



XVI. On orthobaric volumes in relation to pressure and temperature

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XVI. *On Orthobaric Volumes in relation to Pressure and Temperature.* By EDWARD HAIGH, M.A., B.Sc., Senior Master at Monkton Combe School, near Bath *.

[Plates VI. & VII.]

Introduction.

MANY years ago, in connexion with an attempt to obtain a corrected form of van der Waals's equation, the writer commenced a detailed study of the particular case in which a liquid is in equilibrium with its saturated vapour. It is evident from the numerous theorems which have been formulated relating to "corresponding states," that those properties of a substance which depend upon the relations of pressure, temperature, and volume are intimately connected with the values of the three critical constants. Reduced data have accordingly been employed almost exclusively in this paper, the primary aim of the investigation being to ascertain whether any equation could be found connecting pressure, temperature, and volume without the employment of any other constants than simple functions of the critical values of these variables. The problem has long baffled solution, but recently it has been found possible to formulate an equation of the desired type which is in substantial agreement with the results of experiment. On a pressure-volume diagram, the equation connects the coordinates of two isobaric points on each isothermal below the critical point. Since no attempt has been made to take account of the anomalies due directly to polymerization, the equations given below have

* Communicated by Professor Young, F.R.S.

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only reference to that class of substances in which no marked degree of polymerization is apparent.

§ 1. *On a Reduced Equation connecting Orthobaric Volumes with Pressure and Temperature.*

The fundamental proposition which it is the object of this article to establish may be stated as follows :—

The orthobaric volumes of all “normal” substances are connected with vapour-pressures and temperatures of ebullition by the reduced equation

$$\left\{ \pi + (1 - \theta) \left(\frac{1}{\phi\psi} - \pi \right) + \frac{3}{\phi^2} \right\} (3\phi - 1) + \left\{ \pi + (1 - \theta) \left(\frac{1}{\phi\psi} - \pi \right) + \frac{3}{\psi^2} \right\} (3\psi - 1) = 16\theta \quad (1)$$

In the above equation π , θ represent reduced vapour-pressure and temperature, ϕ , ψ are respectively the reduced volumes of the saturated vapour and of the liquid.

Essentially, the equation is a dual form of van der Waals's reduced equation, for if the function $(1 - \theta) \left(\frac{1}{\phi\psi} - \pi \right)$ is removed, it becomes

$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) + \left(\pi + \frac{3}{\psi^2} \right) (3\psi - 1) = 16\theta \quad (2)$$

This latter equation, though approximately true, does not exhibit the close agreement with experimental results which will be shown to be a characteristic feature of equation (1).

At the critical point $(1 - \theta) \left(\frac{1}{\phi\psi} - \pi \right)$ vanishes, and since $\phi = \psi$ the equation reduces to van der Waals's well known form.

Since equation (1), or any of the forms in which it can be expressed, connects the properties of two phases of the same substance, it will be referred to as the “dual” equation.

The introduction of the function $(1 - \theta) \left(\frac{1}{\phi\psi} - \pi \right)^*$ is due to an attempt to take account of the interacting forces between a liquid and its saturated vapour at the surface of separation. It may be well to state at once that the equation obtained must be regarded as an empirical result, since the method of investigation has been necessarily tentative, though with some guidance from theoretical considerations in the selection of the functions employed.

* See paper “On the Variation of Molecular Surface Energy with Temperature,” by W. Ramsay, F.R.S., and Dr. J. Shields, *Phil. Trans.* vol. 184 A. p. 647. (The factor $1 - \theta$ corresponds to τ , the temperature from the critical point measured downwards.)

$$\begin{aligned} & \left\{ \pi + \left(\frac{1}{\theta} - 1 \right) \frac{1}{\phi \psi} + \frac{3}{\theta \phi^2} \right\} (3\phi - 1) \\ & + \left\{ \pi + \left(\frac{1}{\theta} - 1 \right) \frac{1}{\phi \psi} + \frac{3}{\theta \psi^2} \right\} (3\psi - 1) \\ & = 16 \end{aligned} \quad (3)$$
$$F(\phi, \psi) = \left\{ \pi + \left(\frac{1}{\theta} - 1 \right) \frac{1}{\phi\psi} + \frac{3}{\theta\phi^2} \right\} (3\phi - 1),$$
$$F(\psi, \phi) = \left\{ \pi + \left(\frac{1}{\theta} - 1 \right) \frac{1}{\phi\psi} + \frac{3}{\theta\psi^2} \right\} (3\psi - 1),$$
$$F(\phi, \psi) + F(\psi, \phi) = 16 \quad . \quad . \quad . \quad (4)$$
$$\Sigma = 16.$$
$$\pi = \frac{p}{p_0}, \quad \theta = \frac{t}{t_0}, \quad \phi = \frac{v}{v_0}, \quad \psi = \frac{u}{v_0},$$

Equation (1) thus transformed becomes

$$\begin{aligned} & \left\{ \frac{p}{p_0} + \left(1 - \frac{t}{t_0}\right) \left(\frac{v_0^2}{vu} - \frac{p}{p_0} \right) + \frac{3v_0^2}{v^2} \right\} \left(\frac{3v}{v_0} - 1 \right) \\ & + \left\{ \frac{p}{p_0} + \left(1 - \frac{t}{t_0}\right) \left(\frac{v_0^2}{vu} - \frac{p}{p_0} \right) + \frac{3v_0^2}{u^2} \right\} \left(\frac{3u}{v_0} - 1 \right) \\ & = 16 \frac{t}{t_0}. \end{aligned}$$

In compiling these tables the values of the invariant function, which forms the left-hand side of equation (3), have been calculated for various substances from the experimental data supplied by the researches of Young, Ramsay, and their collaborators.

For the sake of comparison, tables for methyl alcohol and

propyl alcohol have been added. Ramsay has proved that these alcohols are polymerized in the liquid state to a high degree, and it will be seen that the agreement of the dual equation with the experimental values is in these cases less precise. In some of the tables the reduced data have been given in full, but where this is not the case, the reduced pressure has been tabulated for convenience of reference, and Young's published papers will supply the remaining data.

A short table has also been annexed giving the critical constants employed in obtaining reduced data, where such results have been directly calculated by the writer from values given in another form.

TABLE I.—*Fluorbenzene.*

	π .	θ .	ϕ .	ψ .	$\Sigma=16$.	Deviation.
1	·0295	·6565	81·36	·3805	15·92	—·08
2	·0442	·6827	55·47	·3887	15·99	—·01
3	·0590	·7028	42·16	·3957	15·98	—·02
4	·0885	·7335	28·40	·4069	16·02	+·02
5	·1179	·7574	21·39	·4166	16·01	+·01
6	·1474	·7771	17·14	·4252	16·01	+·01
7	·1769	·7940	14·26	·4329	15·98	—·02
8	·2064	·8092	12·20	·4406	16·00
9	·2359	·8228	10·62	·4482	16·04	+·04
10	·2949	·8464	8·376	·4624	16·02	+·02
11	·3539	·8667	6·886	·4763	16·02	+·02
12	·4423	·8930	5·352	·4979	16·04	+·04
13	·5898	·9288	3·731	·5365	16·02	+·02
14	·7372	·9579	2·711	·5858	15·98	—·02
15	·8256	·9731	2·223	·6263	15·95	—·05
16	·8846	·9830	1·908	·6635	15·82	—·18
17	·9436	·9919	1·627	·7138	15·87	—·13
Mean value ...					15·98	

TABLE II.—*Isopentane.*

	π .	$\Sigma=16$.	Deviation.
1	·0224	15·95	—·05
2	·04423	15·95	—·05
3	·08847	15·99	—·01
4	·14744	16·04	+·04
5	·2064	15·99	—·01
6	·2949	16·02	+·02
7	·44232	16·00
8	·5898	16·00
9	·7372	15·95	—·05
10	·8257	15·95	—·05
11	·8846	16·01	+·01
12	·9436	15·98	—·02
13	·9731	16·00
Mean	 15·986	

TABLE III.—Benzene and other Hydrocarbons.

	π .	Benzene.		<i>n</i> -Pentane.		Di-isopropyl.		<i>n</i> -Hexane.		Di-isobutyl.		<i>n</i> -Octane.		Hexamethylene.	
		Σ .	Deviation.	Σ .	Deviation.	Σ .	Deviation.	Σ .	Deviation.	Σ .	Deviation.	Σ .	Deviation.	Σ .	Deviation.
1...	·044232	15·85	—·15	15·81	—·19	16·11	+·11	15·77	—·23	15·45	—·55	15·17	—·83	16·14	+·14
2...	·088465	16·00	...	15·98	—·02	16·12	+·12	15·84	—·16	15·51	—·49	15·52	—·48	16·03	+·03
3...	·14744	16·10	+·10	15·94	—·06	16·08	+·08	16·00	...	15·73	—·27	15·75	—·25	16·13	+·13
4...	·20642	16·14	+·14	15·95	—·05	16·10	+·10	16·00	...	15·84	—·16	15·83	—·17	16·11	+·11
5...	·29488	16·12	+·12	15·98	—·02	16·06	+·06	16·00	...	15·87	—·13	15·87	—·13	16·02	+·02
6...	·44232	16·04	+·04	15·99	—·01	16·02	+·02	15·98	—·02	15·90	—·10	15·89	—·11	16·03	+·03
7...	·58978	15·96	—·04	15·97	—·03	15·98	—·02	15·95	—·05	15·94	—·06	15·92	—·08	15·98	—·02
8...	·78721	16·07	+·07	15·93	—·07	15·99	—·01	15·94	—·06	15·95	—·05	15·91	—·09	15·98	—·02
9...	·82568	15·95	—·05	15·95	—·05	15·97	—·03	15·96	—·04	15·92	—·08	15·94	—·06	15·99	—·01
10...	·88465	15·97	—·03	15·96	—·04	15·97	—·03	15·96	—·04	15·95	—·05	15·97	—·03
11...	·94363	15·97	—·03	15·98	—·02	15·97	—·03	15·96	—·04	15·97	—·03
12...	·97313	15·99	—·01	16·00	...	16·00	15·99	—·01
Means ...		16·02	...	15·95	...	16·03	...	15·95	...	15·82	...	15·76	...	16·03	...

TABLE IV.
Carbon Tetrachloride.

	π .	θ .	ϕ .	ψ .	Σ .	Deviation.
1	·04263	·6707	54·20	·3876	15·77	—·23
2	·06995	·7067	34·02	·3998	15·85	—·15
3	·1090	·7426	22·40	·4133	15·97	—·03
4	·1621	·7786	15·23	·4282	15·97	—·03
5	·2311	·8145	10·59	·4457	15·95	—·05
6	·3200	·8505	7·493	·4676	15·94	—·06
7	·4329	·8865	5·347	·4951	15·95	—·05
8	·5774	·9224	3·797	·5322	16·00
9	·7469	·9584	2·590	·5908	15·93	—·07
10	·9604	·9943	1·545	·7282	15·99	—·01
				Mean...	15·93	

Stannic Chloride.

	π .	θ .	ϕ .	ψ .	Σ .	Deviation.
1	·01766	·6304	128·8	·3678	15·33	—·67
2	·03189	·6642	74·69	·3780	15·53	—·47
3	·05331	·6980	45·95	·3892	15·66	—·34
4	·08433	·7318	29·62	·4017	15·76	—·24
5	·12660	·7656	19·75	·4154	15·77	—·23
6	·18323	·7994	13·62	·4310	15·80	—·20
7	·25776	·8332	9·607	·4503	15·88	—·12
8	·35310	·8670	6·852	·4738	15·93	—·07
9	·47339	·9008	4·885	·5034	15·95	—·05
10	·62158	·9346	3·437	·5448	15·94	—·06
				Mean...	15·75	

TABLE V.—*Ether.*

	π .	θ .	ϕ .	ψ .	Σ .	Deviation.
1	·0340	·6702	70·51	·3816	15·66	—·34
2	·0472	·6917	51·80	·3890	15·67	—·33
3	·0641	·7131	38·86	·3952	15·76	—·24
4	·0851	·7345	29·49	·4028	15·79	—·21
5	·1099	·7559	22·78	·4109	15·74	—·26
6	·1415	·7773	17·81	·4209	15·80	—·20
7	·1794	·7987	14·09	·4309	15·95	—·05
8	·2251	·8201	11·20	·4430	15·95	—·05
9	·2776	·8415	8·969	·4565	15·97	—·03
10	·3383	·8630	7·232	·4714	15·97	—·03
11	·4084	·8844	5·861	·4886	16·04	+·04
12	·4901	·9058	4·738	·5080	16·00
13	·5831	·9272	3·807	·5317	16·00
14	·6900	·9486	3·012	·5650	15·99	—·01
15	·8046	·9700	2·319	·6164	16·04	+·04
16	·9428	·9914	1·624	·7128	16·00
				Mean...	15·89	

TABLE VI.—*Alcohols.**Methyl Alcohol.*

	π .	θ .	ϕ .	ψ .	Σ .	Deviation.
1	·0016	·5711	1601·5	·3435	15·60	—·40
2	·00436	·6101	618	·3505	15·61	—·39
3	·01046	·6491	270	·3595	15·83	—·17
4	·02246	·6881	130·33	·3692	15·97	—·03
5	·0439	·7271	68·15	·3804	16·11	+·11
6	·0796	·7661	38·02	·3934	16·19	+·19
7	·1352	·8051	22·33	·4086	16·27	+·27
8	·2182	·8441	13·62	·4282	16·31	+·31
9	·3365	·883	8·525	·4540	16·37	+·37
10	·499	·922	5·349	·4991	16·14	+·14
11	·713	·961	3·141	·5540	16·09	+·09
12	·844	·981	2·287	·6160	16·01	+·01
13	·964	·996	1·618	·7330	16·04	+·04
Mean...					16·04	

Propyl Alcohol.

	π .	θ .	ϕ .	ψ .	Σ .	Deviation.
1	·0221	·6946	121·6	·3756	15·53	—·47
2	·0316	·7132	85·86	·3811	15·58	—·42
3	·0441	·7319	61·64	·3869	15·54	—·46
4	·0602	·7505	45·40	·3935	15·58	—·42
5	·0806	·7691	34·12	·4004	15·65	—·35
6	·1063	·7878	25·81	·4084	15·67	—·33
7	·1381	·8064	19·90	·4169	15·80	—·20
8	·1756	·8250	15·52	·4270	15·72	—·28
9	·2199	·8436	12·25	·4378	15·83	—·17
10	·2746	·8622	9·74	·4504	15·93	—·07
11	·3358	·8808	7·79	·4648	15·86	—·14
12	·4086	·8994	6·233	·4815	15·97	—·03
13	·4900	·9181	4·953	·5016	15·96	—·04
14	·5816	·9367	3·910	·5261	15·87	—·13
15	·6870	·9553	3·043	·5592	15·86	—·14
16	·8076	·9740	2·339	·6082	15·82	—·18
17	·9470	·9926	1·706	·7047	16·05	+·05
Mean...					15·78	

TABLE VII.—Critical Constants and References.

	p_0 in mm.	t_0 Cent.	v_0 in c.c.	Authority.
Fluorbenzene (1)	33,912	286.55	2.822†	Young.
Ether (2)	27,060	194	3.801†	Ramsay & Young.
Methyl alcohol (3)	59,700	240	3.683*	do.
Propyl alcohol (4)	38,120	264	3.634†	do.
Carbon tetrachloride (5).	34,180	283.15	1.799†	Young.
Stannic chloride (5)	28,080	318.7	1.347†	do.
Isopentane.....	} "Thermal properties of Isopentane" (Young, Proc. Physical Soc. vol. xiii. p. 657). (Reduced data.)			
Benzene.....				
<i>n</i> -Pentane	} "Vapour pressures, etc. of di-isopropyl and di-isobutyl" (Young & Fortey, Jour. Chem. Soc. Sept. 1900, pp. 1141-42). (Comparative table of reduced data.)			
di-isopropyl				
di-isobutyl.....				
<i>n</i> -Hexane				
<i>n</i> -Octane	} Jour. Chem. Soc. Sept. 1899, p. 882 (Young & Fortey).			
Hexamethylene.....				

(1) Jour. Chem. Soc. 1889, vol. lv. pp. 486-521.

(2) Phil. Trans. 1897 A, p. 57 *et seq.* "A study of the thermal properties of Ethyl oxide." (Ramsay & Young.)

(3) Phil. Trans. 1887 A, pp. 313-334. "Thermal properties of Methyl alcohol." (Ramsay & Young.)

(4) Phil. Trans. 1889 A, pp. 137-158. "Thermal properties of Propyl alcohol." (Ramsay & Young.)

(5) Jour. Chem. Soc. 1891, vol. lix. pp. 911-936.

† See Dr. S. Young's paper, "On the determination of the Critical Volume," Phil. Mag. Dec. 1892, p. 503.

* See paper (3) named above, Phil. Trans. 1887 A, p. 330.

NOTES ON THE TABLES.

TABLE I.—Fluorbenzene has been frequently employed by Young as a standard substance with which to compare the properties of other compounds which he has experimentally investigated, and this substance was selected by the writer (in 1895) as a typical example for detailed study. From the data of the table here given the properties of a very large number of functions have been examined, and from these results equation (1) was ultimately obtained. For this compound the deviations from the normal value, $\Sigma=16$, are generally small and irregular in sign. It is only in the near neighbourhood of the critical point, where the experimental difficulties are greatest, that the deviation exceeds one per cent., and the mean deviation, $-.02$, is only a small fraction of this amount.

TABLE II.—The maximum deviation for isopentane in no case exceeds one-third per cent., and the mean deviation, $-.014$ in 16, is less than one part in one thousand. These magnitudes are not far removed from the limits of experimental error. In view of the fact that this substance has been investigated in great detail, and with especial care to make due allowance for all known sources of error, it is highly satisfactory to find so close an agreement of the equation with experimental results.

TABLE III.—Benzene, di-isopropyl, and hexamethylene closely resemble each other in the magnitude and character of their deviations, which are small and mainly positive. In four other cases, viz., *n*-pentane*, *n*-hexane, di-isobutyl, and *n*-octane, the deviations are negative in sign and numerically much greater, being highest at the lowest temperature and decreasing numerically as the temperature increases.

TABLE IV.—Carbon tetrachloride closely resembles *n*-hexane in the negative sign and numerical magnitude of its deviations, and consequently in the value of the mean.

Stannic chloride† similarly resembles *n*-octane, the deviations being numerically much greater.

TABLE V.—This table has been calculated at intervals of 10°C . from 40°C . to 190°C . ($\theta = .6702$ to $\theta = .9914$). As a distinctly normal substance the deviations for ether are greater than one would expect to find, being not much less than for propyl alcohol.

Leduc ('Nouvelles recherches sur les Gaz,' Paris, 1899) has similarly found that his calculated results for the isothermals of ether are in defect. He attributes the deficiency to a possible experimental error. ["Il faut remarquer que le volume occupé par la vapeur dans le piézomètre n'est que d'un centimètre cube environ. L'écart . . . doit être attribuée sans hésitation à une erreur de $0,0^{\text{mm}}$ sur la pesée, ce que correspond à 5^{mm} ou 6^{mm} sur la volume observée."]

TABLE VI.—Results for two alcohols have been added as examples of substances for which there is evidence of marked polymerization. It will be seen that even in the case of a highly polymerized substance like methyl alcohol the equation is still approximately true.

TABLE VII.—Many of the numerical calculations required for this investigation were made at a relatively early date, and this table gives only the critical constants actually employed in obtaining "reduced" values of the variables. Some of the critical volumes have since been slightly altered by later determinations of the critical densities. [See Young, "Note on the law of Cailletet and Mathias," Phil. Mag. vol. I, p. 291 (1900). The differences between "old" and "corrected" critical densities usually are so

* See note by Dr. S. Young.

† See note by Dr. S. Young.

small that the general results contained in Tables I.-VI. would hardly be affected. With the necessary alteration the first value of Σ for benzene, Table III., becomes 15.857, and in other cases the correction would be still smaller.]

It is evident from these tables that the initial proposition of this article is substantially true, but there are, in some cases, outstanding deviations of considerable magnitude which remain unaccounted for. It is difficult to say in what proportions such deviations must be ascribed to the inadequacy of the equation, to experimental error, or to circumstances of the problem which have not been taken into account. For example, no allowance has been made for any degree of polymerization whether occurring in the vapour or in the liquid phase of the substance.

Stress may rightly be laid upon the closeness of the agreement in the case of isopentane, for if the dual equation were radically defective, its inadequacy would at once be made evident by employing it to represent the properties of a compound for which the experimental investigation has been of the most exact character. The contrary is, however, the case and in some instances, where the agreement is not so satisfactory, there is reason to believe that the determination of some of the magnitudes involved has been less precise*. Stannic chloride gives values of Σ deviating from the norm to a much greater extent than those of carbon tetrachloride; but reference to Young's paper on the former compound will show that there is some doubt as to the exact value of the critical temperature, and consequently of the critical volume, in this case.

Where the law of Cailletet and Mathias does not strictly hold good a slight uncertainty attaches to the value of the critical volume, if determined by this method, and small errors in the value of this constant have a marked influence on that of the invariant function when calculated for low temperatures. The factor $3\psi - 1$, or $\psi - \frac{1}{3}$ (which in the reduced equation is the analogue of van der Waals's factor, $v - b$), is very sensitive to small variations in the values of its terms when these approach equality. Such variations may be due to small errors in the measurement of the volume of the liquid, in the determination of the critical volume, or may be caused by variations in the value of " b ." In van der Waals's original investigation it is pointed out that the introduction of the factor $v - b$ is subject to the condition that " b " is relatively small compared with " v " and that below the limit $v = 2b$ the formula for gases cannot be expected to hold good owing to the intersection of the spheres of action of the

* See note by Dr. S. Young.

molecules in configurations of greater density *. This condition is violated when the equation is applied to volumes of a liquid at temperatures much below the critical point where the limit $v=b$ (or $\psi=.3333\dots$) is more nearly approached.

Taking a few examples :

Carbon tetrachloride,	Deviation = $-.23$	when $\psi=.3876$
Stannic chloride,	$-.67$	$\psi=.3678$
<i>n</i> -Pentane,	$-.19$	$\psi=.3885$
<i>n</i> -Octane,	$-.83$	$\psi=.3826$
Di-isobutyl,	$-.55$	$\psi=.3864$
Benzene,	$-.15$	$\psi=.3870$

It must, however, be observed that relatively large deviations are not invariably connected with small values of ψ , for we have also

Isopentane,	Deviation = $-.05$	when $\psi=.3908$
Fluorobenzene,	$-.08$	$\psi=.3805$

Whilst, therefore, a diminution in the value of " b " would increase the value of $3\psi-1$, and tend to annul deviations of negative sign, it is evident that such variations can only be of very small magnitude, for otherwise deviations of positive sign would be produced.

As showing the sensitiveness of the invariant function to slight changes in volume, one or two numerical examples may be given. In Table IV. the values for carbon tetrachloride have been calculated, at temperature intervals of 20°C ., from 100°C . to 280°C . inclusive. The calculated value at a lower temperature, $T=90^\circ\text{C}$., gives $\Sigma=15.72$, the volume of unit mass of the liquid being $.6971\text{ c.c.}$ A difference of $.01\text{ c.c.}$ in excess of this value would make $\Sigma=16.01$. The critical volume of unit mass is 1.799 c.c. , and a similar result would be produced on reducing this value by one and a half per cent. Again, in the case of stannic chloride the values of ϕ and ψ have been calculated from the critical volume $v_c=1.347\text{ c.c.}$ If we take the smaller value $v_c=1.325\text{ c.c.}$, the following results for the first and last lines of the table will be obtained:—

Line (1), $\Sigma=15.86$ in place of 15.33 .

(10), $\Sigma=16.10$ in place of 15.94 .

* "There can be no doubt that molecules are not spheres in shape they are more probably, without exception, flattish discs of very small thickness." (O. E. Meyer, 'Kinetic Theory of Gases.' English Translation from 2nd Revised Edition by R. E. Baynes, p. 323.)

Hence it is open to question how far conclusions based upon the hypothesis of the spherical character of molecular action can be pressed to the limit when, as in the liquid state, molecules are densely packed, however convenient the conception may be from a mathematical point of view.

The extreme difference between the values of Σ is reduced by this change from '61 to '24.

Whatever emendation equation (1) may still require, it is obvious, from these examples, that it can only be successfully attempted when data of very great exactitude are available. It certainly does not seem advisable to modify the dual equation by the introduction of small arbitrary constants (which would destroy its generality) until the necessity for their presence has been more fully demonstrated.

It should also be noted that the usual integral value, -273°C. , has been taken as the absolute zero of temperature. The changes in the value of θ which would be produced by using any other admissible value* can only be of minor importance, but yet are not quite negligible, at temperatures much below the critical point, if it is desired to arrive at the closest approximation warranted by experimental evidence.

Analogy with the Law of Cailletet and Mathias.

This well-known law expresses the fact that the means of the densities of a liquid and its saturated vapour are a linear function of the temperature. It is obvious from its form that the dual equation may be similarly stated.

$$\text{Putting } \begin{aligned} f(\phi, \psi) &= \theta \cdot F(\phi, \psi) \quad \text{and} \\ f(\psi, \phi) &= \theta \cdot F(\psi, \phi), \end{aligned}$$

equation (1) may be written

$$\frac{1}{2}\{f(\phi, \psi) + f(\psi, \phi)\} = 8\theta,$$

i. e., for normal substances, the means of the values of the functions $f(\phi, \psi)$ and $f(\psi, \phi)$ are proportional to the absolute temperature.

Or again, taking the invariant form, equation (3) may be written

$$\frac{1}{2}\{F(\phi, \psi) + F(\psi, \phi)\} = 8,$$

i. e., the means of the values of the functions $F(\phi, \psi)$ and $F(\psi, \phi)$ are constant.

The following tables and accompanying diagrams (Plates VI. & VII.) illustrate this relation in the case of Fluorobenzene. As, for this compound, the values of the two functions are rather irregular in the neighbourhood of the critical point, a few corresponding values for isopentane have also been calculated and plotted on an enlarged scale.

* Leduc (*Nouvelles recherches sur les Gaz*) employs the value $-273^{\circ}\cdot 2$. (The following note has been kindly communicated by Dr. S. Young.)

D. Berthelot, "Sur les thermomètres à Gaz,"¹ finds $-273^{\circ}\cdot 09$ and E. Buckingham, "On the establishment of the thermodynamic scale of temperature by the constant volume thermometer,"² $-273^{\circ}\cdot 13$.

¹ *Travaux et Mémoires du Bureau International des Poids et Mesures*, 1903.

² Bulletin of the Bureau of Standards, vol. iii. p. 237 (Washington, 1907).

*Fluorbenzene.*Values of $f(\phi, \psi)$ and $f(\psi, \phi)$ in relation to 8θ .

θ .	8θ .	$f(\phi, \psi)$.	$f(\phi, \psi) - 8\theta$.	$f(\psi, \phi)$.	$8\theta - f(\psi, \phi)$.
·6565	5·252	7·514	2·262	2·936	2·316
·6827	5·462	7·609	2·147	3·306	2·156
·7028	5·622	7·637	2·015	3·596	2·026
·7335	5·868	7·730	1·862	4·018	1·850
·7574	6·059	7·787	1·728	4·351	1·708
·7771	6·217	7·828	1·611	4·613	1·604
·7940	6·352	7·877	1·525	4·835	1·517
·8092	6·474	7·926	1·452	5·023	1·451
·8228	6·582	7·969	1·387	5·227	1·355
·8464	6·771	8·024	1·253	5·547	1·224
·8667	6·934	8·069	1·135	5·813	1·121
·8930	7·144	8·137	0·993	6·195	0·949
·9288	7·430	8·181	0·751	6·701	0·729
·9579	7·663	8·149	0·486	7·169	0·494
·9731	7·785	8·074	0·289	7·436	0·349
·9830	7·864	7·990	0·136	7·547	0·317
·9919	7·935	7·943	0·008	7·792	0·143
Isopentane (in the neighbourhood of the critical point).					
·9800	7·840	8·046	0·206	7·644	0·196
·9918	7·934	7·934	0·100	7·813	0·121
·9963	7·970	8·006	0·036	7·933	0·037

*Fluorbenzene.*Values of $F(\phi, \psi)$ and $F(\psi, \phi)$ in relation to the constant 8.

	θ .	$F(\phi, \psi)$.	$F(\phi, \psi) - 8$.	$F(\psi, \phi)$.	$8 - F(\psi, \phi)$.
1	·6565	11·45	3·45	4·47	3·53
2	·6827	11·15	3·15	4·85	3·15
3	·7028	10·86	2·86	5·12	2·88
4	·7335	10·54	2·54	5·48	2·52
5	·7574	10·27	2·27	5·74	2·26
6	·7771	10·07	2·07	5·94	2·06
7	·7940	9·92	1·92	6·09	1·91
8	·8092	9·80	1·80	6·20	1·80
9	·8228	9·69	1·69	6·35	1·65
10	·8464	9·48	1·48	6·54	1·46
11	·8667	9·31	1·31	6·71	1·29
12	·8930	9·11	1·11	6·93	1·07
13	·9288	8·81	0·81	7·21	0·79
14	·9579	8·50	0·50	7·48	0·52
15	·9731	8·30	0·30	7·65	0·35
16	·9830	8·13	0·13	7·69	0·31
17	·9919	8·01	0·01	7·86	0·14
Isopentane (near the critical point).					
	·9800	8·21	0·21	7·80	0·20
	·9918	8·10	0·10	7·88	0·12
	·9963	8·04	0·04	7·96	0·04

§ 2. *On the Determination of Critical Constants from Observations at Temperatures considerably below the Critical Point.*

The invariant form of the dual equation may be directly employed as a test to ascertain whether given values assigned to the critical constants of a normal substance form a consistent system. If these values are substituted in the function

$$\left\{ \frac{p}{p_0} + \left(\frac{t_0}{t} - 1 \right) \frac{v_0^2}{uv} + \frac{3v_0^2 t_0}{v^2 t} \right\} \left(\frac{3v}{v_0} - 1 \right) \\ + \left\{ \frac{p}{p_0} + \left(\frac{t_0}{t} - 1 \right) \frac{v_0^2}{uv} + \frac{3v_0^2 t_0}{u^2 t} \right\} \left(\frac{3u}{v_0} - 1 \right),$$

the result must approximate to the constant value 16. From the fact that every experimental determination of orthobaric volumes at a known vapour-pressure and temperature gives a relation between the values of the three critical constants, a still more important deduction may be drawn. The law of Cailletet and Mathias makes it possible to express the critical temperature in terms of the critical volume. The critical temperature being thus eliminated, an equation is obtained connecting the two remaining critical constants in which the critical pressure occurs only to the first power. From two such equations the critical pressure is easily eliminated, giving finally a cubic equation in v_0 of the form

$$Pv_0^3 - Qv_0^2 + Rv_0 - S = 0,$$

where P, Q, R, S are functions of the orthobaric volumes, vapour-pressures, and temperatures obtained from any two determinations.

Let u_1, u_2 be the volumes of unit mass of liquid, and v_1, v_2 the volumes of unit mass of saturated vapour, determined respectively at vapour-pressures p_1, p_2 , and temperatures t_1, t_2 . Let A, B be constants in the linear function of the temperature which expresses the sum of the densities, *i. e.*

$$\frac{1}{u} + \frac{1}{v} = A - Bt \\ = f(t),$$

$$\text{or briefly} \quad = f.$$

$$\text{Hence also} \quad \frac{2}{v_0} = A - Bt_0,$$

$$\text{or} \quad t_0 = \frac{1}{B} \left(A - \frac{2}{v_0} \right).$$

Employing the substitutions,

$$\begin{aligned} f_1 &= \frac{1}{u_1} + \frac{1}{v_1}, & f_2 &= \frac{1}{u_2} + \frac{1}{v_2}, \\ g_1 &= \frac{1}{u_1 v_1}, & g_2 &= \frac{1}{u_2 v_2}, \\ H_1 &= 2p_1 t_1, & H_2 &= 2p_2 t_2, \\ K_1 &= 3p_1 t_1 (u_1 + v_1), & K_2 &= 3p_2 t_2 (u_2 + v_2), \\ L_1 &= 3f_1^2 A - 6g_1 A + 2f_1 g_1, & L_2 &= 3f_2^2 A - 6g_2 A + 2f_2 g_2, \\ M_1 &= 9f_1^3 + 9f_1 A - 8g_1, & M_2 &= 9f_2^3 + 9f_2 A - 8g_2, \\ N_1 &= 16A + 8f_1, & N_2 &= 16A + 8f_2, \end{aligned}$$

the critical volume is a root of the cubic

$$\begin{aligned} (H_1 L_2 - H_2 L_1) v_0^3 - (H_1 M_2 - H_2 M_1 + K_1 L_2 - K_2 L_1) v_0^2 \\ + (H_1 N_2 - H_2 N_1 + K_1 M_2 - K_2 M_1) v_0 - (K_1 N_2 - K_2 N_1) = 0. \end{aligned}$$

Deduction of the cubic equation in v_0 .

From equation (1)

$$\begin{aligned} & \left\{ \pi + (1 - \theta) \left(\frac{1}{\psi \phi} - \pi \right) + \frac{3}{\phi^2} \right\} (3\phi - 1) \\ & + \left\{ \pi + (1 - \theta) \left(\frac{1}{\psi \phi} - \pi \right) + \frac{3}{\psi^2} \right\} (3\psi - 1) = 16\theta, \\ \therefore \quad & \theta \pi (3\phi + 3\psi - 2) + (1 - \theta) \left(\frac{3}{\phi} + \frac{3}{\psi} - \frac{2}{\psi \phi} \right) \\ & + 9 \left(\frac{1}{\phi} + \frac{1}{\psi} \right) - 3 \left(\frac{1}{\phi^2} + \frac{1}{\psi^2} \right) = 16\theta, \\ \therefore \quad & \theta \pi (3\phi + 3\psi - 2) + 12 \left(\frac{1}{\phi} + \frac{1}{\psi} \right) - 3 \left(\frac{1}{\phi} + \frac{1}{\psi} \right)^2 \\ & + \frac{4}{\psi \phi} - \theta \left(\frac{3}{\phi} + \frac{3}{\psi} - \frac{2}{\psi \phi} \right) = 16\theta, \\ \therefore \quad & \theta \pi (3\phi + 3\psi - 2) = 16\theta + \theta \left(\frac{3}{\phi} + \frac{3}{\psi} - \frac{2}{\psi \phi} \right) \\ & + 3 \left(\frac{1}{\phi} + \frac{1}{\psi} \right)^2 - 12 \left(\frac{1}{\phi} + \frac{1}{\psi} \right) - \frac{4}{\psi \phi}. \end{aligned}$$

Dividing both sides of the equation by θ ,

$$\frac{1}{\pi} = \frac{3\phi + 3\psi - 2}{\left\{ 16 + \left(\frac{3}{\phi} + \frac{3}{\psi} - \frac{2}{\psi\phi} \right) \right\} + \frac{1}{\theta} \left\{ 3 \left(\frac{1}{\phi} + \frac{1}{\psi} \right)^2 - 12 \left(\frac{1}{\phi} + \frac{1}{\psi} \right) - \frac{4}{\psi\phi} \right\}}.$$

Substituting $\frac{p}{p_0} = \pi$, $\frac{t}{t_0} = \theta$, $\frac{u}{v_0} = \psi$, $\frac{v}{v_0} = \phi$,

$$p_0 = \frac{p t \left(\frac{3v}{v_0} + \frac{3u}{v_0} - 2 \right)}{t \left\{ 16 + 3v_0 \left(\frac{1}{v} + \frac{1}{u} \right) - \frac{2v_0^2}{uv} \right\} + t_0 \left\{ 3v_0^2 \left(\frac{1}{v} + \frac{1}{u} \right)^2 - 12v_0 \left(\frac{1}{v} + \frac{1}{u} \right) - \frac{4v_0^2}{uv} \right\}}. \quad (6)$$

an equation from which p_0 can be found when v_0 and t_0 are known.

Substituting in this equation the values of p , t , u , and v determined by a first observation,

$$\begin{aligned} p_0 &= \frac{p_1 t_1 \left(\frac{3v_1 + 3u_1}{v_0} - 2 \right)}{t_1 \left\{ 16 + 3v_0 \left(\frac{1}{v_1} + \frac{1}{u_1} \right) - \frac{2v_0^2}{u_1 v_1} \right\} + v_0 t_0 \left\{ 3v_0^2 \left(\frac{1}{v_1} + \frac{1}{u_1} \right)^2 - 12 \left(\frac{1}{v_1} + \frac{1}{u_1} \right) - \frac{4v_0}{u_1 v_1} \right\}} \\ &= \frac{\frac{K_1}{v_0} - H_1}{t_1 \{ 16 + 3f_1 v_0 - 2g_1 v_0^2 \} + \left(\frac{A v_0 - 2}{B} \right) \{ (3f_1^2 - 4g_1) v_0 - 12f_1 \}} \\ &= \frac{\frac{B}{v_0} (K_1 - H_1 v_0)}{B t_1 \{ 16 + 3f_1 v_0 - 2g_1 v_0^2 \} + (A v_0 - 2) \{ (3f_1^2 - 4g_1) v_0 - 12f_1 \}}. \end{aligned}$$

From the denominator of this fraction, Bt_1 can be eliminated by means of the relation

$$f_1 = A - Bt_1; \quad \therefore \quad Bt_1 = A - f_1;$$

and, rearranging the terms,

$$\begin{aligned} \frac{p_0 v_0}{B} &= \frac{K_1 - H_1 v_0}{(3f_1^2 A - 6g_1 A + 2f_1 g_1) v_0^2 - (9f_1^2 + 9f_1 A - 8g_1) v_0 + (16A + 8f_1)} \\ &= \frac{K_1 - H_1 v_0}{L_1 v_0^2 - M_1 v_0 + N_1}. \quad \dots \dots \dots (7) \end{aligned}$$

If the law of Cailletet and Mathias holds good, B , and therefore $\frac{p_0 v_0}{B}$, may be regarded as constant; and hence the

value of the ratio on the right-hand side of the equation is the same from whatever set of observations the values of the coefficients are obtained. Hence

$$\frac{H_1 v_0 - K_1}{L_1 v_0^2 - M_1 v_0 + N_1} = \frac{H_2 v_0 - K_2}{L_2 v_0^2 - M_2 v_0 + N_2},$$

from which we obtain the cubic equation

$$(H_1 L_2 - H_2 L_1) v_0^3 - (H_1 M_2 - H_2 M_1 + K_1 L_2 - K_2 L_1) v_0^2 + (H_1 N_2 - H_2 N_1 + K_1 M_2 - K_2 M_1) v_0 - (K_1 N_2 - K_2 N_1) = 0. \quad (8)$$

In the cases which have been examined this cubic has three real and positive roots, but only the mean root is common to all the cubics relating to the same substance. As this method of obtaining the critical volume is new, it will be well to examine its application in detail, taking for the purpose a normal substance whose properties are well known.

Isopentane.

From Young's paper ("Thermal Properties of Isopentane") the following data of five experimental determinations are taken :—

T (Centigrade).	<i>t</i> (Abs. temp.).	<i>p</i> , in mm.	<i>u</i> , in c.c. (from curve).	<i>v</i> , in c.c. (from curve).
10°	283°	390·4 *	1·5885	607·5
30°	303°	815·5 *	1·6413	303·0
60°	333°	2036·5 †	1·7329	127·9
100°	373°	5345·5 †	1·8940	49·45
120°	393°	8018 †	2·0037	32·20

* Dynamical method.

† Mean of experimental values.

The relation between the liquid and vapour densities is expressed by the equation

$$\frac{1}{u} + \frac{1}{v} = A - Bt,$$

where $A = \cdot 8872$ or 8872×10^{-4} ,

$B = \cdot 000908$ or 908×10^{-6} .

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From the above data we obtain

$$\begin{aligned} T = 10^\circ \text{C.} \quad H_1 &= 220,966, \\ K_1 &= 201,882 \times 10^3, \\ L_1 &= 1,052,960 \times 10^{-6}, \\ M_1 &= 859,877 \times 10^{-5}, \\ N_1 &= 19,237,088 \times 10^{-6}. \end{aligned}$$

$$\begin{aligned} T = 30^\circ \text{C.} \quad H_2 &= 494,193, \\ K_2 &= 225,827 \times 10^3, \\ L_2 &= 988,894 \times 10^{-6}, \\ M_2 &= 824,295 \times 10^{-5}, \\ N_2 &= 19,091,808 \times 10^{-6}. \end{aligned}$$

$$\begin{aligned} T = 60^\circ \text{C.} \quad H_3 &= 1,356,310, \\ K_3 &= 263,734 \times 10^3, \\ L_3 &= 891,615 \times 10^{-6}, \\ M_3 &= 771,200 \times 10^{-5}, \\ N_3 &= 18,873,888 \times 10^{-6}. \end{aligned}$$

$$\begin{aligned} T = 100^\circ \text{C.} \quad H_4 &= 3,987,743, \\ K_4 &= 307,120 \times 10^3, \\ L_4 &= 756,698 \times 10^{-6}, \\ M_4 &= 700,224 \times 10^{-5}, \\ N_4 &= 18,583,328 \times 10^{-6}. \end{aligned}$$

$$\begin{aligned} T = 120^\circ \text{C.} \quad H_5 &= 6,302,148, \\ K_5 &= 323,335 \times 10^3, \\ L_5 &= 682,585 \times 10^{-6}, \\ M_5 &= 664,230 \times 10^{-5}, \\ N_5 &= 18,438,048 \times 10^{-6}. \end{aligned}$$

The numerical values of the functions H, K, L, and M vary greatly. H increases rapidly, and K slowly, with rise of temperature; L, M, and N decrease slowly as the temperature rises.

Since n observations can be combined to form $\frac{n(n-1)}{2}$ pairs, these five determinations yield data for the formation of ten cubic equations, of which the values of the coefficients for five have been calculated. As it is important to avoid the introduction of errors due to premature attempts at

approximation, significant figures have been retained in excess of the number probably sufficient for accuracy.

First Cubic.—The first cubic equation calculated by this method was obtained from data at temperatures 60° C. and 120° C., giving the equation

$$469,319 v_0^3 - 14,784,759 v_0^2 + 83,569,800 v_0 - 123,986,496 = 0.$$

This cubic has three positive roots, of which the values are approximately

$$2.397, \quad 4.260, \quad 24.846.$$

Second Cubic, from data at 10° C. and 100° C.

$$403,175 v_0^3 - 20,326,881 v_0^2 + 129,983,430 v_0 - 215,643,367 = 0.$$

The roots of this equation are approximately

$$2.892, \quad 4.277, \quad 43.24.$$

Comparing these results, we infer that the extreme roots of the cubic equation are irrelevant and that the mean root gives the true critical volume. In the equations which follow only the mean root has been calculated.

Third Cubic, from data at 10° C. and 60° C.

$$123,112 v_0^3 - 10,765,884 v_0^2 + 73,280,079 v_0 - 126,317,603 = 0.$$

Mean root, 4.260.

Fourth Cubic, from data at 60° C. and 100° C.

$$254,067 v_0^3 - 9,637,135 v_0^2 + 57,457,144 v_0 - 89,824,667 = 0.$$

Mean root, 4.231.

Fifth Cubic, from data at 10° C. and 30° C. (Low temperatures and a smaller temperature interval.)

$$30,185 v_0^3 - 4,057,493 v_0^2 + 28,301,939 v_0 - 48,996,154 = 0.$$

Mean root, 4.315.

Summarizing these results, we get for v_0 :—

First cubic	. . .	4.260	60° and 120° C.
Second cubic	. . .	4.277	10° and 100° C.
Third cubic	. . .	4.260	10° and 60° C.
Fourth cubic	. . .	4.231	60° and 100° C.
Fifth cubic	. . .	4.315	10° and 30° C.

$$\begin{array}{r} 5)21.343 \\ \hline 4.2686 \end{array}$$

as against Young's value, 4.266 c.c.

Taking Young's value for the critical volume as a standard, the greatest deviation is in the case of the fifth cubic, where the temperatures are both low, and the law of Cailletet and Mathias holds less exactly. The deviations from the norm are not always in the same direction and we may infer that the critical volume will probably lie between the greatest and least of the mean roots of the several cubic equations, and that the mean of their sum will be a close approximation to its actual value *. A value for the critical volume having been obtained, the critical temperature can be deduced from the law of Cailletet and Mathias, and hence also the critical pressure from the dual equation.

The number of substances for which the critical constants can be directly determined by experiment is very small, and the method here described may therefore be useful in obtaining approximate values for these important constants in cases where experimental observations can only be made at temperatures falling considerably below the critical point.

Regarded as a test of the applicability of the cubic equation to determine the critical volume, the foregoing investigation is open to the objection that the value of A which has been employed has been obtained from the complete series of liquid and vapour densities observed between 10° C. and a temperature verging closely upon the critical temperature. If observations are confined within a more limited range, it is conceivable that somewhat different values of A , B may be obtained, and the values of the roots of the cubic correspondingly affected. To this objection it may be replied that Young's investigations have shown that in the case of normal substances such deviations are only of small magnitude, and hence no great alteration in the values of the coefficients of the terms in the cubic equation will be thereby produced. In the hypothetical case in which it is assumed that we have at our disposal only a small number of experimental observations, falling within a restricted range of temperature, mean values of A and B may be determined from the whole series of available observations or, taking each pair of observations independently, values of

* Perhaps a preferable method would be to "weight" the results by multiplying each mean root by the corresponding interval of temperature and divide the total thus obtained by the sum of these temperature intervals. Applied to the five roots given above this method leads to the "weighted" mean value $v_0 = 4.235$.

A and B may be obtained from the equations

$$A = \frac{f_1 t_2 - f_2 t_1}{t_2 - t_1},$$

$$B = \frac{f_1 - f_2}{t_2 - t_1}.$$

From the form of these expressions it will be seen that it is inadvisable to select pairs of observations in which the temperature interval is small. Further to test this point the coefficients of the five cubic equations already investigated have been recalculated, substituting for A the values obtained by treating each pair of observations independently.

For the first cubic $A = .8888$, yielding the equation

$$470,375 v_0^3 - 14,833,255 v_0^2 + 83,786,976 v_0 - 125,483,646 = 0.$$

The coefficients in this equation only differ slightly in value from those previously obtained. The mean roots of the five cubics recalculated in this manner are respectively

First cubic	4.176
Second „	4.230
Third „	4.329
Fourth „	4.226
Fifth „	4.280
<hr/>	
Mean of five roots	4.248

(The “weighted” mean is here only 4.240.)

Compared with 4.266 as a normal value this shows a deviation of about three-sevenths per cent. in defect.

As a test example isopentane is a very favourable case, and generally greater differences in the values of the mean roots of the cubic may be expected to occur. The validity of this method of finding the critical volume depends upon the exactitude with which the law of Cailletet and Mathias is fulfilled by the substance under investigation. Regarded geometrically, if, on a density-temperature diagram, the position of a series of points on the line of mean density has been determined by experiment, the assumption is made that the series of lines obtained by joining pairs of these points will, on being produced, pass through the point representing the critical density. Any slight curvature of the diameter at the extremity, such as Young has observed in many cases, will, to the extent that it occurs, invalidate

the result. Provided, however, that the substance is fairly normal and that an adequate length of the mean-density line has been experimentally constructed, it is very unlikely that the point representing the critical density will lie on the same side of all the lines so obtained. Hence a useful indication will be afforded of the limits within which the true critical volume will most probably lie even when experimental investigation in the neighbourhood of the critical point is not feasible.

To Dr. S. Young (to whom the first manuscript copy of this article was sent), I desire here to tender very cordial thanks for the helpful notes and criticism with which he has favoured me whilst preparing this paper for publication. I am also indebted to Mr. A. G. Wilkinson for careful clerical assistance.

Note by SYDNEY YOUNG, *D.Sc., F.R.S.,*
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The proofs of the correctness of his "dual" equation which Mr. Haigh has brought forward appear to be very complete and satisfactory, and it is probable that some, though not all, of the deviations of the calculated values of Σ from the theoretical value, 16, may be due to experimental errors.

It may be pointed out that such errors are in general most likely to occur in the determinations of the volumes of saturated vapour at the lower temperatures, and it is probable that the single rather large deviation in the case of normal pentane at the lowest temperature may be explained in this way. The results with *n*-pentane should be specially accurate, and the greatest of the remaining deviations, 0.07, is small. Omitting the first result, the mean value of Σ would be 15.965 instead of 15.95.

Serious experimental difficulties were encountered with stannic chloride and carbon tetrachloride, owing to the action of these substances on mercury, stannic chloride under all conditions and carbon tetrachloride at the higher temperatures. In both cases it was necessary to devise special methods for the determination of the vapour pressures and specific volumes, and it is not to be expected that the data for these substances can be so accurate as for the others.

I have pointed out (Phil. Mag. vol. 1. p. 291 (1900)) that although the law of Cailletet and Mathias is applicable to

all the normal substances examined with a close approach to accuracy, yet the deviations are too regular to be ascribed to experimental error. The relation between the mean densities of liquid and saturated vapour and the temperature is represented with great accuracy by the formula

$$D_t = D_0 + \alpha t + \beta t^2,$$

where α is always negative and β may be either positive or negative. The direction and extent of the curvature of the diameter is indicated by the sign and magnitude of the constant β .

The close connexion between Mr. Haigh's dual equation and the law of Cailletet and Mathias is shown by the following table in which the normal substances, excluding carbon tetrachloride and stannic chloride, are arranged in

	Mean value of Σ .	$\beta \times 10^{10}$.
Hexamethylene	16.03	+ 791
Di-isopropyl	16.03	+ 413
Benzene	16.02	+ 693
Isopentane	15.986	+ 463
Fluorbenzene	15.98	+ 293
<i>n</i> -Pentane	15.95	0
<i>n</i> -Hexane	15.95	0
Ether	15.89	- 475
Di-isobutyl	15.82	- 592
<i>n</i> -Octane	15.76	-1046
Carbon tetrachloride	15.93	+1480
Stannic chloride	15.75	+ 977

order of magnitude of the mean values of Σ . It will be seen that with one exception the values of $\beta \times 10^{10}$ follow the same order, Σ falling from 16.03 to 15.76 while $\beta \times 10^{10}$ changes from + 791 to - 1046. The one deviation, that shown by di-isopropyl, is small; and it is probable that the mean value of Σ for *n*-pentane should be slightly higher and of *n*-hexane slightly lower than 15.95, and that $\beta \times 10^{10}$ for the latter substance should have a small negative value.

The connexion seems to break down altogether when the two chlorides are compared with the other substances, but it is possible that a considerable part of the discrepancy may be explained by the relatively large experimental errors to which reference has been made.



