83144 *	1·999
59425	1·612	75673 *	1·392	72344 *	2·999
58501	1·818	70406 *	1·476	62837	4·061
56813	2·954	68035 *	1·532	56311	5·057
55151	3·543	64516	1·624	51012	5·991
54839	3·629	60552	2·511	46675	6·887
53292	4·034	57057	2·549		
42808	6·595	53977	4·233		
		51166	4·831		
		48625	5·396		
		46340	5·935		
		44263	6·432		
		42383	6·917		

Table IV. (*continued*).

(The weight of the second quantity was 0·0018075 gram.)

Temp. 0°.		Temp. 6°-6°·9.		Temp. 63° 6-64°.		Temp. 99°·5-100°·7.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.	millim.	c. c.
25865	10·53	25870	11·25	169420*	1·401	169910 *	1·816
23325	12·36	23291	13·09	110610*	1·907	110530 *	3·161
20800	14·53	20822	15·16	81229*	3·363	80323 *	5·057
18674	16·77	18681	17·11	60422	5·477	59985	7·192
15155	21·73	16777	19·90	48425	7·485	47910	9·391
12277	27·83	15161	22·54	40554	9·462	40169	11·52
9081	39·09	12907	27·16	34806	11·45	34382	13·72
		11093	32·18	30351	13·48	29910	15·96
		9994	36·12	26212	15·99	25930	18·74
		9087	40·06	23568	18·00	23325	21·03
				21106	20·41	20876	23·70
				18866	23·08	18711	26·65
				17000	25·86	16858	29·74
				15356	28·88	15214	33·09
				13288	33·74	13153	38·58

As with ether, these numbers were plotted graphically up to a pressure of 75,000 millim. Above 65,000 millim. no true correction for deviation of Andrews's air-gauge was possible;

* The pressures to which an asterisk is affixed are not corrected.

but approximate corrections were introduced. It was possible to read pressures to within 30 millim. on the scale employed, and volume to within 0·02 cub. centim. per gram. Pressures corresponding to even volumes were read off, as with ether; and on mapping the isochors with temperatures as abscissæ and pressures as ordinates, the resulting points lay in straight lines. The values of b , i. e. of $\frac{dp}{dt}$, were then read off, and smoothed, by mapping them against the reciprocals of the volumes. After smoothing, the values of a were calculated at each volume, making use of the pressures previously read from the curve representing isothermals. The diagram (1) on Plate VII. was then constructed from these smoothed values. The crosses denote our readings of pressures at the temperatures chosen by Andrews for his isothermals. These values of a and b were then made use of in recalculating isothermals at the above temperatures, and the diagram (2) on Plate VII. represents the curves complete so far as Andrews's data allow. The circles represent Andrews's actual measurements; and it is evident that no better concordance could be expected. The tables which follow give the data afforded by Andrews's experiments.

TABLE V.

Pressures read from Curves originally drawn from Andrews's experimental data, and represented by circles in the diagram (2), Plate VII.

Vol.	Temperature.									
	0°.	6°.	13°·1.	21°·5.	31°·1.	32°·5.	35°·5.	48°·1.	64°.	100°.
c. c.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
30	11430	11790	...	...	...	...	...	...	14820	16710
25	13480	13830	...	...	...	...	...	...	17500	19860
20	16200	16570	...	...	...	...	...	...	21450	24300
15	20300	20970	...	...	...	...	...	...	27700	31570
12	23730	24800	...	...	...	...	...	...	33500	38730
10	26715	28000	...	...	...	...	...	...	38970	45330
8	...	...	...	35340	37560?	37800?	38400?	41930	46200	54630
7	...	...	35340	38220?	40970	41370	42060	46200	50850	61500
6	...	...	...	41100?	44700	45060	46000	51000	56700	
5	...	...	...	44100?	48600	49200	50370	56760		
4·5	...	...	...	...	50550	51400	52830	60000		
4·0	...	...	...	...	52420	53430	55140	63500		
3·5	...	...	...	...	54250	55260	57240	67000		
3·0	...	...	...	...	55800	56700	59130	72400		

TABLE VI.

Read and Smoothed Values of b , and Values of a .

Vol.	b , read.	b , smoothed.	$\log b$.	a .
c. c.				
30	52.3	52.5	1.72016	2877
25	63.3	64.0	1.80618	4024
20	81.9	82.0	1.91381	6256
15	113.85	114.5	2.05881	10990
12	150.0	149.9	2.17580	17103
		188.5	2.27531	24718
8	255.0	252.1	2.40175	39120
7	300.0	302.0	2.48001	50970
6	368.1	373.0	2.57171	68877
5	472.3	475.5	2.67715	96008
4.5	553.7	548.5	2.73918	116230
4.0	654.0	638.0	2.80482	141525
3.5	750.0	759.5	2.88053	176860
3.0	933.6	936.5	2.97151	229420

TABLE VII.

Calculated Pressures on Isothermal Curves, at definite volumes.

Vol.	Temperature.									
	0°.	6°.	13°-1.	21°-5.	31°-1.	32°-5	35°-5.	48°-1.	64°.	100°.
c. c.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
30	11456	11771	...	...	13088	...	...	13981	14816	16706
25	13448	13832	...	...	15439	...	...	16526	17544	19848
20	16130	16622	...	...	18680	...	...	20074	21378	24330
15	20269	20956	...	...	23830	...	...	25776	27597	31719
12	23719	24719	25783	27043	28482	...	29140	31030	33413	38810
10	26742	27873	29212	30796	32605	...	33433	35809	38806	45592
8	29731	31244	33036	35155	37576	37928	38684	41862	45872	54952
7	31476	33288	35433	37971	40870	41291	42197	46003	50800	61680
6	32973	35190	37843	40973	44553	45073	46193	50893	56820	70250
5	33802	36652	40032	44032	48592	49262	50682	56672	64232	
4.5	33510	36800	40700	45310	50570	51340	52980	59890	68620	
4.0	32645	36475	41005	46365	52495	53385	55295	63335	73485	
3.5	30480	35040	40440	46820	54110	55170	57440	67020		
3.0	26240	31860	38520	46380	55370	56630	59620	71290		

It will be seen that the highest calculated pressure is about 73,500 millim. Andrews gives measurements at much higher pressures; but these are few in number and uncertain, and the correction for the compressibility of air is moreover unknown. Hence it was impossible to make use of them in determining the values of b .

On reference to Andrews's paper (Phil. Trans. 1876, p. 435)

it will be seen that he compared the relation of increase of pressure to temperature-difference at constant volumes, and came to a conclusion opposed to ours. This is owing to his having made very few observations, and having accidentally chosen those which support his statement. If the coefficients of increase of pressure for unit rise of temperature be calculated by means of Table V., it may be noticed that, although irregular, there is no tendency towards a rise or fall of the coefficient.

Regnault has measured the rise of pressure of gaseous carbonic anhydride at constant volume. He gives the results of four experiments, none of which are available for our purpose, inasmuch as the volumes of a gram are too large.

Reverting to the behaviour of ether, as shown on Plate IV., it will be seen that the curves have been drawn in the region where measurements are impossible. These curves have all the same general form. After rise of pressure and decrease of volume have proceeded for some distance, the curves bend downward, presenting the abnormal feature of decrease of volume with fall of pressure. The pressure continues thus to fall, and at 160° the isothermal touches zero-pressure. At lower temperatures, with small volumes, the pressure becomes negative, and may even represent an enormous tension. At 0° the isothermal at vol. 1.85 cub. centim. per gram reaches the almost incredibly great tension of $-271,700$ millim.; and it has at that volume (the smallest our results allow us to calculate) by no means reached its limit. At still smaller volumes the tension would doubtless still increase, until the curve turned, and further decrease of volume would be represented, as it is at higher temperatures, by increase of pressure.

The existence of these unrealizable portions of such isothermal curves was, we believe, first suggested by Prof. James Thomson, in a paper in the 'Proceedings of the Belfast Natural History and Philosophical Society,' Nov. 29, 1871. Since that time attempts have been made to express relations between the pressure, temperature, and volume of gases and liquids by Van der Waals and by Clausius; and the formulæ which they propose, and which we hope to consider in a subsequent paper, give isothermals of similar form. Portions of these curves have, indeed, been experimentally verified. In

Professor Thomson's paper, above referred to, he points out that Donny, Dufour, and others have observed the phenomenon commonly alluded to as "boiling with bumping." This is usually the effect of a rise of temperature at constant pressure. But it may equally well be produced, as we have frequently had occasion to remark, at constant temperature by lowering pressure. If the diagram on plate iii. in our memoir on alcohol (Phil. Trans. 1886, part i. p. 156) be referred to, it will be seen that our actual measurement of such reduced pressure was made on the isothermal $181^{\circ}4$. Mr. John Aitken, in an extended series of experiments on this subject (Trans. Royal Scott. Soc. of Arts, vol. ix.), has shown that such "superheating" can take place only in absence of a free surface, *i. e.* the existence of gaseous nuclei in the liquid, into which evaporation may take place. And Mr. Aitken has also shown that a gas may be compressed to a volume smaller than that at which liquefaction usually occurs, at any given temperature, without formation of liquid. The space, again, if no nuclei be present on which condensation may take place, remains "supersaturated with vapour." It is evidently, therefore, only the instability of such conditions which prevents their complete realization*.

The formulæ of Clausius and Van der Waals are based on the assumption that two causes are in operation (those referred to in the beginning of this paper), *viz.* the actual size of the molecules, and their mutual attraction. It is possible, by help of these assumptions, to realize the nature of the continuous change from the gaseous to the liquid state of matter. When a gas at a given temperature is reduced in volume its molecules necessarily approach each other, and their attraction for one another increases. This attraction aids the increase of pressure in reducing volume. When a certain volume is reached, the attraction has become so marked that further reduction of volume is accompanied by fall of

* The reasoning of a recent paper by Wroblewski (*Monatsheft der Chemie*, Wien, July 1886, p. 383) rests on the assumption that such conditions are inconceivable. He supposes lines of equal density to be curves, and on their close approach to the vapour-pressure curve to run parallel with it. His conclusions are therefore not borne out by experimental facts.

pressure. If a certain volume be chosen on the descending portion of an isothermal, a state of balance may be imagined where pressure and cohesion unite in maintaining the volume constant against the kinetic energy of the molecules, tending to cause expansion.

The conception of negative pressure, or tension, is that at low temperatures and small volumes the cohesion is such that, in order to overcome it and increase volume, it would be necessary to apply tension to each molecule. But after the lowest pressure or greatest tension has been attained, the actual size of the molecules presents a bar to closer approach; and to cause further decrease of volume pressure must again be applied. It is not to be supposed that at any given volume only one of these factors is operative; the actual size of the molecules exerts its influence even at large volumes, and the cohesion does not disappear, but no doubt immensely increases, as the volume is reduced, even when that reduction requires rise of pressure. Still, a mental picture of the process may, we think, best be attained by directing attention to cohesion, when volume is being decreased with fall of pressure, and to the influence of the actual size of the molecules when volume is small.

When a liquid is converted into gas, heat is absorbed, or work is done on the liquid. We have previously (*loc. cit.*) given tables showing the heats of vaporization of ether at various temperatures. Our experiments have confirmed the prediction that the heat of vaporization of stable liquids decreases with rise of temperature, and in all probability becomes zero at the critical temperature. Now the volume of a fluid may be changed, either keeping the pressure constant or allowing it to vary during the operation; but if the initial pressure and final pressure are the same, the variation of pressure during the operation does not affect the total work done. A liquid may be changed into saturated vapour at any given temperature in the usual manner, when the intermediate states are represented by non-homogeneous mixtures of liquid and saturated vapour. The area enclosed between the vapour-pressure line and lines drawn vertically from its terminal points, cut by the line of zero pressure (or pressure $\times$ change of volume), represents graphically the external work performed in evaporating a liquid. If, however, the change of condition

be not abrupt, but continuous, the area enclosed by the isothermal below the vapour-pressure line must be equal to that above the vapour-pressure line (see Plate IV.). If this were not the case, the amount of work required to effect the continuous change would differ from that required for the abrupt change of state.

Now it is evident that a slight alteration in the position of the vapour-pressure line would have great influence on the relative areas enclosed by the isothermal above and below the vapour-pressure line; and it may also be seen that, when these areas are rendered equal by a horizontal line, the position of that horizontal line must represent the true vapour-pressure.

We have determined the position of the horizontal line in the following manner :—

Knowing approximately the position of the vapour-pressure line at a given temperature, three pressures were chosen—the highest above and the lowest below the experimentally determined vapour-pressure; and by means of a planimeter (by Stanley of Holborn) the areas enclosed between each horizontal line and the curves respectively below and above it, formed by the isothermal lines, were measured. To ascertain what position of the horizontal line would render these areas equal, the values of each set of three areas were mapped on sectional paper as abscissæ, the pressures corresponding to the position of the horizontal lines being ordinates. The curves passing through the resulting points cut each other at a point which represents the true pressure and the true area. This method is rendered clearer by inspection of the following figure :—

It is evident that these vapour-pressures depend entirely on measurements represented in the diagram outside the area bounded by the curve representing orthobasic volumes of gas and liquid. It will be seen, on reference to the table on p. 204, that the agreement between these calculated vapour-pressures and those experimentally determined is a very close one, the greatest difference being about 1 per cent. This agreement between experimentally observed vapour-pressures and those depending on the formula $p=bt-a$ is very remarkable, and it is difficult to believe that, if the isochoric lines were curves, such an agreement could exist.

What are usually termed vapour-pressures, then, are those pressures at which horizontal lines drawn through them render the areas enclosed by the isothermal lines below the horizontal lines equal to those above them. But there are other two conditions of matter, each of which has its characteristic pressures. One of these is represented by the highest pressure attainable on any isothermal, or the summit of the curve above the vapour-pressure line; and the other the apex of the curve below the vapour-pressure line. Each temperature chosen has its particular value for each of these conditions; and it is evident that the relations between the temperatures and pressures corresponding to the inferior or reversed apices, as well as those corresponding to the superior apices, would each form a special curve.

The following Table gives the final results of the calculation of vapour-pressures by the method of areas; and, for the sake of comparison, the actually found vapour-pressures are appended. The pressures at the superior and inferior apices of the isothermal curves, and also the enclosed areas, are given*.

* The areas are in square inches; the scale was 2000 millim. and .2 cub. centim. per gram to the inch. It would be easy, if necessary, to convert these data into actual work.

TABLE VIII.

Temperature.	Vapour-pressures, deduced from areas.	Vapour-pressures, mean of observed.	Pressure, superior apex.	Pressure, inferior apex.	Area above or below vapour-pressure line.
	millim.	millim.	millim.	millim.	sq. in.
192	26350	26331	26490	26125	0·0425
190	25554	25513	25870	24960	0·1245
185	23703	{ Old, 23623 New, 23763 }	24510	21660	0·4550
175	20259	{ Old, 20189 New, 20271 }	22100	14060	1·6520
160	15900	15778	19090	— 20	4·710
150	13405	13262	17380	—10400	7·551

The three pressure-curves—which we shall name the “ordinary” vapour-pressure curve, the “superior” vapour-pressure curve, formed by the superior apices of the isothermal lines, and the “inferior” vapour-pressure curve, produced by the lower apices of the isothermal lines—must, it is evident, meet at the critical point; and on mapping them, it was found that this was the case. Points were chosen on these curves at equal intervals of temperature, and the constants for formulæ of the type $\log p = a + b\alpha^t$ were calculated for each. As the pressures on the inferior curve below a certain temperature were negative, it was found convenient to add 30,000 millim. to each, which was subsequently subtracted from the result. The constants for the curves are —

Superior curve :

$$a = 3\cdot59797 ; \log b = \bar{1}\cdot8343195 ; \log \alpha = 0\cdot00257762.$$

Ordinary vapour-pressure :

$$a = 6\cdot72909 ; \log b = 0\cdot4027232 ; \log \alpha = \bar{1}\cdot99876897$$

(b is here negative).

Inferior curve :

$$a = 4\cdot867404 ; \log b = \bar{1}\cdot5913793 ; \log \alpha = \bar{1}\cdot98382413$$

(b is again negative).

In each case $t = t^\circ \text{ Cent.} - 160^\circ$.

The results are given in the following Table :—

TABLE IX.

Temperature.	Ordinary vapour-pressures.		Superior curve-pressures.		Inferior curve-pressures.	
	Read.	Calculated.	Read.	Calculated.	Read.	Calculated.
	millim.	millim.	millim.	millim.	millim.	millim.
150°	13405	13084	17380	17437	-10400	-10185
160	15900	15900	19090	19090	- 20	- 100
175	20259	20259	22100	22100	+14060	+14060
185	23703	23678	24510	24549	21660	21704
190	25554	25556	25870	25935	24960	24900
192	26350	26341	26490	26523	26125	26065
193		26739		26826		26624
193·83		27075		27077		27077

With exception of the lowest temperature, the agreement between the read and the calculated pressures is close. The extrapolation amounts to only 3°·83. The agreement is close at 192°, and above that temperature the extrapolation is only 1°·83. It will be seen that at that temperature (193°·83) the pressures coincide. The *apparent* critical point was 193°·8.

Isochoric Lines.

Plate VI. represents the whole of the isochors which we have calculated between the volumes of 1·85 and 300 cub. centim. per gram.

If the gas followed Boyle's and Gay-Lussac's laws absolutely, under all conditions, the isochoric lines would all radiate from zero pressure, and would become more and more vertical as the volumes decreased; and the tangents of the angles formed by these lines with the horizontal line of zero pressure would be proportional to c in the equation $p = ct$, where c varies inversely as the volume. But our equation, $p = bt - a$, introduces another term, a , which is negative. These values of a are represented on the diagram by the extremities of the isochoric lines, where they cut the vertical line representing absolute zero of temperature. The tangents of the angles made by these lines with a horizontal line are proportional to the values of b in our equation.

On referring to Plate VI. it will be noticed that, beginning at the largest volume, two adjacent isochors cut each other at a point, as regards pressure and temperature, not far above

zero. With decreasing volumes the points of intersection of adjacent isochors occur at higher and rapidly increasing temperatures and slowly increasing pressures ; and this proceeds until the critical volume is reached. With still smaller volumes, however, the points of intersection of adjacent isochors occur at lower and decreasing temperatures and pressures ; the former decrease slowly, but the latter with great rapidity, and soon extend into the region of negative pressures.

It is evident from the diagram that each isochor between the largest and the critical volume is the tangent of a curve, representing the relations of pressure to temperature ; while the isochors below the critical volume are tangents to another curve, also exhibiting the like relations. Neither of these curves is identical with the vapour-pressure curve, which falls in the area between them.

It will be noticed that, in the area included between the line of zero pressure and these two curves, each isochoric line is cut by two others at every point along its whole length ; but outside this surface, and above the line of zero pressure, no two lines cut each other, and below the line of zero pressure each isochor is cut at each point by one other. The physical meaning of the fact that within the first-mentioned region three isochors intersect each other at one point is, that a gram of the substance may occupy three different volumes at the same temperature and pressure. Now, on referring to the diagram on Plate IV., representing the experimentally unrealizable portions of the isothermal curves, it is evident that on each isothermal line, at pressures limited by the superior or inferior apices of the isothermal, there are, corresponding to each pressure, three volumes. At any pressure above or below these pressures the isothermal line is cut only once, by a horizontal line of equal pressure ; so that, for each pressure, there is only one corresponding volume. At each apex a horizontal line of equal pressure cuts the isothermal line at one point, and is also a tangent to the apex. There are, therefore, two volumes corresponding to each of these pressures. Since no gas can be submitted to a negative pressure, those portions of an isothermal line representing the truly gaseous condition of matter never extend below the horizontal line of zero pressure ; only those portions of the isothermal

which proceed towards the inferior apex fall below this line. An isothermal line below zero pressure is therefore cut only twice by a line of equal pressure, and there are therefore two volumes corresponding to each pressure. At each inferior apex, however, the horizontal line is a tangent to the curve, and there is therefore only one volume corresponding to a given pressure.

On referring back to Plate VI., it will be seen that the pressures corresponding to the superior apices of each isothermal line, when mapped, produce the curve AC; and those corresponding to the inferior apices, the curve BC. The surface bounded by these curves and the line of zero pressure corresponds to portions of the isothermal lines, including pressures between the two apices, and each point in the surface is the locus of intersection of three isochoric lines. Below the line of zero pressure the isochoric lines corresponding to the gaseous state are absent; and hence each point is the locus of intersection of only two isochors. The isothermal lines above and below the limits of pressure given by the apices are cut only once by any line of equal pressure; hence the isochors outside the area ACD, and above the line of zero pressure, do not intersect. The apex C of the curvilinear triangle ACD is the point of highest temperature and pressure at which intersection can take place, and therefore represents the critical point; it is also the common point of intersection of the three pressure-temperature curves.

Referring now to Plate V., in which the isochoric lines in the neighbourhood of the critical point are shown on a larger scale, it will be seen that the isochoric lines above a volume not far removed from 4 cub. centim. per gram cut the ordinary vapour-pressure curve CE on one side, while those below the volume 3.75 evidently cut the vapour-pressure line on its other side. There must therefore be an isochoric line which does not cut the curve at all, but forms a tangent to its end-point. That isochor gives the critical volume. It may be determined by calculating the value of $\frac{dp}{dt}$ at the critical temperature. This value of $\frac{dp}{dt}$ is identical with the value of b in our equation $p = bt - a$ at the critical volume.

Until a mathematical expression is discovered, representing b as a function of volume, the only means at our disposal for ascertaining the true volume corresponding to b is by interpolation of the original curve by which the values of b were smoothed. The common point of intersection of the three pressure-temperature curves has been shown on p. 216 to lie at the temperature $193^{\circ}83$. The value of $\frac{dp}{dt}$ on the vapour-pressure curve at this temperature, calculated by the formula of which the constants have already been given, is 405 millim., which is also the value of b at that temperature. The volume corresponding to this value is 4.06 cub. centim. per gram; and the specific gravity of ether at its critical point is therefore 0.2463.

Unfortunately, Dr. Andrews's measurements of the constants of carbon dioxide are not sufficiently numerous to warrant an attempt to obtain the critical temperature, pressure, and volume by this method. The critical volume of carbon dioxide is evidently less than 3 cub. centim. per gram; but the values of b below that quantity are unascertainable. It may be noticed that the curves below volume 3 are inserted in broken lines, showing a probable course; but no reading from them would be permissible.

The two liquids, ether and carbon dioxide, have no chemical analogy with one another; and we therefore feel justified in concluding that the law which is the subject of this paper is generally applicable to all stable substances. We have, however, other less complete data for methyl and ethyl alcohols, which, so far as they go, are confirmatory of the results described. We have also data available for the examination of acetic acid—a substance which differs from those mentioned, inasmuch as it undergoes dissociation when heated; and we hope shortly to be able to communicate an account of its behaviour.

Professor Fitzgerald, to whom we gave a short account of this law, has recently communicated to the Royal Society a paper in which its thermodynamical bearings are considered.

Bristol, 12th February, 1887.