THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

FEBRUARY 1892.

XVI. *On the Generalizations of Van der Waals regarding "Corresponding" Temperatures, Pressures, and Volumes.*
By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol*.

[Plates I.-III.]

IN his dissertation *Die Continuität des gasförmigen und flüssigen Zustandes* (Roth's translation, Leipzig, 1881, p. 128) Van der Waals has deduced the following generalizations from his fundamental equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = R(1 + \alpha t).$$

If the absolute temperatures of various substances be proportional to their absolute critical temperatures, their vapour-pressures will be proportional to their critical pressures, and their volumes, both as liquid and as saturated vapour, will be proportional to their critical volumes.

At the time, however, that Van der Waals's great work was published, the available experimental data were insufficient to satisfactorily test the accuracy of these generalizations.

Since then the conclusions of Van der Waals have been subjected to a large amount of criticism, both adverse and favourable; and while it is now generally recognized that the relations between the temperatures, pressures, and volumes of liquids and gases cannot be represented by so simple a formula as that quoted above, it has nevertheless been accepted as correct by some authors, who have made it the basis of further generalizations.

And although the general verdict with regard to the strict accuracy of the formula itself can hardly be considered

* Communicated by the Physical Society: read November 6, 1891.

Ratios of Actual to Theoretical Vapour Density at Corresponding Pressures.

favourable, the notion of "corresponding" states has received wide acceptance; and, indeed, the generalizations regarding corresponding temperatures, pressures, and volumes might still be true even though the formula on which they were originally based required some alteration.

In order to study the relations, for instance, between the specific volumes of different substances, determinations were made in the first place at the same temperature, generally at 0° C.; later on it was considered that the conditions would be more uniform if the comparison were made at the boiling-points of the substances under normal atmospheric pressure. It is now, however, usually admitted that in order to obtain the best results the volumes should be determined at "corresponding" temperatures—that is to say, at absolute temperatures proportional to the absolute critical temperatures of the various bodies—or at their boiling-points under corresponding pressures—the two methods of comparison being, according to Van der Waals, identical.

During the last four years I have been engaged in a research on the vapour-pressures and specific volumes—both in the liquid state and as saturated vapour—of the following substances:—benzene, fluorbenzene, chlorobenzene, bromobenzene, iodobenzene*, carbon tetrachloride and stannic chloride†; the vapour-pressures and specific volumes of methyl‡, ethyl§, and propyl alcohols||, and of ethyl ether¶ have also been determined by Dr. Ramsay and myself. We obtained the same constants for acetic acid** up to 280°; and I have recently extended the observations with this substance up to the critical point (*ibid.* lix. p. 903).

The methods employed for the determination of the vapour-pressures of benzene and its halogen derivatives and for the specific volumes of these bodies in the liquid state were, with slight modifications, the same as those made use of by Ramsay and myself in our researches on the alcohols and ether.

Carbon tetrachloride, however, acts on mercury at high temperatures, and stannic chloride renders it unfit for use—though the chemical action is very slight—even at low temperatures; a considerable alteration in the method of determining vapour-pressures was therefore made (*Trans. Chem. Soc.* lix. p. 917).

For the determination of the specific volumes of stannic chloride in the liquid state and of all the substances in the condition of saturated vapour an entirely different method was

* *Trans. Chem. Soc.* lv. p. 486, and lix. p. 125. † *Ibid.* lix. p. 911.

† *Phil. Trans.* clxxviii. A, p. 313.

§ *Ibid.* 1886, part i. p. 123.

|| *Ibid.* clxxx. p. 137.

¶ *Ibid.* clxxviii. A, p. 57.

** *Trans. Chem. Soc.* xlix. p. 790.

employed, and this has been fully described in the *Trans. Chem. Soc.* 1891, p. 37. This method is applicable to substances that attack mercury, and from the data it affords the specific volumes both of liquid and saturated vapour may be calculated; it is also available at any temperature up to the critical point. A modification of the method is described in the *Trans. Chem. Soc.* lix. p. 929.

The object of this paper is to show how far the generalizations of Van der Waals have been verified by the experimental results.

If all the relations were strictly true, it would obviously make no difference whether the specific (or molecular) volumes were compared at corresponding temperatures or corresponding pressures; but it may be stated at once that it is only in a limited number of cases that, when the absolute temperatures are proportional to the absolute critical temperatures, the vapour-pressures are also proportional to the critical pressures. It is therefore necessary to compare the various substances, not only at corresponding temperatures but also at corresponding pressures. The best mode of procedure would probably be to give the temperatures, pressures, and volumes of each substance in terms of the critical constants of that body; but the critical volumes of only a few of the compounds have been directly determined, and it has therefore been necessary to compare the various substances with one of them taken as a standard. The very simple relations observed between the four monohalogen derivatives of benzene (*Trans. Chem. Soc.* 1889, p. 486), and the fact that the constants of fluorobenzene have been determined up to the critical point, render that substance the most suitable for the purpose.

The experimental data and the ratios calculated from them are given in the following tables.

- I. Critical constants—temperature, pressure, volume.
- II. Corresponding pressures.
- III. Corresponding temperatures.
- IV. Boiling-points on absolute scale at corresponding pressures.
- V. Vapour-pressures at corresponding temperatures.
- VI. Molecular volumes of liquids at corresponding pressures.
- VII. Molecular volumes of liquids at corresponding temperatures.
- VIII. Molecular volumes of saturated vapour at corresponding pressures.
- IX. Molecular volumes of saturated vapour at corresponding temperatures.
- X. Ratios of absolute temperatures to those of fluorobenzene at corresponding pressures.

- XI. Ratios of vapour-pressures at corresponding temperatures.
 XII. Ratios of molecular volumes of liquid at corresponding pressures.
 XIII. Ratios of molecular volumes of liquid at corresponding temperatures.
 XIV. Ratios of molecular volumes of saturated vapour at corresponding pressures.
 XV. Ratios of molecular volumes of saturated vapour at corresponding temperatures.
 In calculating the molecular volumes the following molecular weights have been employed :—

C_6H_5F ... 95.8	C_6H_5I ... 203.4	$SnCl_4$ 259.3	C_2H_5OH ... 45.90
C_6H_5Cl ... 112.2	C_6H_6 ... 77.84	$(C_2H_5)_2O$ ... 73.84	C_3H_7OH ... 59.87
C_6H_5Br ... 156.6	CCl_4 ... 153.45	CH_3OH ... 31.93	CH_3COOH 59.86

TABLE I.—Critical Constants.

Substance.	Formula.	Temperature.		Pressure, in millim.	Volume, in c.c.	
		Centi- grade.	Absolute.		of a gram.	Molecular.
Fluorobenzene.....	C_6H_5F .	286.55	559.55	33912	2.43	233
Chlorobenzene	C_6H_5Cl .	(360)	(633)	(33912)	(2.34)	(262)
Bromobenzene	C_6H_5Br .	(397)	(670)	(33912)	(1.76)	(275)
Iodobenzene	C_6H_5I .	(448)	(721)	(33912)	(1.47)	(298)
Benzene	C_6H_6 .	288.5	561.5	36395	2.82	219
Carbon tetrachloride	CCl_4 .	283.15	556.15	34180		
Stannic Chloride ...	$SnCl_4$.	318.7	591.7	28080		
Ether	$(C_2H_5)_2O$.	194.4	467.4	27060		
Methyl Alcohol.....	CH_3OH .	240.0	513.0	59760		
Ethyl Alcohol	C_2H_5OH .	243.1	516.1	47850		
Propyl Alcohol	C_3H_7OH .	263.7	536.7	38120		
Acetic Acid	CH_3COOH .	321.6	594.6	43400	2.46	147

The brackets indicate calculated values. In the case of chlorobenzene, bromobenzene, and iodobenzene the critical temperatures and volumes given depend on the assumption that the critical pressures are equal. The critical constants of chlorobenzene have been observed, but the determinations could not be made with the same degree of accuracy as those of fluorobenzene, and the calculated values have therefore been adopted in this paper. The observed values are :—temperature, 359.2 to 359.45; pressure, 33926 to 33998 millim.; molecular volume, 262 to 275 cubic centim. The temperatures given in the original paper (Trans. Chem. Soc. iv. p. 518) are 360.55–360.8; but the boiling-point of mercury, the vapour of which was employed as a jacket, has since been shown to be lower than was at that time adopted.

TABLE II.
Corresponding Pressures.

Halogen Derivatives of Benzene.	C_6H_5 .	OCl_4 .	$SnCl_4$.	$(C_2H_5)_2O$.	CH_3OH .	C_2H_5OH .	C_3H_7OH .	CH_3COOH .
20	21.46	20.16	16.56	15.96	35.24	28.22	22.48	25.60
50	53.66	50.40	41.40	39.90	88.11	70.55	56.21	63.99
100	107.3	100.8	82.24	79.80	176.2	141.1	112.4	128.0
200	214.6	201.6	165.6	159.6	352.4	282.2	224.8	256.0
400	429.3	403.2	331.2	319.2	704.9	564.4	449.7	511.9
760	815.6	766.0	629.4	606.5	1339	1072	854.3	972.6
1000	1073.0	1008	822.4	798.0	1762	1411	1124	1280
1500	1610	1512	1242	1197	2643	2116	1686	1920
2000	2146	2016	1656	1596	3524	2822	2248	2560
3000	3220	3023	2484	2394	5287	4233	3372	3839
4000	4293	4032	3312	3192	7049	5644	4497	5119
5000	5366	5040	4140	3990	8811	7055	5621	6399
6000	6439	6048	4920	4787	10573	8467	6745	7679
7000	7513	7055	5796	5586	12337	9876	7869	8959
8000	8586	8063	6624	6384	14096	11288	8993	10238
10000	10732	10079	8224	7980	17624	14109	11241	12798
12000	12879	12095	9936	9576	21145	16932	13490	15367
15000	16098	15118	12419	11970	26430	21164	16862	19197
20000	21464	20136	16562	15962	35245	28223	22480	25596
25000	26831	25200	20701	19948	44055	35278	28100	31995
28000	30047	28223	23185	22341	49340	39509	31477	35834
30000	32197	30234	24843	23939	52869	42325	33721	38394
32000	34340	32255	26497	25533	56390	46154	35975	40363
33912	36395	34182	28080	27060	59760	47850	38120	43400

TABLE III.
Corresponding Temperatures (absolute).

Pressure $C_6H_6F.$	$C_6H_6F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$CCl_4.$	$SaCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
20	272.25	308.0	326.0	350.8	273.2	270.6	287.9	227.4	249.6	251.1	261.15	289.3
50	289.3	327.3	346.4	372.8	290.3	287.55	305.9	241.65	265.25	266.85	277.5	307.4
100	303.9	343.8	363.9	391.6	304.95	302.05	321.35	253.85	278.6	280.3	291.5	322.95
200	320.25	362.3	383.45	412.65	321.35	318.3	338.65	267.5	293.6	295.4	307.15	340.3
400	338.75	383.2	405.6	436.5	339.95	336.7	358.2	282.95	310.55	312.45	324.9	359.95
760	358.1	405.1	428.8	461.4	359.35	355.9	378.65	299.15	328.3	330.3	343.45	380.5
1000	367.3	415.5	439.8	473.8	368.6	365.05	388.4	306.8	336.75	338.75	352.3	390.3
1500	382.0	432.15	457.4	492.2	383.35	379.65	408.95	319.1	350.2	352.35	366.4	405.9
2000	393.25	444.85	470.85	506.7	394.6	390.85	415.85	328.5	360.55	362.7	377.2	417.9
3000	410.4	464.25	491.4	528.8	411.85	407.9	434.0	342.8	376.25	378.55	393.65	436.1
4000	423.8	479.4	507.45	546.1	425.3	421.2	448.15	354.0	388.55	390.9	406.5	450.35
5000	434.85	491.95	520.7	.....	436.35	432.2	459.85	363.25	398.7	401.1	417.1	462.1
6000	444.25	502.55	531.95	.....	445.8	441.55	469.8	371.1	407.3	409.75	426.1	472.1
7000	452.8	512.25	542.2	.....	454.4	450.05	478.8	378.25	415.15	417.65	434.3	481.15
8000	460.4	520.85	551.3	.....	462.0	457.6	486.85	384.6	422.1	424.65	441.6	489.25
10000	473.6	535.75	.....	.....	475.25	470.7	500.8	395.6	434.2	436.8	454.25	503.25
12000	484.95	548.6	.....	.....	486.65	482.0	512.8	405.1	444.6	447.3	465.15	515.3
15000	498.7	565.3	.....	.....	501.45	496.65	528.4	417.4	458.15	460.9	479.8	531.0
20000	519.7	587.9	.....	.....	521.5	516.55	549.55	434.1	476.45	479.35	498.45	552.25
25000	536.0	606.35	.....	.....	537.85	532.75	566.8	447.7	491.4	494.35	514.1	569.55
28000	544.5	615.95	.....	.....	546.4	541.2	575.8	454.85	499.2	502.2	522.25	578.6
30000	550.0	622.2	.....	.....	551.9	546.65	581.6	459.4	504.25	507.3	527.55	584.35
32000	555.0	627.85	.....	.....	556.95	551.6	586.9	463.6	508.85	511.9	529.75	589.75
33912	559.55	(633.0)	(670.0)	(721.0)	561.5	556.15	591.7	467.4	513.0	516.1	536.7	594.6

TABLE V.
Vapour-pressures at corresponding Temperatures.

Temp. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$COCl_2.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
272.25	20	19.95	19.75	19.70	26.76	29.21	14.13	.....	.....	.....	.....	9.53
289.3	50	50.40	50.10	50.10	65.46	69.50	36.35	.....	17.95	.....	4.95	24.77
303.9	100	101.7	101.2	101.0	128.8	134.6	74.13	.....	41.69	.....	13.34	56.23
320.25	200	203.0	202.1	202.5	252.9	259.4	151.5	140.9	98.63	50.64	36.48	122.3
338.75	400	405.5	403.2	402.7	495.5	501.2	308.7	291.1	231.7	129.1	98.74	263.0
358.1	700	763.8	758.6	758.6	912.0	916.2	591.6	562.3	515.2	310.5	245.5	538.3
367.3	1000	1001	994.3	997.7	1193	1189	781.3	746.4	726.9	452.9	364.8	739.6
382.0	1500	1498	1491	1495	1766	1740	1191	1130	1211	790.7	651.6	1176
398.25	2000	1995	1982	1989	2325	2272	1598	1515	.....	1175	973.9	1635
410.4	3000	2979	2965	2992	3432	3350	2415	2283	2897	2042	1718	2576
423.8	4000	3967	3967	4027	4545	4406	3240	3076	4198	3027	2550	3589
434.85	5000	4949	4972	.....	5636	5451	4064	3868	5559	4102	3455	4656
444.25	6000	5943	5977	.....	6722	6464	4831	4651	6998	5218	4411	5735
452.8	7000	6982	7015	.....	7834	7516	5715	5476	8521	6449	5445	6894
460.4	8000	7998	8054	.....	8913	8531	6569	6281	10070	7700	6479	8063
473.6	10000	10025	.....	.....	11079	10566	8232	7907	13351	10292	8580	10471
484.95	12000	12050	.....	.....	13228	12560	9897	9539	16788	13017	10952	13002
499.7	15000	15136	.....	.....	16425	15615	12402	12023	22284	17398	14504	16943
519.7	20000	20137	.....	.....	21752	20583	16558	16088	31659	25061	20559	23796
536.0	25000	25206	.....	.....	27071	25498	20725	20045	41543	33037	26761	30726
544.5	28000	28184	.....	.....	30200	28347	23174	22413	47479	37844	30374	34954
550.0	30000	30234	.....	.....	32322	30374	24860	23998	51761	41400	32584	37932
555.0	32000	32211	.....	.....	34435	32285	26516	25615	55847	44668	35481	40691
559.55	33912	(33912)	(33912)	(33912)	36395	34180	28080	27060	59760	47850	38120	43400

TABLE VI.
Molecular Volumes of Liquid at corresponding Pressures.

Pressure. $C_6H_6F_6$	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	C_6H_6	CCl_4	$SnCl_4$	$(C_2H_5)_2O$	CH_3OH	C_2H_5OH	C_3H_7OH	CH_3COOH
20	91.47	102.89	107.99	116.79	86.10	.....	116.17	.....	.....	57.69	74.99	57.85
50	93.30	104.88	110.04	119.03	87.87	94.91	118.66	.....	40.27	58.65	76.19	59.00
100	94.92	106.63	111.89	121.09	89.41	96.58	120.78	.....	40.77	59.51	77.29	60.06
200	96.80	108.75	114.10	123.52	91.23	98.50	123.32	.....	41.56	60.51	78.56	61.33
400	99.05	111.32	116.81	126.48	93.51	100.86	126.51	102.21	42.43	61.72	80.06	62.85
760	101.59	114.26	119.94	129.86	95.91	103.52	129.80	104.94	43.42	63.11	81.81	64.59
1000	102.90	115.75	121.47	131.56	97.12	104.87	131.52	106.31	43.92	63.80	82.70	65.46
1500	105.10	118.23	124.11	134.40	99.20	107.19	134.47	108.60	44.76	64.97	84.20	66.91
2000	107.00	120.24	126.24	136.72	100.96	109.10	136.88	110.46	45.45	65.97	85.47	68.09
3000	110.03	123.69	129.86	140.63	103.89	112.23	140.88	113.49	46.60	67.65	87.65	70.01
4000	112.64	126.65	132.90	143.73	106.35	114.86	144.09	116.08	47.56	69.10	89.50	71.61
5000	114.98	129.27	135.68	.....	108.50	117.16	147.10	118.44	48.42	70.48	91.24	73.04
6000	117.06	131.72	138.23	.....	110.52	119.29	149.82	120.70	49.28	71.67	92.87	74.38
7000	119.14	134.08	140.75	.....	112.48	121.32	152.62	122.91	50.07	72.89	94.45	75.69
8000	121.19	136.33	143.18	.....	114.36	123.88	155.24	125.12	50.88	73.97	96.03	76.94
10000	125.04	140.72	.....	.....	117.95	127.39	160.27	129.33	52.36	76.15	99.01	79.37
12000	128.80	145.10	.....	.....	121.55	131.39	165.56	133.36	53.87	78.33	101.99	81.79
15000	134.64	.....	.....	.....	127.12	137.34	173.87	139.23	56.17	81.63	106.57	85.80
20000	145.08	.....	.....	.....	137.20	148.19	187.29	149.52	60.94	88.22	114.89	91.85
25000	158.40	.....	.....	.....	149.80	161.89	.....	164.15	66.10	96.34	125.67	100.1
28000	169.35	.....	.....	.....	160.20	173.55	.....	176.18	70.92	102.59	134.41	107.4
30000	179.40	.....	.....	.....	169.50	183.37	.....	186.52	75.04	109.10	142.52	113.4
32000	193.0	.....	.....	.....	182.3	196.26	.....	201.80	81.49	118.01	153.99	121.8
33912	233.0	.....	.....	.....	219.0	.....	.....	.....	.....	.....	.....	147.0

Approximate.

TABLE VII.
Molecular Volumes of Liquid at corresponding Temperatures.

Temp. $C_6H_6F_6$	$C_6H_5F_5$	$C_6H_4Cl_4$	$C_6H_3Br_3$	$C_6H_2I_2$	C_6H_6	CCl_4	$SnCl_4$	$(C_2H_5)_2O$	CH_3OH	C_2H_5OH	C_3H_7OH	CH_3COOH
272.25	91.47	102.88	107.95	116.73	86.50	.....	115.78	.....	.....	.....	.....	56.85
289.3	93.30	104.89	110.04	119.03	88.28	95.63	118.24	.....	.....	.....	73.38	57.87
303.9	94.92	106.69	111.93	121.12	89.86	97.33	120.45	.....	.....	.....	74.39	58.83
320.25	96.80	108.80	114.13	123.57	91.73	99.31	122.98	.....	40.36	58.29	75.59	59.99
338.75	99.05	111.37	116.86	126.80	93.95	101.69	125.99	101.86	41.12	59.40	77.09	61.38
358.1	101.59	114.17	119.93	129.85	96.38	104.36	129.47	104.60	42.01	60.66	78.71	62.97
367.3	102.90	115.77	121.44	131.54	97.62	105.76	131.18	105.97	42.47	61.31	79.56	63.81
382.0	105.10	118.21	124.06	134.88	99.73	108.08	134.13	108.26	43.25	62.42	81.02	65.19
393.25	107.00	120.22	126.17	136.67	101.48	109.99	136.55	110.10	43.89	63.33	82.22	66.30
410.4	110.03	123.63	129.76	140.59	104.41	113.11	140.57	113.10	44.97	64.86	84.29	68.12
423.8	112.64	126.56	132.79	144.05	106.90	115.73	143.83	115.72	45.92	66.23	86.11	69.67
434.85	114.98	129.17	135.60	.....	109.04	118.03	146.87	118.11	46.77	67.50	87.80	71.05
444.25	117.06	131.60	138.18	.....	113.05	120.15	149.67	120.32	47.54	68.68	89.42	72.32
452.8	119.14	134.05	140.77	.....	113.05	122.28	152.39	122.61	48.29	69.86	91.00	73.56
460.4	121.19	136.33	143.30	.....	114.90	124.31	155.09	124.86	49.06	71.03	92.50	74.79
473.6	125.04	140.79	.....	.....	118.51	128.32	160.32	129.18	50.53	73.21	95.61	77.16
484.95	128.80	145.29	.....	.....	122.07	132.28	165.43	133.24	52.03	75.37	98.67	79.57
499.7	134.64	.....	.....	.....	127.68	138.29	173.24	139.02	54.36	78.70	103.37	83.31
519.7	145.08	.....	.....	.....	137.81	149.16	187.34	150.26	58.72	85.01	111.87	90.00
536.0	158.40	180.0	.....	.....	150.60	162.81	.....	164.37	64.31	93.52	122.55	98.25
544.5	169.35	192.4	.....	.....	160.70	174.09	.....	176.48	69.13	99.92	131.41	105.45
560.0	179.40	204.0	.....	.....	170.00	184.06	.....	187.11	73.63	106.58	139.50	112.15
555.0	193.0	222.4	.....	.....	183.00	196.57	.....	202.32	80.43	116.13	150.87	120.8
559.55	233.0	.....	.....	.....	219.0	.....	.....	.....	.....	.....	.....	147

Approximate.

TABLE X.
Ratios of Absolute Temperatures (Boiling-Points) to those of Fluorbenzene at corresponding Pressures.

Pressure C_6H_5F .	C_6H_5F .	C_6H_5Cl .	C_6H_5Br .	C_6H_5I .	C_6H_6 .	CCl_4 .	$SnCl_4$.	$(O_2H_2)_2O$.	CH_3OH .	C_2H_5OH .	C_3H_7OH .	CH_3COOH .
20	1.0000	1.1315	1.1985	1.2902	.9890	.9639	1.0679	.....	1.0127	1.0494	1.0997	1.1278
50	"	1.1307	1.1970	1.2885	.9895	.9715	1.0669	.....	1.0081	1.0411	1.0873	1.1258
100	"	1.1300	1.1964	1.2876	.9901	.9724	1.0651	.....	1.0031	1.0394	1.0775	1.1237
200	"	1.1302	1.1961	1.2871	.9903	.9739	1.0648	.8431	.9978	1.0251	1.0667	1.1216
400	"	1.1300	1.1965	1.2874	.9928	.9756	1.0636	.8413	.9919	1.0155	1.0546	1.1185
760	"	1.1307	1.1980	1.2869	.9932	.9774	1.0633	.8411	.9859	1.0061	1.0432	1.1151
1000	"	1.1310	1.1981	1.2891	.9936	.9781	1.0617	.8405	.9829	1.0012	1.0380	1.1133
1500	"	1.1314	1.1985	1.2891	.9944	.9795	1.0618	.8401	.9772	.9937	1.0293	1.1102
2000	"	1.1316	1.1985	1.2893	.9950	.9808	1.0613	.8397	.9704	.9884	1.0229	1.1082
3000	"	1.1321	1.1988	1.2890	.9963	.9826	1.0607	.8394	.9667	.9801	1.0117	1.1045
4000	"	1.1324	1.1986	1.2875	.9969	.9835	1.0599	.8390	.9618	.9798	1.0051	1.1010
5000	"	1.1325	1.1982	.....	.9975	.9844	1.0597	.8382	.9578	.9886	1.0020	1.0981
6000	"	1.1322	1.1977	.....	.9983	.9854	1.0586	.8383	.9544	.9645	.9977	1.0955
7000	"	1.1318	1.1971	.....	.9986	.9856	1.0592	.8375	.9512	.9607	.9937	1.0927
8000	"	1.1315	1.1965	.....	.9987	.9864	1.0585	.8370	.9485	.9577	.9904	1.0905
10000	"	1.1307	.....	.....	.9994	.9878	1.0573	.8362	.9433	.9522	.9848	1.0862
12000	"	1.1304	.....	.....	1.0001	.9888	1.0579	.8366	.9393	.9477	.9807	1.0827
15000	"	1.1299	.....	.....	1.0007	.9893	1.0578	.8346	.9340	.9419	.9754	1.0777
20000	"	1.1300	.....	.....	1.0015	.9910	1.0574	.8343	.9260	.9347	.9690	1.0718
25000	"	1.1301	.....	.....	1.0021	.9925	1.0573	.8348	.9230	.9294	.9649	1.0678
28000	"	1.1299	.....	.....	1.0028	.9933	1.0576	.8351	.9209	.9265	.9631	1.0661
30000	"	1.1300	.....	.....	1.0029	.9932	1.0574	.8349	.9192	.9248	.9618	1.0642
32000	"	1.1301	.....	.....	1.0032	.9937	1.0572	.8350	.9178	.9235	.9606	1.0634
33912	"	.....	.....	.....	1.0035	.9939	1.0575	.8353	.9168	.9223	.9592	1.0626
Mean Ratios.												
	1.1309	1.1976	1.2885	Ratio of Highest to Lowest Ratio.								
	1.002	1.002	1.002	1.002	1.014	1.025	1.010	1.011	1.105	1.138	1.146	1.061

TABLE XI.

Ratios of Vapour-Pressures to those of Fluorobenzene at corresponding Temperatures.

Temp. C_6H_5F .	C_6H_5F .	C_6H_5Cl .	C_6H_5Br .	C_6H_5I .	C_6H_6 .	CCl_4 .	$SnCl_4$.	$(C_2H_5)_2O$.	CH_3OH .	C_2H_5OH .	C_3H_7OH .	CH_3COOH .									
272.25	1.0000	.998	.987	.985	1.338	1.460	.706	.....	.....	.....	.....	.476									
289.3	"	1.008	1.012	1.002	1.309	1.390	.727	.....	.369	.099	.099	.495									
303.9	"	1.016	1.012	1.010	1.288	1.346	.741	.....	.417	.133	.133	.562									
320.25	"	1.015	1.010	1.013	1.265	1.297	.758	.705	.493	.253	.253	.612									
338.75	"	1.014	1.008	1.007	1.239	1.253	.772	.728	.579	.323	.323	.658									
358.1	"	1.005	.998	.998	1.200	1.206	.778	.740	.678	.409	.409	.708									
367.3	"	1.001	.994	.998	1.193	1.189	.784	.746	.727	.463	.463	.740									
382.0	"	.999	.991	.996	1.177	1.160	.794	.753	.807	.527	.527	.784									
393.25	"	.998	.991	.994	1.163	1.136	.799	.758	.....	.587	.487	.817									
410.4	"	.993	.988	.997	1.144	1.117	.805	.761	.966	.681	.573	.859									
423.8	"	.992	.992	1.007	1.136	1.101	.810	.769	1.049	.757	.637	.897									
434.85	"	.990	.994	.....	1.127	1.090	.813	.774	1.112	.820	.691	.931									
444.25	"	.991	.996	.....	1.120	1.077	.814	.775	1.167	.735	.735	.956									
452.8	"	.997	1.002	.....	1.119	1.074	.816	.782	1.217	.921	.778	.985									
460.4	"	1.000	1.007	.....	1.114	1.066	.821	.785	1.259	.962	.810	1.008									
473.6	"	1.002	.....	.....	1.108	1.056	.823	.791	1.335	1.029	.858	1.047									
484.95	"	1.004	.....	.....	1.102	1.047	.825	.795	1.399	1.085	.913	1.083									
499.7	"	1.009	.....	.....	1.095	1.041	.827	.801	1.486	1.160	.967	1.130									
519.7	"	1.007	.....	.....	1.088	1.029	.828	.804	1.583	1.253	1.028	1.190									
536.0	"	1.008	.....	.....	1.083	1.019	.829	.802	1.682	1.322	1.071	1.229									
544.5	"	1.006	.....	.....	1.078	1.012	.828	.800	1.696	1.351	1.085	1.248									
550.0	"	1.008	.....	.....	1.077	1.013	.829	.800	1.725	1.380	1.086	1.264									
555.0	"	1.007	.....	.....	1.076	1.009	.829	.801	1.745	1.396	1.109	1.272									
559.55	"	.....	.....	.....	1.073	1.008	.828	.798	1.762	1.411	1.124	1.280									
Ratio of Highest to Lowest Ratio.																					
	1.026		1.025		1.028		1.247		1.448		1.174		1.140		4.91		7.02		11.35		2.68

TABLE XII.

Ratios of Molecular Volumes of Liquid to those of Fluorobenzene at corresponding Pressures.

Pressure C_6H_5F .	C_6H_5F .	C_6H_5Cl .	C_6H_5Br .	C_6H_5I .	C_6H_6 .	CCl_4 .	$SnCl_4$.	$(C_2H_5)_2O$.	CH_3OH .	C_2H_5OH .	C_3H_7OH .	CH_3COOH .
20	1.0000	1.1248	1.1806	1.2768	.9413	.....	1.2700	.....	.....	.6307	.8198	.6324
50	"	1.1241	1.1794	1.2758	.9418	1.0173	1.2718	.....	.4317	.6287	.8166	.6324
100	"	1.1234	1.1788	1.2757	.9420	1.0175	1.2725	.....	.4295	.6269	.8143	.6327
200	"	1.1234	1.1787	1.2760	.9425	1.0176	1.2740	.....	.4293	.6251	.8115	.6336
400	"	1.1239	1.1793	1.2769	.9441	1.0183	1.2773	1.0319	.4294	.6232	.8083	.6345
760	"	1.1247	1.1806	1.2783	.9441	1.0190	1.2777	1.0330	.4274	.6213	.8053	.6358
1000	"	1.1249	1.1805	1.2785	.9438	1.0191	1.2781	1.0332	.4268	.6200	.8037	.6362
1500	"	1.1238	1.1798	1.2778	.9436	1.0197	1.2793	1.0333	.4259	.6182	.8012	.6366
2000	"	1.1241	1.1802	1.2781	.9442	1.0200	1.2804	1.0324	.4247	.6166	.7987	.6364
3000	"	1.1244	1.1799	1.2760	.9442	1.0197	1.2792	1.0315	.4235	.6148	.7966	.6363
4000	"	1.1243	1.1800	.....	.9436	1.0190	1.2794	1.0305	.4222	.6137	.7953	.6357
5000	"	1.1243	1.1800	.....	.9441	1.0191	1.2799	1.0301	.4211	.6130	.7986	.6359
6000	"	1.1252	1.1808	.....	.9441	1.0183	1.2810	1.0317	.4210	.6123	.7994	.6354
7000	"	1.1254	1.1814	.....	.9436	1.0180	1.2810	1.0324	.4202	.6118	.7927	.6353
8000	"	1.1254	.....	.....	.9433	1.0188	1.2818	1.0343	.4198	.6090	.7918	.6348
10000	"	1.1255	.....	.....	.9437	1.0201	1.2854	1.0354	.4182	.6081	.7918	.6350
12000	"	.....	.....	.....	.9442	1.0200	1.2877	1.0341	.4172	.6063	.7915	.6335
15000	"	.....	.....	.....	.9457	1.0214	1.2910	1.0327	.4173	.6081	.7919	.6331
20000	"	.....	.....	.....	.9457	1.0220	.....	1.0364	.4173	.6082	.7933	.6319
25000	"	1.1310	.....	.....	.9460	1.0248	.....	1.0403	.4188	.6058	.7937	.6342
28000	"	1.1310	.....	.....	.9448	1.0222	.....	1.0397	.4183	.6082	.7944	.6321
30000	"	1.1270	.....	.....	.....	1.0222	.....	1.0397	.4183	.6082	.7944	.6321
32000	"	1.1350	.....	.....	.9446	1.0169	.....	1.0456	.4222	.6114	.7978	.6311
33912	"	.....	.....	.....	.9400	.....	.....	.....	.....	.....	.....	.6310
Mean Ratios.												
	*1.1246	1.1802	1.2772	1.2772	.9439	1.0195	1.2793	1.0342	.4228	.6153	.7995	.6342
Ratio of Highest to Lowest Ratio.												
	*1.003	1.002	1.002	1.002	1.006	1.008	1.017	1.015	1.035	1.041	1.036	1.009

* Omitting approximate values.

TABLE XIII.
Ratios of Molecular Volumes of Liquid to those of Fluorobenzene at corresponding Temperatures.

Temp. C_6H_5F	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	C_6H_6	CCl_4	$SnCl_4$	$(C_2H_5)_2O$	CH_3OH	C_2H_5OH	C_3H_7OH	CH_3COOH
272.25	1.0000	1.1247	1.1802	1.2761	.9437	.....	1.2657	.....	.....	.....	.....	.6215
289.3	"	1.1242	1.1794	1.2758	.9462	1.0250	1.2673	.....	.....	.....	.7865	.6203
303.9	"	1.1240	1.1792	1.2760	.9467	1.0254	1.2689	.....	.....	.6044	.7837	.6198
320.25	"	1.1239	1.1790	1.2765	.9476	1.0260	1.2705	.....	.4169	.6022	.7809	.6197
338.75	"	1.1244	1.1798	1.2772	.9485	1.0267	1.2720	1.0284	.4152	.5997	.7783	.6197
358.1	"	1.1238	1.1805	1.2782	.9487	1.0273	1.2744	1.0297	.4136	.5971	.7748	.6198
367.3	"	1.1250	1.1802	1.2783	.9487	1.0278	1.2748	1.0299	.4127	.5958	.7732	.6201
382.0	"	1.1248	1.1804	1.2784	.9489	1.0283	1.2763	1.0301	.4115	.5939	.7709	.6203
393.25	"	1.1236	1.1792	1.2773	.9484	1.0280	1.2761	1.0290	.4102	.5919	.7684	.6196
410.4	"	1.1236	1.1793	1.2777	.9489	1.0280	1.2775	1.0279	.4087	.5895	.7661	.6191
423.8	"	1.1236	1.1789	1.2789	.9491	1.0275	1.2769	1.0273	.4076	.5880	.7664	.6185
434.85	"	1.1234	1.1793	.....	.9484	1.0266	1.2773	1.0272	.4068	.5871	.7636	.6179
444.25	"	1.1242	1.1804	.....	.9487	1.0264	1.2786	1.0279	.4061	.5867	.7639	.6178
452.8	"	1.1252	1.1815	.....	.9489	1.0264	1.2791	1.0291	.4054	.5864	.7638	.6174
460.4	"	1.1249	1.1824	.....	.9481	1.0257	1.2797	1.0302	.4048	.5861	.7633	.6171
473.6	"	1.1260	.....	.....	.9478	1.0262	1.2822	1.0331	.4041	.5855	.7646	.6178
484.95	"	1.1280	.....	.....	.9477	1.0270	1.2844	1.0345	.4040	.5851	.7660	.6188
499.7	"	.....	.....	.....	.9483	1.0271	1.2867	1.0326	.4038	.5845	.7677	.6204
519.7	"	.....	.....	.....	.9469	1.0281	1.2913	1.0367	.4037	.5859	.7711	.6203
536.0	"	1.1360	.....	.....	.9508	1.0279	.....	1.0377	.4060	.5904	.7737	.6227
544.5	"	1.1360	.....	.....	.9489	1.0280	.....	1.0421	.4082	.5900	.7760	.6251
550.0	"	1.1370	.....	.....	.9476	1.0280	.....	1.0430	.4104	.5941	.7776	.6259
555.0	"	1.1520	.....	.....	.9482	1.0188	.....	1.0483	.4167	.6017	.7817	.6310
559.55	"	.....	.....	.....	.9400	.....	.....	.....	.....	.....	.....	.....
Mean Ratios.												
	*1.1245	1.1800	1.2773	.9479	1.0266	1.277	1.033	.409	.592	.772	.623	
Ratio of Highest to Lowest Ratio.												
	*1.004	1.003	1.002	1.011	1.009	1.020	1.021	1.032	1.030	1.034	1.023	

* Omitting approximate values.

TABLE XIV.

Ratios of Molecular Volumes of Saturated Vapour to those of Fluorobenzene at corresponding Pressures.

Pressure C_6H_5F	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	C_6H_6	CCl_4	$SnCl_4$	$(C_2H_5)_2O$	CH_3OH	C_2H_5OH	C_3H_7OH	CH_3COOH
1000	1.000	1.120	1.168	1.269	.925	.960	1.278	1.036	.533	.706	.903	.545
1500	"	1.128	1.175	1.279	.930	.970	1.276	1.037	.530	.700	.895	.552
2000	"	1.133	1.179	1.283	.933	.976	1.277	1.036	.527	.701	.888	.557
3000	"	1.141	1.189	1.289	.938	.983	1.281	1.038	.525	.697	.880	.565
4000	"	1.143	1.195	1.290	.951	.992	1.287	1.038	.522	.696	.874	.571
5000	"	1.145	1.196	.....	.954	.997	1.282	1.038	.520	.694	.872	.577
6000	"	1.143	1.199	.....	.958	1.002	1.285	1.038	.517	.693	.870	.582
7000	"	1.144	1.199	.....	.961	.999	1.283	1.037	.515	.690	.868	.584
8000	"	1.143	1.200	.....	.961	.995	1.288	1.037	.513	.688	.866	.588
10000	"	1.138	.....	.....	.960	.997	1.302	1.041	.511	.688	.866	.596
15000	"	1.131	.....	.....	.955	.994	1.282	1.040	.507	.675	.857	.599
20000	"	.....	.....	.....	.947	.985	1.272	1.042	.503	.665	.849	.607
25000	"	.....	.....	.....	.944	1.002	1.262	1.042	.495	.645	.829	.622
28000	"	.....	.....	.....	.940	1.000	.....	1.035	.480	.638	.810	.623
30000	"	.....	.....	.....	.936	.993	.....	1.035	.472	.643	.814	.622
32000	"	.....	.....	.....	.946	1.005	.....	1.050	.475	.643	.825	.630
33912	"	.....	.....	.....	.....	1.017	.....	1.032	.473	.625	.836	.625
					.940	.....	.....	.....	.....	.....	.....	.631
Mean Ratios.												
		1.137		1.189		1.282		1.038		.507		.583
		1.022		1.027		1.017		1.032		1.129		1.153
Ratio of Highest to Lowest Ratio.												
		1.137		1.189		1.282		1.038		.507		.583
		1.022		1.027		1.017		1.032		1.129		1.153

TABLE XV.

Ratio of Molecular Volumes of Saturated Vapour to those of Fluorbenzene at corresponding Temperatures.

Temp. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$CCl_4.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
367.3	1.000	1.118	1.174	1.272	.842	.828	1.336	1.101	1.244	2.076	2.678	.894
382.0	"	1.130	1.186	1.286	.853	.852	1.329	1.092	1.126	1.805	2.254	.864
393.25	"	1.135	1.189	1.292	.866	.866	1.322	1.088	1.049	1.635	2.007	.845
410.4	"	1.150	1.201	1.293	.885	.895	1.316	1.083	.945	1.414	1.714	.818
423.8	"	1.150	1.203	1.281	.893	.910	1.313	1.078	.875	1.284	1.541	.797
434.85	"	1.156	1.203	.....	.906	.924	1.308	1.073	.826	1.191	1.422	.782
444.25	"	1.155	1.204	.....	.919	.933	1.305	1.067	.788	1.126	1.337	.769
452.8	"	1.146	1.199	.....	.917	.935	1.300	1.059	.755	1.071	1.266	.756
460.4	"	1.143	1.189	.....	.923	.938	1.300	1.054	.729	1.028	1.216	.745
473.6	"	1.134	.....	.....	.927	.949	1.300	1.048	.689	.962	1.139	.729
484.95	"	1.116	.....	.....	.931	.954	1.291	1.041	.655	.908	1.081	.712
499.7	"	.....	.....	.....	.926	.959	1.275	1.040	.615	.841	1.016	.694
519.7	"	.....	.....	.....	.926	.977	1.262	1.030	.572	.763	.943	.681
536.0	"	.....	.....	.....	.924	.982	.....	1.028	.530	.705	.875	.665
544.5	"	.....	.....	.....	.930	.985	.....	1.030	.508	.690	.861	.653
550.0	"	.....	.....	.....	.940	.995	.....	1.041	.497	.676	.864	.649
555.0	"	.....	.....	.....	.940	1.014	.....	1.025	.484	.648	.866	.639
559.55	"	.....	.....	.....	.940	.....	.....	.....	.....	.....	.....	.631

Mean Ratios.				
1.139	1.194	1.285	Ratio of Highest to Lowest Ratio.	
1.036	1.026	1.017	1.116	1.224
			1.059	1.074
			2.570	3.204
			3.110	1.417

TABLE XVI.
Percentage-differences between Highest and Lowest Ratios in each comparison with Fluorbenzene.

	C_6H_5Cl	C_6H_5Br	C_6H_5I	C_6H_6	CCl_4	$SnCl_4$	$(C_2H_5)_2O$	CH_3OH	C_2H_5OH	C_3H_7OH	CH_3COOH
Absolute temperatures at corresponding pressures	0.2	0.2	0.2	1.4	2.5	1.0	1.1	10.5	13.8	14.6	6.1
Vapour-pressures at corresponding temperatures...	2.6	2.5	2.8	24.7	44.8	17.4	14.0	391.0	602.0	1035.0	168.5
Molecular volumes of liquid at corresponding pressures	0.3	0.2	0.2	0.6	0.8	1.7	1.5	3.5	4.1	3.6	0.9
Molecular volumes of liquid at corresponding temperatures	0.4	0.3	0.2	1.1	0.9	2.0	2.1	3.2	3.0	3.4	2.3
Molecular volumes of saturated vapour at corresponding pressures	2.2	2.7	1.7	3.9	5.9	3.2	1.0	12.9	13.0	11.5	15.8
Molecular volumes of saturated vapour at corresponding temperatures...	3.6	2.6	1.7	11.6	22.4	5.9	7.4	157.0	220.4	211.0	41.7

The degree of deviation from constancy of the various ratios is indicated by the values given at the foot of each table, representing the ratio of the highest to the lowest ratio in each vertical column. These values are collected together in Table XVI. (p. 171), but for the sake of greater clearness they are given as percentage-differences between the highest and lowest ratios in each case, the lowest ratio being always taken as 100.

It will be seen that the halogen derivatives of benzene show very much smaller deviations from constancy than the other compounds; and I have previously suggested (*Trans. Chem. Soc.* 1889, p. 486; 1891, p. 125) that the generalizations of Van der Waals do hold good for these bodies, in which case the deviations of the ratios from constancy may be taken as an approximate measure of the experimental errors to be expected with other compounds. It must, however, be admitted that the mean ratios of the absolute temperatures differ sensibly from the mean ratios of the molecular volumes of liquid, though they should be identical if Van der Waals's generalizations were strictly true, while the errors in these determinations are probably very small. Indeed, in the comparison of bromobenzene with fluorobenzene the difference between the mean ratios amounts to 1.5 per cent. (Table XXI.), while the difference between the highest and lowest ratio in either case is only 0.2 per cent. (Table XVI.). It is probable, therefore, that the generalizations of Van der Waals are not quite, though very nearly, true for these bodies.

The deviations from constancy are smallest in the comparisons of the absolute temperatures at corresponding pressures, and of the molecular volumes of liquid at corresponding pressures and temperatures; and this is no doubt to be expected, since the ratio of the highest to the lowest absolute temperature or volume of liquid for any one substance does not amount to 3 : 1, whereas the ratio of the highest to the lowest pressure is from 1700 to 10000 : 1, and of the highest to the lowest molecular volume of saturated vapour from 3.7 : 1 in the case of iodobenzene, where the range is limited, to 2670 to 1 with acetic acid. It is also impossible to determine the volumes of saturated vapour with anything like the same degree of accuracy as the volumes of liquid, the liability to error by the new method being especially great at the lowest temperatures.

The eleven substances which are compared with fluorobenzene may be arranged in three groups as below :—

1. *Chlorobenzene, Bromobenzene, Iodobenzene.*—As already pointed out, the generalizations of Van der Waals are very nearly true for these bodies when compared with fluorobenzene.

2. *Benzene, Carbon tetrachloride, Stannic chloride, Ether.*—With these substances the generalizations may be taken as

rough approximations to the truth, but the deviations of the ratios from constancy are in most cases much too large to be attributed to error of experiment.

3. *The three Alcohols and Acetic Acid.*—The majority of the generalizations do not hold good at all ; the deviations of the ratios from constancy are, however, not very great in the case of the molecular volumes of liquid at corresponding pressures and temperatures.

Discussion of the Generalizations.

1. *Corresponding Temperatures and Pressures.*—It must, I think, be concluded that the statement that “if the absolute temperatures of various substances are proportional to their absolute critical temperatures their vapour-pressures will be proportional to their critical pressures” has not been proved by experiment to be true except in a very limited number of cases; indeed, when the alcohols and acetic acid are compared with fluorobenzene, the statement is quite wide of the mark. It follows, therefore, that in the comparison of the molecular volumes the ratios at corresponding pressures must differ from those at corresponding temperatures.

2. *Molecular Volumes of Liquid.*—The deviations of the ratios from constancy are smaller in this case than in any of the others, but are certainly not within the limits of experimental error. The comparisons at corresponding pressures seem to be somewhat better on the whole than at corresponding temperatures, but the difference is not very marked.

3. *Molecular Volumes of Saturated Vapour.*—At corresponding pressures the deviations from constancy are within the limits of experimental error in the case of ether and stannic chloride, and are relatively small for benzene and carbon tetrachloride.

There can be no doubt that with the saturated vapours the comparisons at corresponding pressures are very much better than at corresponding temperatures ; and it may therefore be concluded that it is better to compare the molecular volumes both of liquid and of saturated vapour at corresponding pressures than at corresponding temperatures.

Saturated Vapours.

It has been pointed out (Trans. Chem. Soc. 1891, p. 137) that if the generalizations of Van der Waals were strictly true, it would follow that the ratios of the actual densities of the saturated vapours of different substances to their theoretical densities should be equal at corresponding pressures ; and as this method of comparison is a very convenient one I have thought it worth while to tabulate the ratios, although it has already been shown that the relation cannot be strictly true. The values for benzene and its halogen derivatives have

TABLE XVII.

Ratios of Actual to Theoretical Densities of Saturated Vapour at corresponding Pressures.

Pressure. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$COCl_4.$	$SnCl_4.$	$(O_2H_2)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
20	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.907
50	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.829
100	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.770
200	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.718
400	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.678
760	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.657
1000	1.037	1.047	1.063	1.053	1.037	1.047	1.040	1.029	1.071	1.019	1.025	1.654
1500	1.056	1.059	1.077	1.065	1.052	1.059	1.063	1.054	1.084	1.042	1.060	1.659
2000	1.073	1.072	1.091	1.079	1.066	1.073	1.079	1.070	1.105	1.059	1.081	1.669
3000	1.107	1.099	1.116	1.107	1.091	1.098	1.107	1.122	1.122	1.075	1.099	1.690
4000	1.138	1.127	1.142	1.136	1.112	1.122	1.136	1.153	1.157	1.103	1.132	1.713
5000	1.166	1.153	1.168	.....	1.136	1.147	1.162	1.180	1.189	1.129	1.164	1.735
6000	1.193	1.181	1.192	.....	1.159	1.173	1.187	1.207	1.219	1.153	1.192	1.759
7000	1.217	1.206	1.217	.....	1.180	1.197	1.213	1.233	1.277	1.203	1.242	1.781
8000	1.247	1.233	1.242	.....	1.206	1.233	1.238	1.260	1.306	1.230	1.267	1.805
10000	1.300	1.291	.....	.....	1.260	1.275	1.287	1.308	1.360	1.275	1.315	1.852
12000	1.349	1.347	.....	.....	1.316	1.329	1.343	1.358	1.419	1.343	1.373	1.904
15000	1.431	.....	.....	.....	1.408	1.410	1.435	1.436	1.507	1.437	1.462	1.983
20000	1.600	.....	.....	.....	1.582	1.571	1.619	1.605	1.700	1.643	1.664	2.153
25000	1.818	.....	.....	.....	1.806	1.790	.....	1.837	1.985	1.876	1.927	2.434
28000	2.011	.....	.....	.....	2.006	1.994	.....	2.032	2.228	2.054	2.116	2.691
30000	2.206	.....	.....	.....	2.180	2.164	.....	2.199	2.420	2.250	2.282	2.920
32000	2.450	.....	.....	.....	.....	2.376	.....	2.455	2.699	2.561	2.504	3.252
33912	4.400	.....	.....	.....	4.370	.....	.....	.....	.....	.....	.....	5.792
		(4.43)	(4.46)	(4.43)		(4.30)	(4.35)	(4.40)	(5.18)	(4.65)	(4.70)	

The bracketed values are calculated from the molecular critical volumes given in Table XXII.

already been published (*loc. cit.*); but there are one or two obvious small irregularities, and I have therefore mapped the ratios against temperature and constructed curves for each substance (Plate I.). The smoothed values read from the curves are given in this paper, and the molecular volumes of saturated vapour have also been recalculated from the density ratios. The same method of procedure has been adopted with the other substances.

The close similarity in the behaviour of the halogen derivatives of benzene and the approximate agreement in the case of the members of Group II. is very clearly shown in Table XVII.

It is generally admitted that gaseous acetic acid at low temperatures contains molecules more complex than those corresponding to the ordinary formula $C_2H_4O_2$, and from the very high density at the critical point it would appear that many of these complex molecules have escaped dissociation even at this high temperature.

It will be seen that with the alcohols the differences from the other substances become generally more marked as the critical point is approached. At the highest pressure the vapour-density of methyl alcohol is very distinctly higher than that of any member of the first or second group at the corresponding pressure; and this fact appears to favour the conclusion of M. Guye and others, that some of the molecules of methyl alcohol at the critical point and in the liquid state at all temperatures are more complex than in the ordinary gaseous state. On the other hand, by a comparison of the densities of the saturated vapours of acetic acid with those of the alcohols and ether, Dr. Ramsay and I were led to the conclusion that the molecules of ordinary substances, including the alcohols, are not more complex in the liquid than in the gaseous state. This conclusion, so far as the members of Groups I. and II. are concerned, is strengthened by the results given in the preceding Table; but it is certainly weakened to some extent in the case of the alcohols, or at any rate of methyl alcohol.

There is no doubt that these bodies do show marked differences in many of their properties from the majority of compounds; and the most plausible explanation of these differences seems to be the existence of complex molecules in the liquid state, although there is ample proof that they are not present in the saturated vapours at low temperatures.

As the alcohols differ so widely from other substances, it is of interest to find whether the relations of Van der Waals hold good when they are compared among themselves. I have therefore calculated the ratios of the absolute temperatures, pressures, and volumes of ethyl and propyl alcohol to methyl alcohol and of propyl alcohol to ethyl alcohol. The results are given in the following Tables:—

TABLE XVIII.—Alcohols at corresponding Pressures.

Pressures of C_6H_5F .	Absolute Temperatures.			Molecular Volumes of Liquid.			Molecular Volumes of Vapour.		
	$\frac{C_2H_5OH}{CH_3OH}$.	$\frac{C_2H_5OH}{CH_3OH}$.	$\frac{C_3H_7OH}{C_2H_5OH}$.	$\frac{C_2H_5OH}{CH_3OH}$.	$\frac{C_3H_7OH}{CH_3OH}$.	$\frac{C_3H_7OH}{C_2H_5OH}$.	$\frac{C_2H_5OH}{CH_3OH}$.	$\frac{C_3H_7OH}{CH_3OH}$.	$\frac{C_3H_7OH}{C_2H_5OH}$.
20	1.0363	1.0860	1.0479	.....	.....	1.2998	.....	.....	.....
50	1.0327	1.0785	1.0443	1.4565	1.8918	1.2989	.....	.....	.....
100	1.0302	1.0741	1.0427	1.4597	1.8960	1.2989	1.310	.....	.....
200	1.0274	1.0690	1.0405	1.4562	1.8903	1.2981	1.311	.....	.....
400	1.0238	1.0632	1.0385	1.4546	1.8866	1.2971	1.317	1.707	1.296
760	1.0205	1.0581	1.0368	1.4535	1.8840	1.2962	1.321	1.697	1.284
1000	1.0187	1.0561	1.0367	1.4527	1.8831	1.2962	1.323	1.693	1.279
1500	1.0169	1.0533	1.0358	1.4515	1.8812	1.2960	1.321	1.688	1.277
2000	1.0186	1.0541	1.0349	1.4490	1.8806	1.3033	1.328	1.687	1.271
3000	1.0139	1.0465	1.0322	1.4493	1.8765	1.2977	1.328	1.676	1.262
4000	1.0125	1.0450	1.0321	1.4584	1.8838	1.2959	1.332	1.673	1.256
5000	1.0113	1.0461	1.0344	1.4555	1.8843	1.2946	1.335	1.677	1.256
6000	1.0106	1.0454	1.0344	1.4543	1.8841	1.2958	1.339	1.682	1.256
7000	1.0100	1.0447	1.0344	1.4558	1.8864	1.2957	1.340	1.685	1.257
8000	1.0097	1.0442	1.0341	1.4588	1.8874	1.2983	1.339	1.687	1.280
10000	1.0094	1.0440	1.0343	1.4543	1.8864	1.3001	1.345	1.692	1.259
12000	1.0090	1.0441	1.0348	1.4541	1.8833	1.3021	1.331	1.683	1.271
15000	1.0084	1.0443	1.0356	1.4534	1.8874	1.3054	1.321	1.688	1.278
20000	1.0093	1.0465	1.0368	1.4572	1.8978	1.3023	1.304	1.679	1.285
25000	1.0070	1.0455	1.0382	1.4576	1.9013	1.3044	1.330	1.688	1.269
28000	1.0061	1.0458	1.0394	1.4466	1.8953	1.3102	1.363	1.687	1.266
30000	1.0061	1.0464	1.0400	1.4540	1.8994	1.3063	1.352	1.736	1.284
32000	1.0063	1.0467	1.0402	1.4482	1.8897	1.3049	1.324	1.768	1.335
33912	1.0060	1.0462	1.0399	.. ..	.....	.....	.....	.....	.....
Mean Ratios									
	1.030	1.040	1.015	1.4534	1.8890	1.2999	1.329	1.693	1.274
Ratio of Highest to Lowest Ratio.									
	1.030	1.040	1.015	1.012	1.013	1.012	1.040	1.057	1.063

TABLE XIX.—Alcohols at corresponding Temperatures.

Absolute Temperatures of C_2H_5F .	Vapour-Pressures.		Molecular Volumes of Liquid.				Molecular Volumes of Saturated Vapour.			
	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_2H_7OH}{CH_3OH}$	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_2H_7OH}{CH_3OH}$	$\frac{C_2H_5OH}{C_2H_7OH}$	$\frac{C_2H_7OH}{C_2H_5OH}$	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_2H_7OH}{CH_3OH}$	$\frac{C_2H_5OH}{C_2H_7OH}$	$\frac{C_2H_7OH}{C_2H_5OH}$
272.25	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
289.3	.483	.276	.....	.....	.....	.....	.....	.....	.....	.....
303.9	.518	.320	1.4443	1.8730	1.2968	1.2968	.....	.....	.....	.....
320.25	.557	.370	1.4444	1.8746	1.2968	1.2968	.....	.....	.....	.....
338.75	.557	.426	1.4439	1.8735	1.2975	1.2975	1.851	.....	.....	.....
358.1	.602	.476	1.4435	1.8734	1.2978	1.2978	1.718	.....	.....	.....
367.3	.623	.502	1.4431	1.8734	1.2981	1.2981	1.669	2.153	1.290	1.290
382.0	.653	.538	1.4430	1.8734	1.2983	1.2983	1.603	2.002	1.249	1.249
393.25	.....	.....	1.4422	1.8743	1.2995	1.2995	1.560	1.914	1.227	1.227
410.4	.705	.593	1.4380	1.8753	1.3041	1.3041	1.496	1.813	1.212	1.212
423.8	.721	.607	1.4307	1.8755	1.3030	1.3030	1.471	1.760	1.189	1.189
434.85	.738	.622	1.4433	1.8807	1.3031	1.3031	1.442	1.722	1.194	1.194
444.25	.747	.630	1.4433	1.8807	1.3031	1.3031	1.429	1.696	1.187	1.187
452.8	.757	.639	1.4465	1.8844	1.3027	1.3027	1.419	1.677	1.182	1.182
460.4	.765	.643	1.4478	1.8854	1.3023	1.3023	1.409	1.667	1.183	1.183
473.6	.771	.643	1.4489	1.8922	1.3060	1.3060	1.396	1.654	1.184	1.184
484.95	.775	.652	1.4485	1.8964	1.3092	1.3092	1.387	1.652	1.191	1.191
499.7	.781	.651	1.4476	1.9015	1.3135	1.3135	1.368	1.652	1.208	1.208
519.7	.792	.649	1.4478	1.9052	1.3160	1.3160	1.354	1.648	1.236	1.236
536.0	.795	.644	1.4509	1.9058	1.3104	1.3104	1.329	1.650	1.242	1.242
544.5	.797	.640	1.4455	1.9010	1.3151	1.3151	1.327	1.656	1.247	1.247
550.0	.800	.644	1.4475	1.8946	1.3089	1.3089	1.360	1.738	1.278	1.278
555.0	.800	.635	1.4488	1.8758	1.2992	1.2992	1.398	1.786	1.335	1.335
559.55	.801	.638	.....	.....	.....	.....	.....	.....	.....	.....
Ratio of Highest to Lowest Ratio.										
	1.658	2.362	1.276	1.009	1.018	1.015	1.395	1.306	1.129	1.129

The percentage difference between the highest and lowest ratios in the various comparisons—including those with fluorbenzene—are given in the following Table:—

TABLE XX.

	$\frac{\text{CH}_3\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{CH}_3\text{OH}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{CH}_3\text{OH}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{C}_2\text{H}_5\text{OH}}$
Absolute temperatures at corresponding pressures.....	10.5	13.8	14.6	3.0	4.0	1.5
Vapour-pressures at corresponding temperatures.....	391.0	602.0	1035.0	65.8	136.2	27.6
Molecular volumes of liquid at corresponding pressures	3.5	4.1	3.6	1.2	1.3	1.2
Molecular volumes of liquid at corresponding temperatures	3.2	3.0	3.4	0.9	1.8	1.5
Molecular volumes of saturated vapour at corresponding pressures	12.9	13.0	11.5	4.0	5.7	6.3
Molecular volumes of saturated vapour at corresponding temperatures	157.0	220.4	211.0	39.5	30.6	12.9

When the alcohols are compared with one another, the deviations of the ratios from constancy are much smaller than when fluorbenzene is taken as the standard substance, but they are still far outside the limits of experimental error. It may, perhaps, be said—as with the members of Group II. in the comparisons with fluorbenzene—that the generalizations offer a rough approximation to the truth.

Here, again, the comparison of the molecular volumes of saturated vapour at corresponding pressures is very much more satisfactory than at corresponding temperatures.

In the *Philosophical Magazine* for November 1890, p. 417, it was pointed out by Prof. Orme Masson that the ratio of the molecular volumes (in the liquid state) of any two members of certain groups of nearly related carbon compounds, at their boiling-points under equal pressure, is equal to the ratio of those boiling-points, expressed on the absolute scale of temperature, or

$$\frac{V}{V'} = \frac{T}{T'}.$$

In the same number of the *Philosophical Magazine* (p. 423) I showed that Masson's relation is a special case of a more general one which should hold good if the generalizations of

Van der Waals were strictly true. This relation may be expressed by the equations

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p},$$

where v and v' are the molecular volumes of saturated vapour, V and V' those of liquid, and T and T' the boiling-points on the absolute scale of any two substances at corresponding pressures p and p' .

When the critical pressures are equal $p=p'$ and the equations become

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'},$$

or the molecular volumes, whether of liquid or saturated vapour, at the boiling-points under equal pressure are proportional to the boiling-points expressed on the absolute scale.

That the relation cannot be strictly true when the critical pressures are different is obvious, since it is not generally true that the vapour-pressures at corresponding temperatures are corresponding pressures. It is still possible, however, that the relation may be true for the critical temperatures, pressures, and volumes. Unfortunately, the critical volumes have only been determined in a few cases, but it has been shown that the ratios of the molecular volumes at corresponding pressures do not vary within very wide limits; and it is, therefore, possible to test the relation in a limited form, taking the critical temperatures and pressures and the mean ratios of the molecular volumes at corresponding pressures.

A preliminary comparison was given in the paper referred to, but it was very incomplete, and there was a small error in some of the calculations owing to the misplacement of a figure in the critical pressure of fluorbenzene, which was given as 33190 instead of 33910.

As the experimental results have been considerably extended since that time and now include the molecular volumes of the saturated vapours, it is possible to give the Table in a complete form.

TABLE XXI.

Comparison of Values of $\frac{T}{T'} \times \frac{p'}{p}$ with Mean Ratios of
Molecular Volumes at corresponding Pressures.

Substances compared.	$\frac{T}{T'} \times \frac{p'}{p}$	Mean Ratios of Molecular Volumes.		Percentage difference between highest and lowest of the three values.
		Liquid.	Saturated Vapour.	
C_6H_5Cl/C_6H_5F	1.1308	1.1246	1.137	1.1
C_6H_5Br/C_6H_5F	1.1974	1.1802	1.189	1.5
C_6H_5I/C_6H_5F	1.2884	1.2772	1.282	0.9
C_6H_5Br/C_6H_5Cl	1.0589	1.0495	1.047	1.1
C_6H_5I/C_6H_5Cl	1.1394	1.1358	1.132	0.7
C_6H_5I/C_6H_5Br	1.0760	1.0822	1.080	0.6
C_6H_5/C_6H_5F	.9351	.9439	.946	1.2
CCl_4/C_6H_5F	.9861	1.0195	.993	3.4
$SnCl_4/C_6H_5F$	1.2771	1.2793	1.282	0.4
$(C_2H_5)_2O/C_6H_5F$	1.0468	1.0342	1.038	1.2
CH_3OH/C_6H_5F	.5203	.4228	.507	23.1
C_2H_5OH/C_6H_5F	.6537	.6153	.676	9.9
C_3H_7OH/C_6H_5F	.8533	.7995	.859	7.4
CH_3COOH/C_6H_5F	.8303	.6342	.593	40.0
C_2H_5OH/CH_3OH	1.2564	1.4534	1.329	15.7
C_3H_7OH/CH_3OH	1.6401	1.8890	1.693	15.2
C_3H_7OH/C_2H_5OH	1.3054	1.2999	1.274	2.5

For the halogen derivatives of benzene $p=p'$.

It will be seen that the differences between the three values are not very great, except in the comparisons of the three alcohols and acetic acid with fluorbenzene, and of ethyl and propyl alcohol with methyl alcohol. In the other cases, including the comparison of propyl with ethyl alcohol, the relation

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p}$$

may be considered as approximately true with the limitations already stated.

The two substances—methyl alcohol and acetic acid, and to a small extent ethyl and propyl alcohol—are clearly exceptional in their behaviour, and it is of interest to note, in comparing these substances with fluorbenzene, that while with acetic acid the ratios of the molecular volumes both of liquid and saturated vapour are very low, with methyl alcohol it is only in the liquid state that this is to be observed. This

may again point to the existence of complex molecules of acetic acid in both the liquid and gaseous states, but of methyl alcohol in the liquid state only, except possibly very near the critical point.

With ethyl and propyl alcohols the ratios of the molecular volumes of liquid to those of fluorbenzene are also low, though not nearly to the same extent as with methyl alcohol.

Note on the Determination of Critical Constants.

Of the three critical constants, temperature, pressure, and volume, the first is the most easily determined, for by employing as heating-agents the vapours of pure liquids boiling under known pressures, the temperature is perfectly under control and is easily measured. Moreover, the presence of a very small amount of impurity does not influence the critical temperature of a substance to nearly the same extent as the critical pressure.

The critical pressure may also as a rule be determined without very much difficulty, provided that absence of impurity is ensured, but this point is of the utmost importance. In the case of substances that attack mercury at high temperatures, such as carbon tetrachloride and stannic chloride, the ordinary method of operation requires modification, and the calculations become more laborious, but otherwise the difficulty is not greatly increased.

The determination of the critical volume of a substance, even when perfectly pure and without action on mercury,

Fig. 1.

Fig. 2.

is, however, a much more difficult matter. That this is so is evident from the form of the curves representing the relation

of the volumes of liquid and of saturated vapour to the temperature or pressure, as shown in the accompanying diagrams constructed from the results with ethyl alcohol.

A very small alteration of temperature, such as 0.1° , at or just below the critical point, produces a considerable alteration in the volume; therefore in order to obtain a direct reading of the critical volume it is necessary that the substance shall be exactly at its critical temperature.

I have assumed that a substance is in this state when on rapidly increasing the volume somewhat above the critical volume the fall of temperature due to the expansion causes a momentary separation of liquid and vapour.

In order to determine the critical volume, I note the position of this temporary mark of division and then diminish the volume slightly. After waiting a few minutes for the temperature to become constant again, I increase the volume very slightly but rapidly, and again note the position of the mark of division, which is now nearer to the top of the tube. Proceeding in this way it is possible under favourable conditions to make the substance occupy such a volume that a very slight but rapid expansion gives a temporary mark of division of liquid and vapour almost exactly at the top of the tube. This volume I take to be the critical volume, and I have succeeded in determining it directly in the case of benzene, fluorbenzene, and acetic acid; while with chlorobenzene, for which mercury vapour was employed as a jacket, it was only possible to obtain a rough approximation to the true volume on account of the slight unsteadiness of the temperature.

The critical volumes of the other substances may probably be ascertained with fair accuracy in the following manner:—

At low temperatures and pressures the ratios of the molecular volumes of liquid and saturated vapour of any one substance to those of fluorbenzene at corresponding temperatures and pressures differ somewhat widely as a rule, but as the critical point is approached the differences diminish and at the critical point itself all four values should, of course, be identical. It follows, therefore, that by mapping the ratios against temperature, four straight lines or curves should be obtained, which, when produced, should cut one another at the critical temperature, and the point of intersection should give the ratio of the molecular critical volume to that of fluorbenzene.

It will be seen from the accompanying diagrams, figs. 3 to 6, Plates II. & III., that in the case of benzene and acetic acid the four curves do very nearly cut one another at the critical temperature, and the ratios of the critical volumes thus

obtained agree very well with those calculated from the experimental results. The other substances will be considered in their order.

Halogen Derivatives of Benzene.—Accurate determinations of the volumes of liquid have been obtained only up to 280° , but the ratios are very nearly constant and are practically identical at corresponding temperatures and pressures; the extrapolation may therefore be considered justifiable. In the case of chlorobenzene a few approximate determinations have been made near the critical temperature; they give slightly higher ratios than those at lower temperatures, and agree rather more closely with the mean ratio of the absolute temperatures at corresponding (equal) pressures.

The molecular volumes of the saturated vapours give generally higher ratios than those of the liquid; this may be partly due to experimental error; but as the deviations are nearly all in the same direction, it seems hardly justifiable to attribute them entirely to this cause. It is evidently impossible to make use of these ratios in determining the critical volumes; but the mean ratios of the molecular volumes of liquid may probably be relied on to give fairly accurate results (Trans. Chem. Soc. lv. p. 517).

Carbon Tetrachloride.—As the observations extend to within a few degrees of the critical temperature, there does not seem to be much room for error.

Stannic Chloride.—The molecular volumes of saturated vapour cannot be made use of, as the results at the highest temperatures are a little doubtful owing to slight decomposition of the substance; considerable extrapolation would also be necessary. The ratios for the liquid state give, however, very nearly straight lines, which may therefore probably be extrapolated without much error.

Ether.—The four curves would evidently be very close together at the critical temperature, but as the results with the saturated vapour are somewhat irregular it seems best to rely only upon those with the liquid.

Methyl Alcohol.—In this case the curves for the liquid state do not seem to agree well with those for the saturated vapour; I have taken the mean value, but it is evidently open to some doubt.

Ethyl and Propyl Alcohols.—The agreement is better with these alcohols, but the volumes of saturated vapour are somewhat irregular near the critical point.

Acetic Acid.—The four curves meet very satisfactorily at the critical temperature.

The mean ratios of the molecular volumes to those of fluor-

benzene are given in the following Table, together with the molecular and specific critical volumes calculated from them, taking the observed critical volume of fluorbenzene as correct. For the sake of comparison the specific volumes directly observed and also those previously adopted by Ramsay and myself are given.

TABLE XXII.

Substance.	Mean Ratio.	Molecular Volume. Calculated.	Specific Volume.		
			Calculated.	Observed.	Ramsay and Young.
C_6H_5F	.....	.....	.....	2.43	.....
C_6H_5Cl	1.1246	262	2.34	2.34-2.45	.....
C_6H_5Br	1.1802	275	1.76	.....	.....
C_6H_5I	1.2772	298	1.47	.....	.....
C_6H_6	.944	220	2.83	2.82	.....
CCl_4	1.010	235	1.53	.....	.....
$SnCl_4$	1.290	301	1.16	.....	.....
$(C_2H_5)_2O$	1.047	244	3.30	.....	4.06
CH_3OH	.440	103	3.21	.....	3.7
C_2H_5OH	.620	144	3.15	.....	3.5
C_3H_7OH	.800	186	3.11	.....	3.6
CH_3COOH ...	.630	147	2.45	2.46	.....

It will be seen that the values for benzene and acetic acid, calculated from the mean ratios, agree very well with those directly observed, and this may be taken as evidence in favour of the accuracy of the method of direct measurement adopted. On the other hand, the calculated values for ether and the alcohols are considerably lower than those previously given by Ramsay and myself. But it may be pointed out that the critical temperature of ether was almost certainly slightly underestimated, owing to the employment of the vapour of methyl salicylate as a jacket. There is no reason to suspect any error in the determination of the critical pressure; and if the constants for Biot's formula be taken as correct, the calculated temperature corresponding to the critical pressure would be 194.4 instead of 193.8, and the higher value agrees well with a more recent determination by Ramsay, who in this case employed the vapour of quinoline as a jacket. The correction of the critical temperature of ether would give a lower value to the critical volume.

Again, Professor Tait has recently made an exhaustive mathematical investigation of the relations of pressure, temperature, and volume of several substances, including ether,

and he has pointed out that the critical temperature is probably a little higher than 193·8, and that the critical volume of this substance is certainly lower than 4 cubic centim., and is more probably about 3·5 cubic centim., a value that agrees fairly well with that calculated by the method described.

In the case of the alcohols the critical volumes given by Ramsay and myself were estimated by inspection of the curves representing the relation of the specific gravities of liquid and saturated vapour to the temperature, and of the specific volumes to the pressures, and they were admittedly only approximate values.

M. Guye has shown (*Comptes Rendus*, cxii. p. 1257) that an approximate relation exists between the critical temperature, pressure, and volume of a substance and its theoretical vapour-density compared with air. This is expressed by the equations

$$d = 1146 \frac{\delta\theta}{\pi(1070 + \theta)} = \frac{M}{28\cdot87};$$

where δ is the specific gravity at the critical point compared with water at 4°, θ the absolute critical temperature, π the critical pressure, and M the molecular weight. The critical volumes of ether and the alcohols previously given by Ramsay and myself are certainly in better agreement with this relation than those which I now find; but it may be mentioned that, with the exception of iodobenzene, all the substances referred to in this paper give somewhat higher values

of d than the quotient $\frac{M}{28\cdot87}$ if the molecular volumes in Table XXII. be taken as correct.

It may, I think, be safely stated that the true critical volumes are not lower than those directly observed, but it is possible that they may be a little higher. It is therefore perhaps too much to say that the values given in the table are definitely established, but I am inclined to think that they may be accepted as fairly close approximations to the truth.

If that is so, it would appear from Table XVII. that *the ratio of the actual critical density to the theoretical density is for very many substances about 4·4*. Ethyl and propyl alcohol give somewhat higher values, while for methyl alcohol and acetic acid, especially the latter, the ratios are extremely high.