The Gladstone "Law" in Physical Optics, and the True Volume of Liquid Matter

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LV. *The Gladstone "Law" in Physical Optics, and the True Volume of Liquid Matter.* By WALTER HIBBERT, F.I.C.

ONE of the curious results established in Chemical Optics is that two independent formulæ (those of Gladstone and Lorentz respectively) can be used in the discussion of experimental data relating to the refractive index and the density of a given substance. Neither of them can claim any special advantage. They both have a wide range of application, yet neither holds universally good. Still more curiously, they break down under quite different conditions of experiment.

The Lorentz formula,

$$\frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d} = \text{constant},$$

which is able to cover the large variation in density separating a liquid and its vapour, gives erroneous results in the simple case of a liquid whose density is changed by pressure. On the other hand, the Gladstone formula,

$$\frac{\mu - 1}{d} = \text{constant},$$

is unique in its power to deal with liquids under varying pressure, but fails in the jump from liquid to vapour.

Hitherto no light has been thrown on these anomalies, but this present paper attempts to explain the exceptions in the case of the Gladstone expression, and, incidentally, introduces a physical magnitude which is conveniently described as the "actual volume occupied by one gramme of the substance."

The suggestion of the present argument arose out of a number of experiments carried out by Dr. Gladstone and myself during the last two years. We have examined a great variety of salt-solutions, whose strength varied from saturation down to about 5 per cent.—a dilution limit imposed by experimental error when the hollow-prism method is adopted for obtaining the refractive index.

Our main conclusion, to the effect that the value of $\frac{\mu-1}{d}$ for the salt is practically constant, has received special confirmation by the publication of a paper by Kohlrausch and Hallwachs*, in which they extend the work on about 10 salts to extremely dilute solutions. They used an interference method for determining μ , and a special apparatus for getting d with the necessary accuracy, so that the experimental error is not larger than usual, even when the amount of salt present is not greater than 0.05 per cent. of the solution.

An examination of this body of evidence proved to me that the constancy of $\mu-1/d$ was much greater for an ordinary dissolved salt than for a simple liquid whose density is changed by heat. For example:—

When heptane is heated from 12° to 88° its density changes by about 10 per cent., and the value of $\mu-1/d$ by 0.55 per cent.

Sodium chloride, diluted from 13 per cent. down to 0.03 per cent. (a concentration change of 400 to 1), has its value for $\mu-1/d$ changed by 0.22 per cent. only.

In speculating on this far greater constancy in the case of a dissolved salt, it seemed not unreasonable to regard the solution in the light of Van't Hoff's theory, attributing a pseudo-gaseous condition to the dissolved salt. This at once suggested other comparisons, and led to the following summary statement of all experimental results on the subject:—

1. The Gladstone expression is true in the case of gases whose density is changed by varying pressure†.
2. It is true in the case of liquids whose density is changed by varying pressure‡.
3. It is true (or a *very* close approximation) in the case of dissolved salts, especially in dilute solution.
4. It is a less close approximation in the case of simple liquids undergoing thermal expansion.
5. It altogether fails when a liquid is changed into vapour.

* Wied. *Ann.* 1894, liii. p. 1.

† Biot and Arago, *Mém. d. l'Inst.* vii. p. 301 (1806), and Chappuis and Rivière, *Compt. Rend.* ciii. Biot and Arago express their results $(\mu^2-1)v = \text{const.}$ But μ^2 is only slightly greater than unity, and therefore $(\mu-1)v$ must also be constant.

‡ Quincke, *Phil. Mag.* 1884, xvii. p. 65.

On studying the results included in 4, it appeared that they had one point in common. If the variation be expressed in symbols, it may be put in the form

$$e_t = e_0(1 \pm at),$$

where e_0 and e_t are the values of $\frac{\mu-1}{d}$ at 0° and t° respectively.

Examination showed that all good experiments gave a negative sign for the coefficient a . In other words, the value of e always diminishes as the density diminishes. If we put $(\mu-1)/d = (\mu-1)v$, where v is the volume of unit mass, we may say that $(\mu-1)v$ always diminishes as v increases. This statement is still more emphatically true when the liquid becomes a vapour.

Therefore, in classes 4 and 5, whenever v increases the product $(\mu-1)v$ diminishes. In liquids, where the change in v is not very great, the diminution of the product is small; but in passing to vapour, where the change in v is enormous, the product $(\mu-1)v$ undergoes a large diminution. To put the same thing in the inverse sense, the results show that when v becomes comparatively small, there is a marked increase in the product. So stated, they afford criteria by which we may possibly find the cause of the deficiency. The conditions are almost a reproduction of those which led to the second approximation in the case of Boyle's law. Experiment showed that the product pv was only constant when v was comparatively large. As v diminished, there was a tendency for the product to increase, and it became necessary to suppose that the expression pv referred not to the whole space symbolized by v , but to v minus the space occupied by the particles. Hence $p(v-b)$, where b is the actual volume of the matter, has taken the place of pv .

It appeared to me, that the similar experimental results would warrant the introduction of a similar symbol in the Gladstone expression, thus transforming it into

$$(\mu-1)(v-\beta) = \text{constant}.$$

It is at once apparent that the introduction of β tends to remove the anomalies, and also evident why cases 1, 2, and 3 in the above summary are satisfied by the uncorrected formulæ.

In 1 and 3, that is in the case of gases and dissolved salts respectively, the value β is negligible compared with v .

In 2, owing to the very slight compressibility of the liquids, the changes in v are always exceedingly small. Hence $v - \beta$ will change almost as much as v , if, as is probable, β is not a large fraction of v .

In 4, the case of liquids undergoing thermal expansion, the changes in v are great enough, as compared with the value of β , to cause an appreciable difference between the ratios v/v_1 and $(v - \beta)/(v_1 - \beta)$.

In 5, the case of vaporization, we have v for the liquid comparatively small, changing into a very large value in the vapour. Here there is a decided and altogether disturbing difference between the ratios v/v_1 and $(v - \beta)/(v_1 - \beta)^*$.

Evidently, then, if the numerical data are found to be of the right order, the introduction of β will remove the reservations with which the Gladstone law is usually stated. Moreover, the physical conditions under which β needs to be introduced render it probable that β has, or may have, a physical meaning, and is not merely of the nature of an arbitrary constant. But the real justification for introducing β must be, *à posteriori*, by showing that the calculated values are not improbable, and that they have relations to other physical quantities.

We can determine β for any one substance from observations on a liquid at two different temperatures.

Let μ_1, μ_2 be the refractive indices; v_1, v_2 the volumes of

* This paper was written out before I recalled the fact that Ketteler suggested the same solution for the discrepancies experienced in applying the expression $(\mu^2 - 1)v = \text{constant}$. Writing it $(\mu^2 - 1)(v - \beta)$ he examined a series of experiments made by Weegmann (*Zeit. phys. Chem.* ii. p. 905). The result was not very encouraging. But I am of opinion that there are two reasons for that discouragement. First, Weegmann happened to work on substances of exceptional density, a fact which ought to foreshadow the probability of exceptional results in any volume deduced from them. Secondly, the expression $(\mu^2 - 1)v$ is surely not so good a basis for the investigation as the simpler one due to Gladstone and Dale. In ordinary liquids it is not so constant; it is not supported by Quincke's experiments on liquids under pressure (*comp. Sutherland, Phil. Mag.* 1888); nor does it render such service in Physical Chemistry as either the Gladstone or Lorentz expression.

unit mass $\left(= \frac{1}{d} \right)$ at the temperatures of two experiments, and let β have the meaning suggested, then

$$(\mu_1 - 1)(v_1 - \beta) = (\mu_2 - 1)(v_2 - \beta),$$

and

$$\beta = \frac{(\mu_1 - 1)v_1 - (\mu_2 - 1)v_2}{\mu_1 - \mu_2}.$$

This equation shows that the measure of β will depend on differences which we know to be small, and it is at once evident that the best experiments only will be serviceable. Thus, a table of results for carbon disulphide gives the following figures for the temperatures of 0° and 40° Centigrade; the data are Ketteler's:—

$$\mu_1 = 1.64375, \mu_2 = 1.61187; v_1 = .77314, v_2 = .81103.$$

Therefore

$$\beta = \frac{0.497709 - 0.496245}{0.03188} = \frac{0.001464}{0.03188} = 0.0459.$$

Here the difference between the two terms of the numerator is only $\frac{1}{350}$ of either, and as each term involves only the fractional part of the index, any error in μ is multiplied about 900 times in its effect on β .

This makes it imperative to attach weight only to those experiments where special appliances have been adopted to keep the temperature constant during the observations. For this reason I simply allude to the few results I have myself obtained in a few preliminary experiments, reserving data for a fuller discussion. The results here presented depend almost entirely on the work of three sets of observers, namely, Nasini and Bernheimer, Perkin, and Ketteler. It would be invidious for me to single out one of these as more accurate than the others; their papers show that all the experiments are of a high order of accuracy. It is doubtful, however, whether Perkin's data are not the most serviceable for our present purpose, if only for the reason that the interval of temperature he employed is greater, with the consequence that the differences on which β depends become more marked, and thereby afford greater accuracy.

Table I. is drawn up from a paper by Nasini and Bernheimer*. They were the first to use a jacketed prism, so that their results are the earliest of those suitable for deducing β . One substance in their list—bromonaphthalene—has been omitted, as it stands alone in giving an increase in $(\mu-1)v$ on heating. It is probable that the limit of experimental error is reached with that substance.

TABLE I.

Substance.	Temp.	Density.	μ_{α} .	$\beta = \frac{(\mu-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$.	v at lower temp.	$\frac{\beta}{v}$.
Thymol, $C_{10}H_{14}O$.	24°	0·96895	α 1·51453	0·0563	1·0320	0·058
	77·3	0·92838	α 1·49189	0·0600		
				0·0623		
				Mean 0·0600		
Cinnamic Alcohol, $C_9H_{10}O$.	24·8	1·04017	1·57311	0·077	0·96055	0·083
	77·3	1·00027	1·54939	0·086		
				0·011		
				0·080		
Anethol, $C_{10}H_{12}O$.	14·9	0·99132	1·55559	0·066	1·0087	0·0655
	77	0·94041	1·52526	0·063		
				0·069		
				0·066		
α -Methyl α -Naphthol, $C_{11}H_{10}O$.	14	1·09636	1·61474	0·0566	0·9121	0·0680
	77	1·04661	1·58508	0·0570		
				0·0850		
				0·0620		
Dimethylnaphthalene, $C_{12}H_{12}$.	16·4	1·01803	1·60765	0·0869	0·9823	0·09
	77	0·97411	1·57901	0·0899		
				0·0893		
				0·0890		

Column 2 gives the temperatures, 3 the densities, and 4 the indices for the line α . Col. 5 gives three values of β as calculated from the two indices for each of the lines α , D, and β . The indices for D and β will be found in the original paper.

* *Gaz. Chim. Ital.* xv., 1885.

The third value (that given by $H\beta$) for cinnamic alcohol appears to be wrong, and the third value for methyl α -naphthol also, though to a less degree. In calculating the means, I have ignored the first and allowed only half weight to the second of these.

The next table contains all the observations made by Perkin*, whose apparatus was still more perfect than that of Nasini and Bernheimer. The index is quoted here for the line D only, but the quantity β has been calculated from the lines A, C, D, and F. Where a fifth value is given, it is calculated from the line G.

Tables I. and II. contain the results yielded by substances of very varied chemical types. It may be stated at once that, although the last six substances have been put in the Table, the discussion of the figures they yield will be deferred. It is known that they are of very exceptional character; for example, that they change in chemical constitution when heated, so that it is not strictly the same substance we are dealing with at the two temperatures given in the Table†. Excluding these compounds, the values of β are of a satisfactory order. They do not vary largely, the extreme values being 0.09 and 0.043, most of them lying between 0.065 and 0.045. That is to say, on the hypothesis which led to the calculation, the actual space filled by one gramme of the substance is about one twentieth of a cubic centimetre.

Column 7 shows the value of β/v , that is the ratio of the actual to the apparent volume of a liquid. The extremes are 0.15 and 0.054. If we exclude methylene di-iodide, a substance of exceptional density, the extremes are 0.09 and 0.054, and twelve out of the sixteen liquids lie between 0.076 and 0.054; the average value is 0.064.

These results are promising, both with regard to the absolute magnitude and the approach to similarity of value for the different liquids. This last fact was to be expected, for it is probable that ordinary liquids, under similar conditions of temperature and pressure, have volume constitutions of a fairly uniform type.

* Chem. Soc. Journ. 1892, pp. 287 & 800.

† Compare Perkin, Chem. Soc. Journ. 1892, p. 840.

TABLE II.

Substance.	Temp	Density.	μ_D .	$\beta = \frac{(\mu-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$	v at lower temp.	$\frac{\beta}{v}$.
Heptane, C_7H_{16}	12.2	0.69026	1.39220	0.0808		
	88.8	0.62301	1.35197	0.0810 0.0813 0.0814		
				Mean 0.0810	1.4487	0.056
Octyl Iodide, $C_8H_{17}I$.	14	1.34096	1.4922	0.0467		
	88	1.25332	1.4579	0.0476 0.048		
				0.0475	0.7457	0.063
Methylene Iodide, CH_2I_2 .	8	3.3480	1.74935	0.0425		
	87	3.1390	1.69500	0.0429 0.0442 0.0445		
				0.0440	0.29868	0.15
Toluene, C_7H_8	10.7	0.87532	1.5028	0.0677		
	90	0.79949	1.45673	0.0683 0.0688 0.0709		
				0.0688	1.1424	0.06
Phenyl Chloride, C_6H_5Cl .	9.6	1.1167	1.53103	0.0421		
	89.2	1.0302	1.48731	0.0533 0.0572 0.0543 0.0577		
				0.0540	0.8955	0.06
Phenyl Bromide, C_6H_5Br .	4.2	1.5100	1.56845	0.0458		
	89.2	1.39638	1.52235	0.0440 0.0464 0.0487 0.052		
				0.047	0.66225	0.071
Phenyl Iodide, C_6H_5I .	8	1.8482	1.62755	0.0444		
	88	1.7272	1.58301	0.0441 0.0450 0.0461 0.0465		
				0.0452	0.54107	0.083
Aniline, C_6H_7N	11.2	1.02792	1.5912	0.0490		
	90.1	0.95783	1.54867	0.0513 0.0546 0.0537 0.0538		
				0.0525	0.97283	0.054

Table II. (*continued*).

Substance.	Temp.	Density.	μ_D .	$\beta = \frac{(\mu-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$	v at lower temp.	$\frac{\beta}{v}$.
Dimethylaniline, $C_9H_{11}N$.	8	0.96688	1.56535	0.0610	1.03425	0.065
	89.7	0.89961	1.52345	0.0665 0.0671 0.0850 <hr/> 0.068		
α -Naphthylamine, $C_{10}H_9N$.	51	1.10043	1.67084	0.060	0.90873	0.076
	88.4	1.07207	1.65209	0.0678 0.0704 0.0800 <hr/> 0.069		
Ethyl Cinnamate	12.9	1.05560	1.56351	0.060	0.94733	0.071
	91.1	0.98815	1.52500	0.0663 0.0684 0.080 <hr/> 0.068		
Acetyl-acetone	11	0.98506	1.44493	0.211	1.0152	0.235
	99.3	0.89787	1.39634	0.222 0.224 0.251 0.278 <hr/> 0.240		
Methyl-acetyl-acetone.	8.34	0.99189	1.44210	0.173	1.0081	0.185
	99.2	0.90324	1.39526	0.178 0.185 0.207 <hr/> 0.186		
Ethyl-acetone-oxalate.	17	1.12879	1.46503	0.0676	0.8859	0.080
	100	1.04109	1.42617	0.0700 0.0772 0.0760 <hr/> 0.0710		
Ethyl-diaceto-acetate.	17.6	1.09313	1.45729	0.0476	0.9148	0.0564
	99.8	1.0675	1.41932	0.0479 0.0487 0.0530 0.0603 <hr/> 0.0515		

Table II. (*continued*).

Substance.	Temp.	Density.	μ_D .	$\beta = \frac{(u-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$	$\frac{v}{\text{at lower temp.}}$	$\frac{\beta}{v}$.
Diacetyl-acetone	60	1.04248	1.46691	0.292	0.96146	0.326
	99.8	1.00615	1.44386	0.291		
				0.309		
				0.350		
				0.314		
Allyl-acetyl-acetone ...	13.5	0.97671	1.46156	0.1515	1.0238	0.1709
	99.2	0.89832	1.41868	0.1614		
				0.1680		
				0.1894		
				0.205		
				0.175		

It may be objected that the average values obtained for β and β/v are much too small, seeing that other estimates of these quantities give much larger figures. The ratio

$$\frac{\text{actual volume of molecules}}{\text{apparent volume of liquid}}$$

is generally estimated to be about 0.2 or 0.3; that is, about four times greater than the value now found by the new hypothesis.

To this objection it may be replied:—

1. Prof. Tait has expressed the opinion that "the estimates hitherto made can hardly be called even rough approximations. But probably the particle does not occupy so much as 5 per cent. of its share of the whole content"*. This estimate is not far from the 6 per cent. yielded by the foregoing calculations.

2. It will be suggested at a later stage that the expressions which give 0.2 or 0.3 for the ratio β/v probably measure, not the molecular volume itself, but that part of the apparent volume which may be called the molecular domain.

Postponing further consideration of this argument, we may inquire whether the value of β is dependent on the particular

* Tait, 'Properties of Matter,' p. 90.

temperatures employed in the observations. That is to say, presuming that it is a measure of molecular volume, does it show any change in value at higher or lower temperatures? Very few series of observations are accurate enough to stand the severe test imposed on them by an attempt to answer this question. Of the few that seem suitable, I shall give two examples, taken from the work of Ketteler*. From these it will appear that the answer varies, carbon disulphide showing a constant value for β at different temperatures, while water gives a *diminishing* value as the temperature rises.

Carbon Disulphide, CS₂.

Temperature.	v .	μ_D .	β .	$(\mu-1)(v-\beta)$.
-20°	0.75582	1.65950	0.0476	0.46879
-10	0.76442	1.65158	0.0476	0.46878
0	0.77314	1.64375		0.46874
10	0.78207	1.63593	0.046	0.46872
20	0.79131	1.62806	0.046	0.46873
30	0.80093	1.62004	0.0464	0.46871
40	0.85515	1.61187	0.0459	0.46871

Here it is evident that the value of β remains practically constant through a range of 60° C. The values given were calculated from 0° as one of the temperatures in each case.

If β has the meaning here assigned to it, the above measurements indicate that 1 gram of carbon disulphide actually occupies 0.046 cubic centimetre. Moreover, if we take the ratio β/v , we find it to be 0.062 at 0° C., which is again very near the average value yielded by the many liquids already given.

* *Ann. Phys. Chem.* xxxv. p. 693.

Water.

Temperature,	v .	μ_D .	β calculated from first.	β calculated for each pair.
20.9	1.00196	1.33287		} .204 } .114 } .085 } .067
31.0	1.0044	1.33177	0.204	
56.0	1.0149	1.32776	0.150	
87.0	1.0336	1.32107	0.114	
94.0	1.0386	1.31943	0.108	

The result here is quite different from that shown by carbon disulphide ; β varies with every change in the temperature. It is given in two columns, the first containing values obtained by taking each observation in conjunction with that at the lowest temperature. The next column contains values obtained by taking each pair of observations. This last series is the more suggestive.

1st. It shows β to be *diminishing* as the temperature rises, and gives the value it has between 87° and 94°. At this temperature, where the water is approaching its boiling-point, the value of β becomes 0.067 cubic centim., a close approximation to that given by the other liquids.

2nd. The ratio β/v at the high temperatures is 0.063, almost exactly the ratio 0.064 given by the other liquids.

These results are suggestive, and at once raise a question as to the meaning of the diminution in β as the temperature rises towards boiling-point. Any one acquainted with recent researches on the physical properties of liquids will at once recall those of Ramsay and Shields on Molecular Complexity; those of Thorpe and Rodger on Viscosity of Liquids, &c., as bearing on this question. The investigations mentioned, along with others, have rendered it almost certain that the molecule of water is a complex of the form nH_2O , and that the value of n in this expression diminishes as the temperature rises. Consequently the high value now found for the volume of the water molecule, as measured by β , appears to be another indication of its greater molecular complexity, and

the fall towards normal value as boiling-point is approached points to a molecular simplification as indicated by the other methods.

Somewhat similar, though more erratic, is the available evidence with regard to other liquids of known molecular complexity, such as the alcohols and acetic acid. The figures are not now quoted, as they must be redetermined with greater accuracy and perfect exclusion of atmospheric moisture during the experiments.

We may now test the value of β in another way. It has already been mentioned that the ordinary Gladstone expression fails to deal with the transition from liquid to gas, and the suggestion is now made that the discrepancy is due to the neglect of the volume of the particles, a quantity which practically vanishes in the case of vapours.

The question arises, will the value of β deduced from a liquid bring the liquid and gaseous numbers into agreement? Not many observations are available for this comparison. Obviously the same specimen ought to serve for the liquid and vapour. The work of Lorenz* and Prytz almost exhausts the published data of this sort.

Lorenz gives two observations on the liquid at different temperatures, and also an observation on the vapour formed by the liquid. Unfortunately Lorenz selected the temperatures of 10° and 20° C. for the observations on the liquids, which are too near one another to afford a very satisfactory basis for calculating β . Notwithstanding this, the results as shown in the following table (p. 683) are very encouraging.

This table shows that the difference between the specific refraction of a liquid and its vapour as calculated by the Gladstone expression may be 10 per cent. of the whole; also that if the value of β as calculated from the liquid be employed in the modification now proposed, the difference between the liquid and vapour falls to less than 1 per cent. With a more accurate estimate of β this difference might be still further reduced. The modified expression gives practically a constant for both liquid and vapour.

One remark ought to be made. The value of β for carbon

* Wied. *Ann.* 1880.

Substance.	Temp.	Specific Refraction ($\mu - 1$) v .		β calculated from Liquid.	Specific Refraction ($\mu - 1$) ($v - \beta$).	
		Liquid.	Vapour.		Liquid.	Vapour.
Carbon Disulphide ...	10	·4889	} ·4289	0 0886	·4334	·4289
...	20	·4882				
Chloroform	10	·2979	} ·2681	0 0672	·2677	·2681
...	20	·2975				
Ethyl Iodide	10	·2634	} ·2334	0 0685	·2282	·2334
...	20	·2629				
Ethyl Acetate	10	·4148	} ·401	0 030	·4035	·401
...	20	·4147				
Ethyl Ether	10	·4905	} ·4561	0 098	·4554	·4561
...	20	·4900				

disulphide is much greater than that deduced from Ketteler's figures already quoted; a fact which is difficult to explain, though difference of specimen may have something to do with it.

There is another set of observations by which β can be tested. Prytz has given data for nine liquids and their vapours; but as he only took one observation on the liquid his work is only available for calculating β from the liquid and vapour values. This can be compared with the average values previously obtained.

Substance.	β calculated from Liquid and Gas.
Methyl Alcohol	0·09
Ethylene Chloride	0·116
Ethedene „	0·085
Acetone	0·091
Methyl Acetate	0·0655
Ethyl Formate	0·093
Propyl Iodide	0·112
Methyl Propionate	0·096
Benzene.....	0·16

These values are slightly higher than those deduced from two observations on the liquid, but the difference is not great.

A *prima facie* case having been shown for attaching some physical significance to the symbol β , it appeared probable that the values for different substances would show definite

relationships between themselves; or that the value of β for a given substance would be related to the value of v at the freezing, boiling, or critical temperature.

Of these the boiling-point is the one for which data are mostly available, and a little examination suggested a close relation between the absolute temperature of the boiling-point and the two volumes v and β . It may conveniently be written

$$\beta \propto \frac{v_T}{\sqrt{T}}.$$

For the Centigrade scale the relation indicated seems to approach one of equality.

There are ten substances for which β , v_T , and T are known with sufficient (or apparently sufficient) accuracy. The above equation is here used to find the value of β from v and T , and the value so obtained is compared with that given by the optical data.

The following table shows that the results are in fair agreement, if we remember that the three data compared together are mostly due to different observers using different specimens.

Substance.	v_T .	$\sqrt{T}$.	$v_T \div \sqrt{T}$	β from refraction.
Heptane	1.629	19.3	0.084	0.081
Carbon Disulphide ...	0.818	17.89	0.0457	0.0460
Aniline	1.146	21.2	0.054	0.0525
Toluene	1.282	19.62	0.065	0.068
Water	1.043	19.34	0.054	{ 0.067 ? 0.060
Phenyl Chloride	1.044	20.1	0.052	0.054
Phenyl Bromide	0.766	20.7	0.0365	0.047
Phenyl Iodide	0.6388	21.5	0.03	0.045
Ethyl Cinnamate	1.2005	23.15	0.052	0.068
Ethylene Dibromide...	0.5178	20.13	0.026	0.031

Many other figures might be given but they are of inferior accuracy, and ought not to be placed along with those just quoted. The examples are sufficient to establish a case for further inquiry, inasmuch as the agreement is close enough in six or seven cases to preclude the notion of accidental coincidence.

If additional data confirm the foregoing result, it affords

us another method of calculating the quantity β when the boiling-point and the density at that temperature are known. I propose to get β for other substances by this method, and test several deductions by the result. It is evident, on general grounds, that values of β calculated by this method will be of the same order of magnitude as that given by the optical data. All ordinary liquids boil between, say, 50° and 300° Centigrade, or 320° and 470° absolute; and the square roots range between 18 and 22, with average about 19, which is fairly near the average ratio for v_1/β .

It is hardly necessary to point out that this relation may possibly supply a hint as to the unknown law between volume-relationships of liquids and the temperatures. For example, I was tempted to compare the varying value of β in the case of water with its very varied coefficient of thermal expansion α .

Apparently, these two quantities are inversely proportional, as shown in the following table by the comparative constancy of the product $\beta \times \alpha$.

Water.

Temperature-range.	β .	α .	$\beta \times \alpha$.
20.9 to 31	0.203	$.00025$	$.0000505$
31 „ 56	0.144	$.0004$	$.0000576$
56 „ 87	0.082	$.00059$	$.0000482$
87 „ 94	0.067	$.00072$	$.0000482$

In reading this table the approximate character of the value for β must be kept in mind. The last column then indicates the probability of some connexion between β and α . α is calculated from data given by Thorpe.

Slight though this evidence may appear it seems to me to warrant further careful investigation, in view of the desirability of finding some method of obtaining a general law governing the thermal expansion of liquids, and the admitted difficulty of the problem.

Note.—I have quite recently calculated the value of β from another series of figures due to Ketteler, and quoted in Landolt and Bornstein's tables. The general tendency is as above, but the product $\beta \times \alpha$ varies from $\cdot 0_428$ to $\cdot 0_4600$. There is perhaps internal evidence, however, for regarding the figures as less accurate than the foregoing, so that I let the matter stand, subject to correction.

Summing up the general results obtained so far, we find:—

1. In simple liquids the quantity β lies between narrow limits, the average being $0\cdot 05$ cubic centim.
2. The ratio β/v averages $0\cdot 064$. That is, the actual volume of the molecules is about 6 per cent. of the apparent volume.
3. Liquids known to have exceptional physical properties, such as water &c., give higher values of β than usual. This higher value changes with temperature, and is probably a measure of molecular complexity.
4. There is reason to think that some liquids, like carbon disulphide, yield a constant value for β at different temperatures.
5. The value of β given by a liquid enables us to apply the Gladstone formula (amended) during the transition from the liquid to the gaseous state.
6. There are grounds for believing that the value of β is related to other volume-relationships of the substance, as, for example, the specific volume at the boiling-point.
7. In some cases there may be a connexion between β and the coefficient of thermal expansion.

A further argument for the introduction of the quantity β is the fact that it will remove certain anomalies in molecular refractions, bringing the value for hydrogen, chlorine, &c. into harmony with that given by the gaseous elements. This point, together with others of a like nature, is reserved for another paper.

So far as the suggestions thrown out are probable, it would appear that "the actual volume of the particles" is not a correct expression for β . In the case of water, β has a varying value, which is attributed to the resolution of its

complex molecule into simpler forms. But such resolution could not diminish the volume of the particles, unless we mean by this phrase “the true volume of the atoms + the inter-atomic space.” If we imagine a surface drawn to enclose the molecule, it will include such space as lies between the atoms in that molecule. Similarly, when two molecules coalesce to form one of greater complexity the space occupied by the two is greater than before. They do not actually touch, so that the enclosing surface has a greater volume than twice that which encloses one molecule.

The results obtained so far show that the modified Gladstone expression promises to cover all ranges of density*. This wide range of applicability is obtained by emphasizing the volume-relationships involved in the formula—a fact which acquires further significance when we remember that it is as a measure of a volume that the Gladstone expression has proved so useful. For the specific refraction of a substance, $(\mu - 1)v$, is evidently a fractional part of the specific volume v . Moreover, both Dufet (*Journ. de Phys.* 1885) and Sutherland (*Phil. Mag.* 1888), in developing a theoretical basis for the Gladstone law, have shown that “volume of molecules” is involved, though the exact definition of the phrase is not arrived at.

It seemed worth while asking whether this fractional part of the volume had a physical meaning. If the quantity β may be regarded as a measure of true molecular volume, and there still remain a certain element of volume to be measured, it will most probably be found by accepting a well-known kinetic constitution for the liquids. If temperature be constant, we may assume that each molecule of a liquid vibrates as a whole over a certain region called its domain, the centre of this region being defined as the centre of the molecule when in its mean position.

The extent of the domain, and the relation between it and the total volume, will depend on the energy of molecular motion, and on the law of molecular force with regard to distance.

* Except perhaps in the case of certain solids. See data for refraction of solids collected in the paper by Dr. Gladstone and myself already mentioned, *Chem. Soc. Trans.* 1895, p. 831.

Thus the apparent volume is made up of fractional parts, one of which may be called the sum of the volumes of the molecules, another the sum of the volumes of the domains, and a third the interstitial spaces. A satisfactory theory for evaluating these can perhaps not be found till more is known of the magnitude and law of the molecular forces, but an empirical examination suggested that $(\mu-1)v$ might possibly serve as a basis for finding the domain. At any rate it gives by transposition a part of v which fairly answers to the only criterion of the domain which I can lay down.

Nothing is known as to possible change of the dimensions of the molecules themselves, but it seems highly probable that the domain of a given substance will most certainly differ under different physical conditions. Still further does it seem probable that the domain of different substances, heated between the same temperature-limits, may change in the same ratio. Figures in the tables which follow will prove this for the new expression, to what may be called a first approximation.

The transformation referred to is

$$(\mu-1)v = \mu \left[v - \frac{v}{\mu} \right],$$

the value of the square bracket on the right being equal to $\frac{\mu-1}{\mu} \cdot v$.

It was evident to me, and will be to any one familiar with the data given by molecular refractions, that this last expression gives a fraction of v tolerably near that obtained by the use of the other well-known expression

$$\frac{\mu^2-1}{\mu^2+2} \cdot v.$$

I can best illustrate this by taking a table from a lecture on the "Range of Molecular Forces" delivered to the Chemical Society by Rücker (Chem. Soc. Journ. 1888, p. 253).

Using Hopkinson's data, Rücker compares the values of

$$\frac{K-1}{K+2} \quad \text{and} \quad \frac{\mu^2-1}{\mu^2+2}$$

for five substances (K = specific inductive capacity). His object is to show that the figures justify well-known theories due to Clausius, Clerk-Maxwell, and others. Assumptions underlying these expressions make them a measure of the ratio

$$\frac{\text{true volume of molecules}}{\text{apparent volume of liquid}},$$

though the expression "true volume of molecules" is a quantity depending on what is better known as the "diameter of the molecule," *i. e.* the smallest distance between the centres of molecules.

The table is quoted bodily, with an additional column to show the value of $\frac{\mu-1}{\mu}$, this last being the factor of v in the square bracket of the transposed expression.

Substance.	Formula.	K.	μ^2 .	$\frac{K-1}{K+2}$.	$\frac{\mu^2-1}{\mu^2+2}$.	$\frac{\mu-1}{\mu}$.
Amylene	C_5H_{10} .	2.05	1.9044	0.260	0.232	0.245
Benzol	C_6H_6 .	2.38	2.2614	0.315	0.296	0.334
Toluol	C_7H_8 .	2.42	2.2470	0.321	0.291	0.333
Xylol.....	C_8H_{10} .	2.39	2.2238	0.317	0.290	0.329
Cymol	$C_{10}H_{12}$.	2.25	2.2254	0.294	0.290	0.295

Here it is evident that there is a close agreement among the three sets of figures, amply sufficient to justify further examination. So far as differences occur, $\frac{\mu-1}{\mu}$ is nearer $\frac{K-1}{K+2}$ than is $\frac{\mu^2-1}{\mu^2+2}$.

In pursuing this comparison I shall introduce β , so that

$$(\mu-1)(v-\beta) = \mu \left[(v-\beta) - \frac{v-\beta}{\mu} \right].$$

The square bracket is equal to

$$\frac{\mu-1}{\mu} (v-\beta),$$

and it is under this head that the figures appear in the following tables :—

Carbon Disulphide.

Temperature.	$\frac{\mu^2-1}{\mu^2+2} \cdot v.$	$\frac{\mu-1}{\mu} \cdot (v-\beta).$	$\frac{v-\beta}{\mu}.$	$\frac{v-\beta}{\mu}$ calculated.
-20°	0.2788	0.2821	0.4277	0.4259
-10	0.2793	0.2835	0.4349	0.4341
0	0.2798	0.2847	0.4424	0
10	0.2803	0.2867	0.4494	0.4502
20	0.2808	0.2875	0.4578	0.4581
30	0.2813	0.2890	0.4659	0.4659
40	0.2819	0.2904	0.4746	0.4735

The experimental data are Ketteler's, and have already been given.

On comparing columns 2 and 3, it is seen that the figures are remarkably close to one another. The difference is just over 1 per cent. at -20°, and though it increases as the temperature rises, it only just exceeds 3 per cent. at +40° C.

Column 4 contains the values of the second term in the bracket, or $\frac{1}{\mu}$ th of $v-\beta$; and column 5 contains the "calculated" values for the same expression. The calculation is made by taking the value at 0° C. and multiplying by the square root of the ratio of absolute temperatures. Thus the value at -20° is equal to

$$0.4424 \times \sqrt{\frac{254}{274}} = 0.4259.$$

I was led to try this by the results obtained in the first part of the present paper, and the extremely close approximation of the calculated to the other numbers is surely of some importance. The quantity $\frac{v-\beta}{\mu}$ will be referred to as the interstitial space.

The next table contains data for substances already mentioned.

Substance.	Temp.	$\frac{\mu-1}{\mu} (v-\beta)$	$\frac{\mu^2-1}{\mu^2+2} v$	Difference.		Ratio of New Values.
				Actual.	per cent.	
Thymol	24.4	0.39022	0.3110	0.079	20	1.0154
	77	0.39542	0.3124	...	...	
Cinnamic Alcohol.....	24.8	0.3208	0.3168	0.004	1.2	1.0152
	77	0.3261	0.3182	...	...	
Anethol	14.9	0.3378	0.3241	0.0137	4	1.0199
	77	0.3445	0.3260	...	...	
α -Methyl α -Naphthol	14	0.3255	0.3182	0.007	2	1.0187
" "	77	0.3316	0.3202	...	...	
Dimethyl Naphthalene	16	0.3377	0.3395	-0.0018	-0.6	
	78	0.3438	0.3412			
Heptane.....	12	0.3853	0.3451	0.04	10	1.030
	89	0.3968	0.3471	...	...	
Octyl Iodide	14	0.2303	0.2164	0.014	6	1.024
	88	0.2358	0.2177	...	-11	
Methylene Iodide.....	8	0.1091	0.1216	-0.012	...	1.0318
	87	0.1126	0.1225	...	...	
Toluene	10.7	0.3591	0.3376	0.021	6	1.0312
	90.3	0.3703	0.3403	...	...	
Phenyl Chloride	9.6	0.2922	0.2771	0.015	5	1.029
	89	0.3007	0.2793	...	...	
Phenyl Bromide	4.2	0.2230	0.2168	0.006	3	1.031
	89.2	0.2296	0.2185	...	...	
Phenyl Iodide	8	0.1913	0.1919	-0.0006	-0.3	1.028
	88	0.1967	0.1935	...	...	
Aniline	11.2	0.3417	0.3288	0.018	4	1.0273
	90.1	0.3511	0.3319	...	...	
Dimethylaniline	8	0.3462	0.3336	0.0126	3.6	1.0304
	89.7	0.3567	0.3363	...	...	
Ethyl Cinnamate	12.9	0.3169	0.4210	0.104	33	1.0255
	91.1	0.3250	0.4378	...	...	
α -Naphthylamine	51	0.3370	0.3396	-0.0026	0.8	1.0349
	88.4	0.3408	0.3409	...	...	
Acetyl-acetone	11	0.2387	0.2702	0.0315	13	1.033
	99.3	0.2488	0.2678	...	...	
Methyl-acetyl-acetone	8.34	0.2560	0.2668	-0.0108	4	1.0322
	99.2	0.2800	0.2656	...	...	
Ethyl-acetyl-acetone.....	15.4					1.0272
	100.3					
Ethyl-acetone-oxalate	17.0	0.2587	0.2449	0.0138	5	1.0287
	100.0	0.2665	0.2545	...	...	
Ethyl-diacetol-acetate	17.6	0.2710	0.2493	0.0217	8	1.0322
	99.8	0.2615	0.2387	...	...	
Diacetyl-acetone	60.0	0.2065	0.2667	-0.0602	29	1.0322
	99.8	0.2089	0.2639	...	...	
Allyl-acetyl-acetone ...	13.5	0.2681	0.2812	-0.0131	5	1.0039
	99.2	0.2769	0.2809	...	...	
Ethyl Acetate	10	0.2909	0.2546	0.0363	12	1.0040
	20	0.2920	0.2549	...	...	
Chloroform	10	0.1848	0.1990	0.0058	3	1.0029
	20	0.1855	0.1791	...	...	
Ethyl Alcohol	10	0.3266	0.2804	0.046	14	1.0046
	20	0.3276	0.2807	...	...	
Ethyl Iodide	10	0.1514	0.1557	-0.0043	3	1.0049
	20	0.1521	0.1558	...	...	
Carbon Disulphide ...	10	0.2668	0.2805	-0.013	5	1.0049
	20	0.2681	0.2809	...	...	

On examining this table we find that the new expression gives results which very fairly agree with those derived from Lorentz's formula. The average difference between the two is about 5 per cent., a difference not greater than that which would be yielded by the expressions of Clausius and Maxwell. So far as this agreement goes we may regard

$$\frac{\mu-1}{\mu}(v-\beta)$$

as a fair approximation to a volume quantity, which I may be allowed to call "molecular domain."

The value, as given by either formula, increases with the temperature. The highest increase by the μ^2 expression is about one per cent. in the case of aniline. Whether such an increase could be attributed to the molecule proper, is an unsolved problem. It is usual to regard the values yielded by the Lorentz formula as more constant than here appears, but the figures are too numerous and too reliable to leave any doubt about the magnitude of the change.

As I have already said, it seems probable that domains will change in the same ratio between the same temperature limits. This can be tested for the new expression by the figures in the last column, which gives the ratio of the two values for

$$(v-\beta) - \frac{v-\beta}{\mu} \text{ or } \frac{\mu-1}{\mu}(v-\beta)$$

found at two temperatures.

To facilitate comparison, the substances are arranged in groups, marked off by a line. The members of each group are heated between approximately the same temperatures. Thus thymol is heated between 24°·4 and 77°, cinnamic alcohol between 24°·8 and 77°. The domain of the first increases in the ratio 1·0154, that of the second in the ratio 1·0152.

The members of the large group beginning with heptane and ending with ethyl cinnamate are heated between limits the lower of which lies between 4° and 12°, while the upper limit lies between 87° and 90°. The new domain rises generally in this group by 3 per cent. Out of the ten substances, seven give a ratio of increase very near to 1·030, the other three are near 1·027.

The next group includes eight substances heated between, say, 12° and 100° . Three give ratios close to 1.033, two yield 1.027. The last group is heated from 10° to 20° only, and gives ratios close to 1.004, except in the case of alcohol.

These results seem to afford a reasonable presumption in favour of the figures being regarded as a measure of domain. There is evidently a tendency for the ratio of increase to be the same for the different liquids, although their densities vary in the ratio of 5 to 1. It is surely improbable that molecules of very varying atomic structure should have the same temperature increase, but the same improbability does not attach to "domain."

There is, however, one aspect of this question which may prove to be still more important. It may be objected that the empirical * expression here used for obtaining the domain is too fanciful to be regarded with serious consideration. It may further be pointed out that it is equivalent to

$$(\mu-1)(v-\beta) \times \frac{1}{\mu},$$

as we have seen, and that the first two factors give a constant. Any relationships like those just alluded to must therefore be dependent on a more or less common temperature function for the refractive index.

* In the June number of the Chem. Soc. Journal appears an abstract of a paper by W. F. Edwards (American Chem. Journ.), who obtains the expression now proposed, as a new formula for specific refraction, thus:—If V and V_1 are the velocities of light in space and the substance respectively, $\mu = \frac{V}{V_1}$. Let $A = V - V_1$, then $A = \frac{\mu-1}{\mu} V$. If the difference A is proportional to the amount of substance, and assuming as unit one gramme of substance in 1 cub. centim., and that X is the retardation of velocity for unit substance, then

$$X = \frac{\mu-1}{\mu} V \times \frac{1}{d}.$$

This is the same expression as that I propose for domain, multiplied by V . As will be seen from my tables, and as Edwards shows, the value of X is not a constant. It cannot therefore serve as a measure for specific refraction unless under stated conditions of temperature. He promises to return to this, but will, I believe, only find the solution by substituting "volume of domain" for volume of substance. As will be seen, I obtain his expression by a transformation of the Gladstone expression.

It is evident, apart from arithmetic error, that this must be so. But such an objection, while having weight against an expression obtained by the method we have pursued, at once raises a very suggestive question. Does the evidence really justify the idea that the refractive indices of various substances change in the same ratio between the same temperature limits? In other words, Is the ratio magnitude of the change independent of the nature of the liquid? The following table gives the evidence available. The substances quoted are those already dealt with, but the comparison deals directly with the refractive indices, and is therefore free from all objections which might be urged against the hypothesis of this paper.

To facilitate comparison, the substances are again divided into groups, the order being slightly different from that previously given. The refractive indices are given in column 3; column 4 gives the ratio of the two indices, which are slightly corrected in column 5. This is done by calculating from columns 2 and 3 the average change in the index per degree, as shown in column 6. The figure thus obtained is used to calculate the change of index for 80° exactly, which means an alteration of only a degree or two for most substances. The ratio in column 5 is calculated then for a common interval of 80° , and will be somewhat nearer the truth than the uncorrected ratio in column 4.

Column 7 gives the exponent of μ in the statement $\mu^x \propto \frac{1}{T}$, where T is the absolute temperature. It therefore

equals
$$\log \frac{T_2}{T_1} \div \log \frac{\mu_1}{\mu_2}.$$

The ratio $\frac{\mu_1}{\mu_2}$ is about 1.03, so that the different powers of it do not vary so much.

An examination of this table will show that for the same temperature limits there is a fair approach to constancy in the ratio $\frac{\mu_1}{\mu_2}$.

Thus the indices of the first seven substances all give

Substance.	Temp.	μ .	$\frac{\mu_1}{\mu_2}$.	$\frac{\mu_1}{\mu_2}$ corrected.	$\frac{\mu_1 - u_2}{T_2 - T_1}$.	$x = \lg \frac{T_2}{T_1} \div \lg \frac{\mu_1}{\mu_2}$.
Heptane.....	12°	1.3922	} 1.0297	1.0317	.000522	8.1
".....	89	1.35197				
Methylene Iodide.....	8	1.74935	} 1.0321	1.0325	.000671	8.0
".....	87	1.69500				
Toluene.....	10.7	1.5028	} 1.0316	1.0318	.000576	8.05
".....	90	1.45673				
Phenyl Chloride.....	9.6	1.53103	} 1.0293	1.0295	.000546	8.84
".....	89.2	1.48731				
Acetyl-acetone.....	11	1.44493	} 1.0349	1.0314	.000552	7.92
".....	99.3	1.39634				
Methyl-acetyl-acetone.....	8.34	1.4421	} 1.0334	1.0295	.000514	8.49
".....	99.2	1.39526				
Ethyl-acetyl-acetone....	15.4	1.44066	} 1.0324	1.0307	.000535	8.0
".....	100.3	1.3952				
Phenyl Bromide.....	4.2	1.56845	} 1.0303	1.0285	.000543	9.46
".....	89.2	1.52235				
Phenyl Iodide.....	8	1.62755	} 1.0279	1.0279	.000557	9.17
".....	88	1.58301				
Aniline.....	11.2	1.5912	} 1.0274	1.0278	.000538	9.23
".....	90.1	1.5487				
Dimethylaniline.....	8	1.5583	} 1.0270	1.0265	.000510	9.6
".....	89.7	1.51704				
Ethyl-acetone-oxalate.....	17	1.46503	} 1.0272	1.0262	.000536	9.35
".....	100	1.4263				
Ethyl-diaceto-acetate.....	17.6	1.4573	} 1.0270	1.0261	.000463	9.29
".....	99.8	1.4193				
Ethyl Cinnamate.....	12.9	1.5479	} 1.0253	1.0259	.000476	9.93
".....	91.1	1.5108				
Octyl Iodide.....	14.5	1.4922	} 1.0236	1.0254	.000463	9.99
".....	88.5	1.4579				
Thymol.....	24	1.5145	} 1.0154	1.0154	.000427	10.7
".....	77.3	1.4919				
Cinnamic Alcohol.....	24.8	1.5731	} 1.0153	1.0153	.000447	10.6
".....	77.3	1.5494				

ratios very near to 1.031. This is specially striking if we take particular cases like the first two on the list—heptane and methylene di-iodide—as shown in the following short table (p. 696).

It is also noteworthy that this same ratio (1.03) holds good in the case of those substances whose tendency to tautomerism is productive of anomalies. These are acetyl-acetone, methyl-acetyl-acetone, and ethyl-acetyl-acetone, which give abnormal values for β , and which differ from all other substances, even when tested by the Lorentz formula. Of course the ratio 1.03 is not preserved all the way down this group; the lower

	Temp.	Density.	Between the same temp. limit.	
			Ratio of Densities.	Ratio of Indices.
Heptane	12	0.6903	}	1.11
„	89	0.6230		
Methyl Di-iodide.....	8	3.348	}	1.07
„ „	87	3.139		

members fall to about 1.026. Whether this means only a slight departure from the other value, or whether it indicates a breakdown of the suggested constant relationship can only be decided when many more accurate temperature observations are obtainable. The ratio altogether breaks down in the case of such substances as water, which, as I have suggested, show special relations to refractive index by reason of varying molecular complexity.

The last column in the foregoing table gives the ratio of the logarithms of temperatures and indices. Further research may make this column more valuable than it now appears.

Taken altogether, the table affords ground for believing that there are close relationships between refractive index and temperature, and, further, that the ratio of change for a particular temperature interval may be the same for many different liquids.

The question then arises, whether this last relation is direct, or arises from some material property changing with the temperature? Is it possible that the velocity of light may vary with temperature, apart from any relation to material substances, or is the foregoing relationship dependent upon some molecular function like that suggested, that is “molecular domain?”

It seems impossible to answer the first part of this question. The second part can be judged by analogy, which would appear to suggest that a molecular function is more probable. Thus, one might expect that the kinetic energy of the particles is the property directly increased by rise of temperature, and

that many or all other properties of the molecule are consequential upon that. The apparent volume of course increases. That fraction of the volume which is measured by

$$\frac{\mu^2 - 1}{\mu^2 + 2}v, \text{ or } \frac{\mu - 1}{\mu}(v - \beta)$$

also increases, whatever it may be called. This constant fact appears to be a decided argument in favour of these expressions, giving “domain” and not “volume of matter” simply. But again, if the plea for “domain” be granted, there ought to be increase, not only when the liquid is heated, but also when it is changed into a vapour. This is actually the case for $\frac{\mu - 1}{\mu}v - \beta$, the value of which increases in the ratio 1 to 1.4 or 1.5. This variability may be compared with that found by van der Waals for his constant “*b*” (‘Continuity &c.’, Phys. Soc. translation, p. 409).

Correction.

On page 286 of this volume (xiii.) of the ‘Proceedings’ in the report of the discussion upon Dr. Larmor’s paper, Professor Lodge is represented as criticising Dr. Larmor’s summary of Herr Wiener’s paper. It appears that Professor Lodge intended to refer to a summary made some time ago by Herr Wiener and not by Dr. Larmor.