

XV.—*The Molecular Volumes of the Saturated Vapours of Benzene and of its Halogen Derivatives.*

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IN a previous paper (Trans., 55, 1889, 486), an account was given of determinations of the molecular volumes of benzene and of its monohalogen derivatives in the liquid state, and it was pointed out that certain simple relations are to be observed between the boiling points, vapour pressures, and molecular volumes of the four substances fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene; when any one of these substances, however, is compared with benzene, the corresponding relations are not so simple.

Briefly recapitulated, the relations between the halogen derivatives of benzene are as follows:—

1. When the four substances are compared at their boiling points under equal pressures, these temperatures—on the absolute scale—and also the corresponding molecular volumes, bear a constant ratio to each other, whatever the pressure.

2. The critical pressures of fluorobenzene and chlorobenzene, and in all probability those also of bromobenzene and iodobenzene, are equal.

3. The relations of Van der Waals, as regards “corresponding” temperatures, pressures, and volumes of liquid hold good accurately in the case of the halogen derivatives of benzene, but since the critical pressures are equal, *corresponding* pressures are in this case *equal* pressures.

4. A comparison of benzene and fluorobenzene showed that whereas at corresponding pressures the boiling points, measured on the absolute scale, are far from showing a constant ratio to each other, yet when the molecular volumes of these substances are compared either at corresponding temperatures or at corresponding pressures, the ratios of the volumes are nearly constant, though the two methods of comparison are not equivalent and necessarily give somewhat different results.

It has been pointed out by Professor Orme Masson (*Phil. Mag.*, November, 1890) that when the halogen derivatives of similar hydrocarbons are compared together at their boiling points under normal pressure, their molecular volumes bear the same ratio to each other as the boiling points (expressed on the absolute scale), but that inorganic compounds, even when closely related, do not, as a rule, exhibit such simple relations.

In a short paper published in the same number of the *Phil. Mag.* (p. 423), I showed that Orme Masson's relation is really a special case of a more general one which should be applicable to all substances if the generalisations of Van der Waals were strictly true. This relation may be expressed as follows:—The molecular volumes of any two substances, both in the liquid state and as saturated vapour, at their boiling points under "corresponding" pressures *should be* directly proportional to their absolute critical temperatures and inversely proportional to their critical pressures; or

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

where V and V' are the molecular volumes of the liquids, v and v' the molecular volumes of their saturated vapours, T and T' the absolute critical temperatures, and p and p' the critical pressures.

When the critical pressures are equal (as in the case of the halogen derivatives of benzene, and possibly also of some of the groups of halogen compounds cited by Orme Masson), corresponding pressures become equal pressures, and we then have the simple law:—The molecular volumes of the members of any group of chemically related compounds whose critical pressures are equal, measured at their boiling points under any equal pressure, are directly proportional to their absolute critical temperatures, and therefore to their absolute boiling points under any equal pressures; or

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

The wider generalisation appears to be approximately true for the liquid state for nearly related substances whose critical pressures are different; in the case of benzene and fluorobenzene, for instance, the difference between the observed and calculated molecular volumes is very little over 1 per cent., but considerable differences are in some cases to be observed when the substances are not closely related, and even when the higher alcohols are compared with methyl alcohol.

The experimental work described in the present paper was undertaken in order to find whether the relations which have been shown to hold good for the molecular volumes of the liquids are also applicable to those of the saturated vapours.

The method employed was that recently described to the Society (this vol., p. 37), but, as the molecular volumes of the liquids had already been carefully determined, it was only necessary to measure the volume of liquid and of saturated vapour at each temperature when the whole tube was heated.

The ratio of the specific volume of the saturated vapour to that of the liquid at any temperature is given by the equation

$$r_T = \frac{V_c}{V_T - V'_T},$$

where V_T is the true volume of liquid, supposing all vapour to be condensed, and V_c and V'_T are the observed volumes of saturated vapour and of liquid. The values of V_T were calculated from the molecular volumes previously determined.

The observed values of V'_T were mapped and curves drawn through the points; the values read from these curves, which differed, however, very slightly from the observed values, were employed in the calculations.

The specific volumes of the saturated vapour are given by the equation $s_T = r_T \times S_T$, where S_T is the specific volume of the liquid at T° . The molecular volumes of the saturated vapours $= v_T = Ms_T$, where M is the molecular weight of the substance.

Before describing the results obtained, it may be well to point out the chief sources of error which are likely to occur.

1. *Errors of Reading*.—Since in the formula $r_T = \frac{V_c}{V_T - V'_T}$ the volume ratio r_T , and therefore the molecular volume depends on the difference between two volumes of liquid V_T and V'_T , any small error in the determination of either of these values will introduce a relatively large error in the calculated value of the molecular volume. It is important, therefore, to find what accuracy in reading has usually been attained, and to get some idea of the influence of the errors of reading on the molecular volumes.

A fair test of the accuracy attained is afforded by the determinations of the weights of the various quantities of liquid employed, for the weights were calculated in each case from the results of volume readings at several different temperatures, and therefore the differences of the individual values from the means afford the required data. There are in all 47 readings, giving nine weight determinations. The differences of the individual weight determinations from the mean values correspond to errors in reading of volume, and these errors are tabulated below.

TABLE I.

Number of readings.	Errors in reading.
1	between 0.15 and 0.2 mm.
1	„ 0.1 „ 0.15 „
5	„ 0.05 „ 0.1 „
40	less than 0.5 mm.

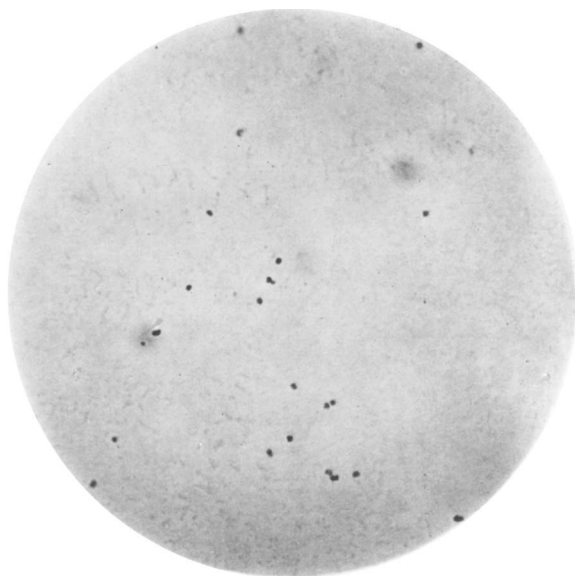
It will be seen, therefore, that the error of an individual reading is rarely so great as 0.1 mm.

In the tables of results, I have given in each case the percentage error in the molecular volume corresponding to an error of 0.1 mm. in the reading of the volume of liquid. These columns are headed E in the tables. Errors in the calibration of the tubes and in the previous determinations of the molecular volumes of the liquids would similarly affect the values of the molecular volumes of the saturated vapours.

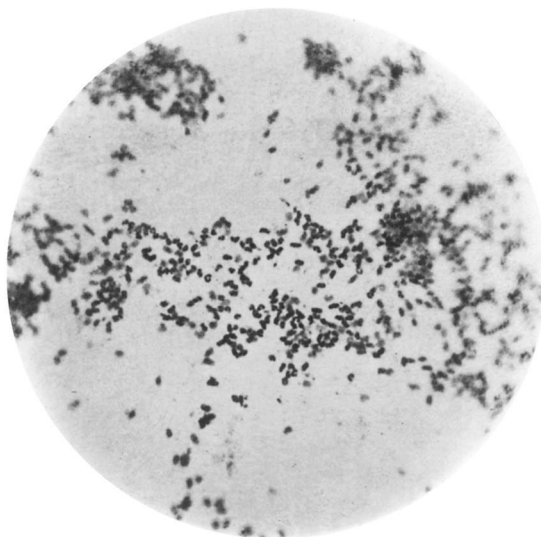
Effect of Air or permanent Gas in Tube.—Although the amount of saturated vapour in a given space is theoretically independent of the presence or absence of a permanent, indifferent gas, yet, in practice, there can be no doubt that the presence of such a gas does influence the results, inasmuch as it increases the time that elapses before the space above the liquid becomes completely saturated with vapour. To take an extreme case, suppose that the whole tube is at first at a constant temperature, t° , at which the vapour pressure of the liquid is extremely small and practically negligible; and that the tube is then raised to a much higher temperature, T° . Vapour will be evolved from the surface of the liquid, and, the tube being very narrow, the air will be driven forward and will occupy the upper part of the tube, the effect being at first the same as if the tube were shortened. The amount of vapour evolved will therefore be too small, and if readings are taken too quickly, the observed volume of liquid, V'_T , will be too great. In course of time, the air will diffuse through the vapour, and if there were no other disturbing factor a correct result would finally be obtained; but if saturated, or nearly saturated, vapour be allowed to remain for a considerable time at a constant temperature, there is danger of condensation taking place to a slight extent on the walls of the tube, and I have observed that the presence of a permanent gas tends to cause such condensation. Any variations of temperature, even if very minute, would increase this danger.

It is, therefore, of great importance that air should be expelled from the tube as completely as possible; and, in fact, one set of observations was rendered inaccurate owing to the incomplete expulsion of air. Moreover, bromobenzene appears to undergo slight decomposition at temperatures above 240° or 250° , a small amount of permanent gas being formed; and it was found that whereas up to 240° the readings of volume became constant almost immediately, at higher temperatures the alteration of volume did not cease until the tube had been kept at a constant temperature for from 10 to 20 minutes. The determinations of the molecular volumes of the saturated vapour of bromobenzene above 250° are also irregular and obviously inaccurate, a slight deviation from the curve being noticeable even at 250° .

NITROUS ORGANISM $\times 1000$.

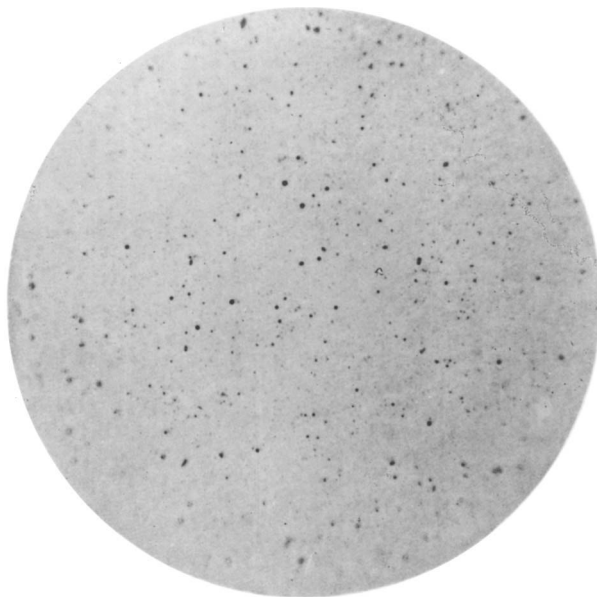


IN AMMONIUM CARBONATE SOLUTION.

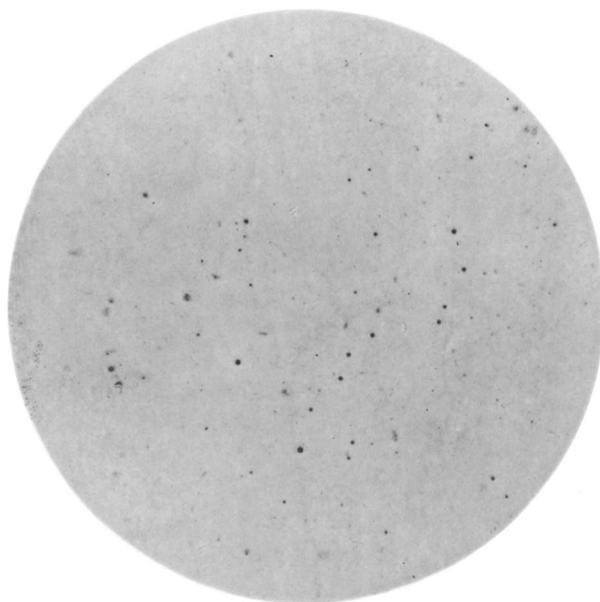


SUNK COVER-GLASS
IN AMMONIUM CARBONATE SOLUTION.

NITROUS ORGANISM $\times 1000$.

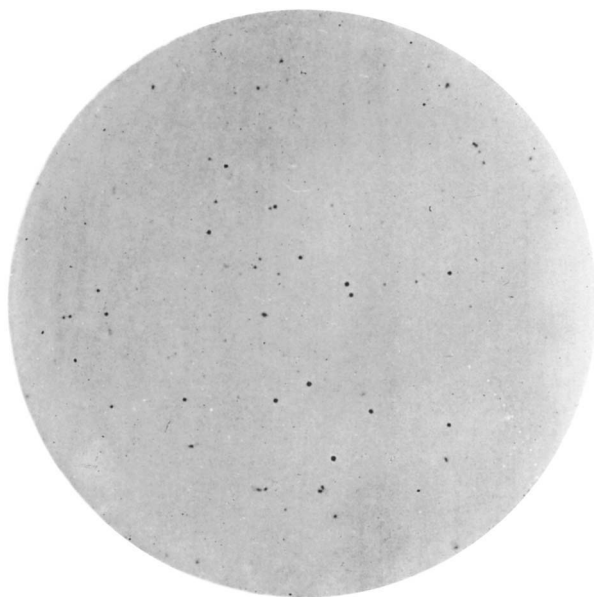


IN BEEF BROTH AT 22°.



IN HALF PER CENT. MILK AT 22°.

NITRIC ORGANISM $\times 1000$



IN POTASSIUM NITRITE SOLUTION.

Effect of Impurity of Jacketing Vapour.—If the substance employed to heat the tube were impure, the temperature of its vapour would be higher at the bottom than at the top of the tube. Such a difference of temperature, even if very slight, would cause evaporation of liquid in the volume tube and condensation in the upper part of the tube. This would make it quite impossible to obtain accurate results, but errors due to this cause could hardly fail to be detected, and they were certainly absent from my results.

Two tubes were employed in these experiments: in the first, A, the volume of saturated vapour was from 8 to 12 times as great as that of the liquid; in the second, B, the volume of saturated vapour was about twice as great as that of the liquid. The volumes of liquid were read at 0° and at two or three temperatures between 8° and 15°, and, after correction, when necessary, for the small amount of substance present as saturated vapour, the weights were calculated from the known molecular volumes of the liquid at the observed temperatures. The weight determinations are given in the table below.

Substance.	Tube.	Temp.	Volume of liquid.	Molecular volume.	Weight.
Fluorbenzene....	A	0·0°	·2000	91·54	·2093
„		8·5	·2020	92·45	·2093
„		11·1	·2025	92·73	·2092
„		12·3	·2028	92·85	·2093
„		14·5	·2032	93·08	·2091
					Mean.. ·20924
Fluorbenzene....	B	0·0°	·3869	91·54	·4050
„		10·45	·3915	92·65	·4048
„		11·9	·3924	92·82	·4050
					Mean.. ·40493
Chlorobenzene...	A	7·3°	·1845	100·18	·2067
„ ...		8·25	·1846	100·27	·2066
„		10·7	·1850	100·51	·2065
„		11·2	·1851	100·56	·2065
„		13·4	·1855	100·77	·2066
					Mean.. ·20660
Chlorobenzene...	B	0·0°	·3681	99·48	·4152
„		10·8	·3720	100·50	·4153
„		11·7	·3722	100·58	·4152
„		12·8	·3734	100·70	·4160
„		14·0	·3734	100·81	·4156
					Mean.. ·41530*

* The observation at 12·8° was omitted in calculating the mean weight.

Substance.	Tube.	Temp.	Volume of liquid.	Molecular volume.	Weight.
Bromobenzene ...	A	0·0°	·2408	102·90	·3665
"		9·55	·2430	103·76	·3667
"		11·7	·2432	103·96	·3663
"		12·2	·2433	104·00	·3663
" ..		13·7	·2435	104·13	·3662
"		14·75	·2437	104·23	·3662
"		15·35	·2439	104·30	·3662
					Mean.. ·36635
Bromobenzene ...	B	0·0°	·3395	102·90	·5167
"		8·8	·3422	103·69	·5168
"		12·5	·3434	104·04	·5169
"		14·5	·3440	104·21	·5169
					Mean.. ·51682
Iodobenzene	A	5·0°	·1870	109·75	·3466
"		6·7	·1870	109·90	·3461
"		7·6	·1872	109·98	·3463
"		8·2	·1872	110·03	·3461
"		9·3	·1874	110·13	·3462
"		9·8	·1875	110·17	·3463
"		9·8	·1876	110·17	·3464
"		10·6	·1878	110·25	·3464
					Mean.. ·34630
Benzene	A	0·0°	·1892	86·48	·1703
"		7·3	·1907	87·23	·1702
"		11·3	·1918	87·67	·1703
"		13·4	·1921	87·88	·1702
"		14·6	·1923	87·99	·1701
					Mean.. ·17022
Benzene	B	0·0°	·3363	86·48	·3027
"		6·9	·3394	87·19	·3030
"		9·5	·3403	87·46	·3029
"		10·6	·3407	87·57	·3028
"		12·0	·3413	87·73	·3028
					Mean.. ·30284

The actual determinations of the molecular volumes of the saturated vapours are given in the following tables. The data given are—

T. The temperature of the tube.

V_c. The observed volume of vapour.

V_T. The true volume of liquid, supposing all vapour to be condensed. These values were calculated from the known specific volumes of the liquids.

OF THE SATURATED VAPOURS OF BENZENE, ETC. 131

V'_T . The observed volume of liquid.

r_T . The ratio of the specific volume of saturated vapour to that of liquid at T° .

v_T . The molecular volume of the saturated vapour at T° .

E. The percentage error corresponding to a hypothetical error of 0.1 mm. in the reading of volume.

$T^\circ \text{C.}$	$V_{\text{c.}}$ c.c.	V_T c.c.	V'_T c.c.	r_T	v_T c.c.	E. p.c.
Fluorbenzene. Tube A.						
80	2.3374	.2204	.2133	329.0	33200	3.1
90	2.3377	.2234	.2138	244.0	24900	2.3
100	2.3383	.2266	.2139	184.0	19100	1.8
110	2.3396	.2299	.2132	140.0	14750	1.3
120	2.3418	.2355	.2117	107.5	11500	1.0
130	2.3448	.2374	.2093	83.5	9070	0.8
140	2.3490	.2414	.2058	66.0	7290	0.6
150	2.3544	.2456	.2010	52.8	5940	0.5

Fluorbenzene. Tube B.

130	.8883	.4594	.4486	82.30	8940	3.5
140	.8839	.4672	.4534	64.10	7080	2.7
150	.8794	.4753	.4582	51.40	5780	2.2
160	.8749	.4841	.4631	41.70	4770	1.8
170	.8704	.4936	.4680	34.00	3970	1.5
180	.8659	.5038	.4728	27.95	3330	1.2
190	.8621	.5153	.4770	22.50	2745	1.0
200	.8583	.5277	.4811	18.42	2300	0.8
210	.8548	.5415	.4849	15.10	1935	0.7
220	.8519	.5573	.4882	12.33	1626	0.6
230	.8501	.5755	.4903	9.98	1359	0.5
240	.8492	.5966	.4916	8.09	1141	0.4
250	.8503	.6228	.4908	6.44	949	0.3
260	.8548	.6566	.4866	5.03	781	0.2
270	.8684	.7057	.4734	3.74	624	0.2
275	.8838	.7414	.4582	3.12	547.5	0.1
280	.9172	.7891	.4249	2.52	470.2	0.1

Chlorobenzene. Tube A.

130	2.4297	.2099	.2015	289.0	33000	2.6
140	2.4303	.2125	.2017	225.0	26000	2.0
150	2.4312	.2152	.2015	177.0	20700	1.6
160	2.4328	.2179	.2006	141.0	16600	1.3
170	2.4351	.2208	.1990	112.0	13400	1.0
180	2.4380	.2239	.1968	90.0	10900	0.8
190	2.4417	.2272	.1938	73.1	9020	0.6
200	2.4464	.2307	.1897	59.7	7480	0.5
210	2.4529	.2344	.1839	48.6	6180	0.4

T° C.	V _c c.c.	V _T c.c.	V' _T c.c.	τ_T	ν_T c.c.	E. p.c.
Chlorobenzene. Tube B.						
160	·9050	·4381	·4317	141·00	16700	5·9
170	·9010	·4439	·4360	114·00	13700	4·9
180	·8971	·4501	·4403	91·00	11100	3·9
190	·8931	·4567	·4416	74·00	9100	3·2
200	·8892	·4637	·4489	60·00	7500	2·6
210	·8853	·4712	·4531	49·00	6200	2·1
220	·8816	·4790	·4572	40·50	5250	1·7
230	·8777	·4875	·4614	33·60	4430	1·5
240	·8740	·4968	·4654	27·80	3740	1·2
250	·8705	·5068	·4693	23·20	3180	1·0
260	·8674	·5179	·4727	19·20	2680	0·8
270	·8645	·5301	·4759	15·95	2280	0·7
275	·8634	·5339	·4772	14·45	2100	0·7
280	·8622	·5440	·4786	13·18	1938	0·6

Bromobenzene. Tube A.

160	2·2780	·2819	·2726	247·0	29800	2·4
170	2·2978	·2852	·2735	196·0	23900	1·9
180	2·2980	·2886	·2740	157·0	19400	1·5
190	2·2987	·2922	·2740	126·0	15800	1·2
200	2·3000	·2960	·2734	102·0	12900	1·0
210	2·3015	·3000	·2725	83·7	10700	0·8
220	2·3039	·3042	·2708	69·0	8970	0·7
230	2·3071	·3087	·2683	57·1	7540	0·5
240	2·3115	·3134	·2645	47·3	6330	0·4

Bromobenzene. Tube B.

190	·9511	·4123	·4049	129·0	16100	5·1
200	·9479	·4176	·4085	104·0	13200	4·2
210	·9447	·4232	·4120	84·0	10800	3·4
220	·9414	·4292	·4157	70·0	9070	2·8
230	·9383	·4354	·4191	57·5	7600	2·3
240	·9355	·4421	·4223	47·2	6330	1·9
250	·9330	·4491	·4251	38·9	5290	1·6
260	·9308	·4569	·4276	31·8	4400	1·3
270	·9290	·4653	·4298	26·2	3700	1·1
280	·9272	·4746	·4319	21·7	3120	0·9

Iodobenzene. Tube A.

190	2·3756	·2214	·2124	264·0	34300	2·5
200	2·3759	·2239	·2127	212·0	27900	1·9
210	2·3766	·2264	·2126	172·0	22900	1·6
220	2·3779	·2290	·2121	141·0	18900	1·3
230	2·3796	·2317	·2111	115·5	15700	1·1
240	2·3816	·2345	·2097	96·0	13200	0·9
250	2·3845	·2375	·2074	79·2	11050	0·7
260	2·3885	·2407	·2041	65·3	9230	0·6
270	2·3932	·2441	·2000	54·3	7780	0·5
280	2·3987	·2478	·1952	45·6	6640	0·4

T° C.	V _c . c.c.	V _T . c.c.	V' _T . c.c.	τ_T .	v_T . c.c.	E. p.c.
Benzene. Tube A.						
80	2·3875	·2090	·2010	298·0	28500	2·8
90	2·3881	·2118	·2012	225·0	21800	2·0
100	2·3894	·2148	·2007	169·0	16600	1·6
110	2·3910	·2180	·1995	129·0	12900	1·2
120	2·3938	·2214	·1975	100·0	10100	0·9
130	2·3972	·2249	·1947	79·4	8160	0·7
140	2·4021	·2288	·1905	62·7	6560	0·6
150	2·4082	·2328	·1851	50·5	5370	0·5
Benzene. Tube B.						
140	·9153	·4070	·3926	63·60	6650	2·6
150	·9119	·4142	·3963	50·90	5420	2·1
160	·9086	·4215	·3999	42·10	4560	1·8
170	·9057	·4296	·4032	34·30	3790	1·4
180	·9031	·4385	·4061	27·90	3140	1·2
190	·9011	·4481	·4085	22·70	2620	1·0
200	·8997	·4585	·4102	18·65	2195	0·8
210	·8989	·4703	·4113	15·23	1842	0·6
220	·8989	·4838	·4117	12·47	1550	0·5
230	·9003	·4994	·4107	10·15	1303	0·4
240	·9038	·5176	·4075	8·21	1092	0·3
250	·9107	·5399	·4009	6·55	909	0·2
260	·9229	·5684	·3890	5·14	751	0·2
270	·9494	·6076	·3629	3·88	606	0·2
275	·9727	·6344	·3397	3·30	538	0·1
279·65	1·0117	·6676	·3009	2·76	473	0·1

The molecular volumes of saturated vapour do not lend themselves to graphical representation; but the logarithms of these values, mapped against the temperature, give serviceable curves. These were accordingly drawn, and the smoothed values for each 10° read off. They are given in the following table:—

Molecular Volumes of Saturated Vapours from Curves.

Temp.	Fluor- benzene.	Chloro- benzene.	Bromo- benzene.	Iodo- benzene	Benzene.
80°	33200	—	—	—	28600
90	25000	—	—	—	21800
100	19000	—	—	—	16600
110	14700	—	—	—	12900
120	11500	—	—	—	10200
130	9080	32900	—	—	8180
140	7250	26000	—	—	6630
150	5860	20800	—	—	5420
160	4810	16600	29800	—	4490
170	3970	13500	23900	—	3730
180	3290	11000	19400	—	3130
190	2740	9050	15800	33800	2615
200	2290	7480	13000	27800	2195
210	1928	6240	10800	22900	1850
220	1622	5230	8950	19000	1552
230	1361	4410	7530	15700	1302
240	1140	3740	6310	13100	1091
250	950	3170	5350	11000	910
260	781	2690	4570	9250	650
270	624	2280	3900	7810	705
280	471	1940	3300	6620	469

These values agree very well with those observed with the exception of the volumes of bromobenzene at temperatures above 250°. These were inaccurate, for reasons already stated (p. 128), and the curve above 250° was therefore extrapolated. The error at 280° amounts to 5.5 per cent.

The molecular volumes of the saturated vapours at the boiling points of the substances under "corresponding" pressures (which, for the halogen derivatives, are equal pressures) were then read from the curves, and are given in the following table:—

Pressures.		Temperatures.					Molecular volumes of saturated vapour.				
Halogen derivatives.	Benzene.	C ₆ H ₅ F.	C ₆ H ₅ Cl.	C ₆ H ₅ Br.	C ₆ H ₅ I.	C ₆ H ₆ .	C ₆ H ₅ F.	C ₆ H ₅ Cl.	C ₆ H ₅ Br.	C ₆ H ₅ I.	C ₆ H ₆ .
1000	1073	94·3	142·4	167·05	200·5	91·95	22300	24600	25500	27500	20500
1500	1610	109·0	159·2	184·8	219·45	106·85	15100	17000	17500	19200	13900
2000	2146	120·25	172·0	198·3	234·0	118·3	11400	13030	13450	14600	10560
3000	3220	137·4	191·6	219·0	256·0	135·9	7670	8760	9150	9910	7230
4000	4293	150·8	206·9	234·95	272·65	149·5	5750	6600	6910	7460	5480
5000	5366	161·85	219·45	248·95	—	160·75	4630	5280	5530	—	4420
6000	6439	171·25	230·0	259·1	—	170·5	3870	4410	4630	—	3690
8000	8586	187·4	247·95	277·9	—	186·8	2870	3280	3450	—	2770
10000	10732	200·6	262·35	—	—	200·3	2265	2575	—	—	2183
12000	12879	211·95	274·75	—	—	212·0	1862	2106	—	—	1782
15000	16098	226·7	—	—	—	227·05	1447	—	—	—	1371
20000	21464	246·7	—	—	—	247·5	1009	—	—	—	953
25000	26831	263·0	—	—	—	264·1	733	—	—	—	689
30000	32197	277·0	—	—	—	278·6	516	—	—	—	489
33912	36395	286·55	—	—	—	288·5	233*	—	—	—	219*

* From previous results with the liquids ; direct readings.

The ratios of the molecular volumes at corresponding pressures are given in the table below.

Ratios of Molecular Volumes of Saturated Vapours at Corresponding Pressures.

Pressures.		Ratios.						
Halogen derivatives.	Benzene.	$\frac{C_6H_5Cl}{C_6H_5F}$	$\frac{C_6H_5Br}{C_6H_5F}$	$\frac{C_6H_5I}{C_6H_5F}$	$\frac{C_6H_5Br}{C_6H_5Cl}$	$\frac{C_6H_5I}{C_6H_5Cl}$	$\frac{C_6H_5I}{C_6H_5Br}$	$\frac{C_6H_6}{C_6H_5F}$
1000	1073	1.105	1.145	1.235	1.035	1.120	1.080	0.925
1500	1610	1.125	1.160	1.270	1.035	1.130	1.095	0.925
2000	2146	1.135	1.180	1.280	1.040	1.130	1.090	0.930
3000	3220	1.145	1.195	1.295	1.045	1.130	1.085	0.945
4000	4293	1.145	1.200	1.295	1.045	1.130	1.080	0.955
5000	5366	1.140	1.195	—	1.045	—	—	0.955
6000	6439	1.140	1.195	—	1.050	—	—	0.955
8000	8586	1.145	1.205	—	1.050	—	—	0.965
10000	10732	1.140	—	—	—	—	—	0.965
12000	12879	1.130	—	—	—	—	—	0.955
15000	16098	—	—	—	—	—	—	0.945
20000	21464	—	—	—	—	—	—	0.945
25000	26831	—	—	—	—	—	—	0.940
30000	32197	—	—	—	—	—	—	0.945
33312	36395	—	—	—	—	—	—	0.940
Mean ratios ..		1.140	1.195	1.290	1.046	1.130	1.085	0.949

With the exception of the comparisons at the lowest pressures, it is evident that the molecular volumes of the saturated vapours bear an approximately constant ratio to each other at all corresponding pressures. In calculating the mean ratios, the results at 1000 and 1500 mm. have been omitted on account of the relatively large errors involved in their determinations.

It has been already pointed out that if Van der Waals' generalisations were strictly true, the following relation should hold good:—

$$\frac{V}{V'} = \frac{v}{v'} = \frac{T}{T'} \cdot \frac{p'}{p}.$$

Or in the case of the halogen derivatives of benzene, the critical pressures of which are equal, the simpler relation

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

In the following table, the mean ratios of the observed molecular

volumes, both of the liquids V/V' and of the saturated vapours v/v' , are compared with those calculated from the above formulæ. In the case of the halogen derivatives, the ratios T/T' are the mean ratios of the boiling points (on the absolute scale) at equal pressures. For benzene and fluorobenzene, the absolute critical temperatures are taken.

Substances compared.	$\frac{T}{T'}$	$\frac{T}{T'} \cdot \frac{p'}{p}$	Mean ratios of molecular volumes at corresponding pressures.	
			Liquids.	Saturated vapours.
C_6H_5Cl/C_6H_5F	1·1308	—	1·1244	1·140
C_6H_5Br/C_6H_5F	1·1974	—	1·1800	1·195
C_6H_5I/C_6H_5F	1·2884	—	1·2772	1·290
C_6H_5Br/C_6H_5Cl	1·0589	—	1·0494	1·046
C_6H_5I/C_6H_5Cl	1·1394	—	1·1359	1·130
C_6H_5I/C_6H_5Br	1·0760	—	1·0824	1·085
C_6H_6/C_6H_5F	—	0·9351	0·9435	0·949

It will be seen that the three ratios are in each case approximately equal, the greatest differences being between the ratios of the molecular volumes of liquid and saturated vapour in the first comparison, and between the ratio of the molecular volumes of the saturated vapour and the value $T/T' \times p'/p$ in the last. Both these differences are, however, under 1·5 per cent.

In conclusion, it may be pointed out that—assuming the truth of Van der Waals' generalisations—the ratio of the actual density of the saturated vapour to the theoretical density ($\frac{1}{2}$ molecular weight) should be the same for all stable substances at their boiling points under corresponding pressures.

For the vapour density of a substance is the ratio of its weight to that of the same volume of hydrogen at the same temperature and pressure; and if for any saturated vapour the volume taken (in c.c.) is the molecular volume (v), then the weight of substance will be its molecular weight M (in grams). Calling the boiling point on the absolute scale T and the pressure p , we have

$$\text{Density of saturated vapour} = \frac{M}{0\cdot0000896 \times v \times \frac{273}{T} \times \frac{p}{760}},$$

and since the theoretical vapour density = $M/2$, the ratio of the actual to the theoretical vapour density will be

$$R = \frac{2 \times 760}{0\cdot0000896 \times 273} \times \frac{T}{vp} = c \frac{T}{vp}.$$

Pressures.		Densities of saturated vapours ($H = 1$ at same temperature and pressure).					Ratio of actual to theoretical vapour density at corresponding pressures.				
Halogen derivatives.	Benzene.	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$
1000	1073	49.12	58.86	84.07	108.6	40.06	1.025	1.042	1.074	1.088	1.029
1500	1610	50.20	59.21	84.77	108.3	40.96	1.048	1.056	1.083	1.065	1.052
2000	2146	51.33	60.00	85.39	109.7	41.68	1.072	1.070	1.091	1.079	1.071
3000	3220	53.13	61.63	87.19	112.5	42.49	1.109	1.099	1.114	1.106	1.092
4000	4293	54.80	63.38	89.41	115.5	43.41	1.144	1.130	1.142	1.136	1.115
5000	5366	55.86	65.05	91.74	—	44.25	1.166	1.159	1.172	—	1.137
6000	6439	56.88	66.26	93.21	—	45.09	1.188	1.181	1.190	—	1.159
8000	8586	59.74	69.19	97.08	—	46.70	1.247	1.233	1.240	—	1.200
10000	10732	62.25	72.44	—	—	48.81	1.300	1.291	—	—	1.254
12000	13879	64.60	75.55	—	—	51.10	1.349	1.347	—	—	1.313
15000	16098	68.52	—	—	—	54.80	1.431	—	—	—	1.408
20000	21461	76.64	—	—	—	61.55	1.600	—	—	—	1.582
25000	26831	87.08	—	—	—	70.30	1.818	—	—	—	1.806
30000	32197	105.70	—	—	—	84.84	2.206	—	—	—	2.180
33912	36395	210.60	—	—	—	170.2	4.397	—	—	—	4.374

For any other substance at its boiling point under the corresponding pressure p' , the ratio of the actual to the theoretical vapour density is $R' = c \frac{T'}{v'p'}$.

But it has been already shown that for any two substances at corresponding pressures p and p'

$$\frac{v}{v'} = \frac{T}{T'} \cdot \frac{p'}{p}, \quad \text{or} \quad \frac{T}{vp} = \frac{T'}{v'p'}; \quad \text{therefore} \quad R = R'.$$

As this is a very convenient method of comparing the saturated vapours of different substances, I have calculated the densities of the saturated vapours at the "corresponding" pressures which have already served as the basis of comparison, and also the ratios to the theoretical vapour densities.

The results are given in the table (p. 138):—

At pressures above 1500 mm. there is a remarkably close agreement between the four halogen derivatives; the larger differences in the ratios at the lowest pressures may be due, in part at any rate, to errors of experiment. With regard to benzene and fluorbenzene, the general agreement throughout, even including the direct observations at the critical points, is very striking; the differences, however, which reach a maximum of nearly 4 per cent. at a pressure of 8000 mm., cannot be explained by experimental errors, and are certainly real.

The results obtained may be summarised as follow:—

1. The molecular volumes of the saturated vapours of benzene and its halogen derivatives bear an approximately constant ratio to each other at all "corresponding" pressures.

2. The molecular volumes of the saturated vapours of these substances at their boiling points under "corresponding" pressures are, approximately, directly proportional to their absolute critical temperatures, and inversely proportional to their critical pressures.

3. The ratios of the actual densities of the saturated vapours (compared with hydrogen at the same temperature and pressure) to the normal vapour densities ($\frac{1}{2}$ molecular weight) are approximately equal for these substances at their boiling points under "corresponding" pressures.

4. The critical pressures of the halogen derivatives being equal, "corresponding" pressures are equal pressures. For these substances the deviations from constancy are small, and may be due to errors of experiment. In the comparisons of benzene with fluorbenzene, however, the deviations, though not very great, are certainly not entirely due to experimental error.

The first two relations have already been found to hold for the molecular volumes of the liquids.