XI. The variation in the density of water with the temperature

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those obtained by Matthiessen, we find that he fixes the maximum point of his curve at an alloy containing 37 per cent. of tin. This number agrees pretty closely with the formula AuSn if we take tin as having an atomic weight of 118, and gold as having an atomic weight of 197. The formula, then, AuSn, the maximum point of the electric conductivity-curve, and the point where the E.M.F. abruptly rises, lie between the alloys containing 36 per cent. and 38 per cent. respectively of tin. This method, then, confirms the existence of one of Matthiessen's supposed compounds, but has not confirmed the existence of the other two. It agrees, however, with the results obtained with the copper-tin alloys, and taken in conjunction with them shows that the point of maximum conductivity is the point where a compound exists. This does not seem an unreasonable result. Compounds of the formula Au_4Sn and Au_2Sn_5 are not very probable. Furthermore, the most common form for the curve of electric conductivity to take in the case of metals not combining is a **U**. If we regard the compound AuSn as practically a new metal of fairly good conductivity, we should expect two regions of depression between AuSn and gold, and between AuSn and tin to make the results correspond to those usually obtained. But we may derive a further conclusion from the E.M.F. measurements in the case of these alloys. The change in E.M.F. in passing over the compound amounts to ·25 volt. Now this is a measure of the energy absorbed in the cell in decomposing the compound and may, therefore, be taken as an approximate measure of the heat of formation of the compound itself.

XI. *The Variation in the Density of Water with the Temperature. By* D. MENDELÉEFF *.

THE expansion of water with change of temperature, although presenting great scientific interest, both for the comprehension of the action of heat upon matter and also for many experimental investigations, cannot yet be considered as elucidated in its theoretical aspect nor sufficiently worked out experimentally. It will be seen from Tables I. and II. that in the best existing determinations, and after the introduction of possible corrections †, we encounter discrepancies which,

* Translated by G. Kamensky. Communicated by Prof. Crum Brown, F.R.S.

† For instance, possible corrections for the value of the true coefficient of expansion of mercury, for the readings of the mercury thermometer, for weighing in air, for the increase of the expansion of the vessel with a rise of temperature, &c. Further on I consider certain of these correc-

even for ordinary temperatures, exceed hundred-thousandths *
while the accuracy of gravimetric and volumetric measurements can now be carried to millionths.

The publication of the present paper previous to my having been able to undertake a series of fresh and properly instituted determinations of the expansion of water, is accounted for by the fact that the collation and elaboration of the existing data referring to this subject has led me to the following somewhat simple expression :—

$$S_t = 1 - \frac{(t-4)^2}{(A+t)(B-t)C}, \quad \cdots \quad (1)$$

which embraces all that is known for the variation of the density of water (S_t) between $-10°$ C and $+200°$ C † with all the accuracy now attainable. A general expression for the variation of the density of water, while presenting a means for

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tions in detail. I have introduced some of them into the existing data of many observers, but I do not give the results thus obtained in this article, because in the first place I wish to preserve the original results of the experimenters, knowing that the greatest interest is always attached to them, and in the second place because many of these corrections are of doubtful value, unless they are made by the observers themselves. When studying the literature of the subject, it becomes a matter of regret that the majority of observers do not give their original experimental numbers (for example, the apparent volumes or weights of water). If these were known, it would be easier to introduce the necessary corrections and to form an estimate of the magnitude of the errors inherent in the figures thus given.

    * For example, at 25° the volume of water, according to Jolly, is equal to 1·002856; according to Matthiessen it is 1·002982. The first number approaches to the values given by Rosetti, Hagen, and others; the second is nearer to Despretz's determination.

    † In his admirable determinations of the expansion of water from 100° to 200°, Hirn plainly states that at these temperatures the expansion of water is expressed differently and more simply than at lower temperatures. Kopp and the majority of investigators give empirical expressions (by interpolation) for the expansion of water for only small variations of temperature, for instance from 75° to 100°, their endeavours to obtain a general expression, comprising the whole range of volumes from 0° to 100°, having been fruitless. Frankenheim (Pogg. *Ann.* 1852, lxxxvi. p. 463), in undertaking the great labour of making a series of fresh calculations for all the experimental data of Pierre, had in view to seek out a general expression (" Ausdruck des Naturgesetzes ") answering to the " conflict between heat and cohesion which evinces itself in the variation of the density of water," but was unsuccessful in finding a general algebraical expression for the dependence which is here concealed. He concludes his memoir with the words " Das Problem ist noch ungelöst." From this we see that the great importance of having a simple general algebraical expression for the expansion of water with a rise of temperature was long since recognized by many scientists.

working up experimental data, may also have a certain theoretical significance, inasmuch as it may assist in explaining the general law of the expansion of liquids *. For all liquids except water the rate of change of the density with the temperature (*i. e.* the differential coefficient $\frac{ds}{dt}$) varies but little, either rising or falling slightly with considerable variations of temperature ; for example :—

	Amyl alcohol.	Sulphuric acid ($93\frac{1}{4}$ p.c.).	Phosphorus tribromide.	Mercury.
$S_0 =$	0·8248	1·8525	2·92311	13·5956
$\frac{ds}{dt}$ at 0° ...	−0·00076	−0·00106	−0·00244	−0·002447
„ 25° ...	−0·00077	−0·00102	−0·00245	−0·002439
„ 50° ...	−0·00080	−0·00099	−0·00245	−0·002431
„ 100° ...	−0·00094	−0·00092	−0·00246	−0·002415
According to	Kopp (1855).	Kremers (1863).	Thorpe (1880).	Regnault.

In the case of water, on the other hand, the differential coefficient $\frac{ds}{dt}$ not only changes its sign at 4°, but in general varies with extraordinary rapidity, even (judging from Hirn's data, 1867) at temperatures far removed from 0°, above 100° :—

	0°.	25°.	50°.	100°.	160°.	200°.
$10^5 \frac{ds}{dt} =$	+6	−25	−45	−72	−100	−120

Although I do not desire here to touch upon the question of a first approximation towards the general law of the expansion of liquids, I consider it necessary to state that the

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* In the Journal of the Russian Physico-Chem. Soc. for 1884 (and also in the Journal of the Chem. Soc. London, 1884), I stated that the expansion of liquids may be approximately expressed (at a point far removed from their passage into another state and within the range of the ordinary accuracy of determinations) by an equation of the form $S_t = S_0 (1 - kt)$; and although in various quarters doubts were entertained as to the generality of such a law (especially by Avenarius and Grimaldi), on the other hand, not less weighty proofs of its applicability were brought forward (notably by Thorpe and Rücker, Kraiewicz and Konovaloff) ; so that the question of a general law for the expansion of liquids must be considered as having just entered upon its first phases of historical development. Just as when elaborating my first article (Journal of the Russ. Physico-Chem. Soc. 1884, p. 7), I then considered the question of the expansion of water as unique, and as requiring special determination, so now I maintain that the working out of this problem will advance the very idea of the general law of the expansion of liquids. I trust to return to this subject shortly.

aspect of formula No. 1 bears a certain relation to this subject, as will be seen from the method by which I arrived at it.

In order to obtain an expression fulfilling the condition that the density of water at 4° be taken as $=1$, it was necessary in the empirical formula

$$S_t = a + bt + ct^2 + dt^3 + \ldots \ldots$$

to take $a = 1$ and to make the sum of all the remaining members of the series divisible by $(t-4)$. But in order to comply with the fact that the density of water attains a maximum at 4°, it was necessary to admit that the remaining members are once more divisible by $(t-4)$, because then, when $t = 4$, the differential coefficient is equal to zero [*]. Therefore the formula

$$S_t = 1 - (t-4)^2 \, F \, (t), \quad \ldots \ldots \quad (2)$$

where $F(t) > 0$ and < 1, should be taken. Having determined the values of $F(t)$ or the magnitudes $(1 - S_t)/(t-4)^2$ from the aggregate of existing data, I became convinced from

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[*] As far as I know (from a notice in Pogg. *Ann.* 1853, xc. p. 628) Hassler, in America in 1832, was the first to apply an expression of the form

$$S_t = S_0 - A(t - t_m) - B(t - t_m)^2,$$

where t_m is the temperature of maximum density, for calculating the density of water. The necessity for discarding the term $(t - t_m)$ in the first degree, and for taking it only in the second degree, was already recognized by Miller (Phil. Trans. 1856), and is repeated by Hagen and Rosetti. But these observers, in their calculations for the expansion of water according to the formula

$$S_t = 1 - (t - t_m)^2 A + B(t - t_m)^{2+n} - C(t - t_m)^{2+k},$$

&c., have up till now always only adopted such functions where t invariably has a positive exponent, *i. e.* only enters into the numerator; whereas I have become convinced that formulæ of this kind satisfy the aggregate of known facts only when taken with a large number of terms, even if fractional indices be adopted, as done by Hagen and Rosetti. And if the number of the terms of the expression be great, then it loses that simplicity which alone fulfils the requirements we have a right to claim in a natural expression for the phenomena of nature. In addition to this, Hagen expressed the variation of specific gravity by a formula of the aspect

$$S_t = 1 - (t - t_m)^2 [A - B(t - t_m)^{1 \cdot 6}]^2,$$

while Rosetti had recourse to a similar formula for the expression of the volumes :

$$V_t = 1 + A \, (t - t_m)^2 - B(t - t_m)^{2 \cdot 6} + C(t - t_m)^{3 \cdot 2},$$

and since $V_t S_t = 1$, a comparison of both expressions, as well as a trial of them, convinces one of the total unsatisfactoriness of both or at least one of them.

numerous calculations that $F(t)$ is expressed by the sum of the terms $a + bt + ct^2 + dt^3 + \ldots$ with coefficients consecutively changing their signs, *i. e.* from $+$ to $-$, and decreasing in magnitude [*]. This indicated the convergent nature of the series and the possibility of expressing $F(t)$ in a simpler form which would rapidly converge. But I did not consider it as sufficiently exact, for the admission of terms with t^3 and even t^4 in $F(t)$ did not yet express the entire phenomenon of the expansion of water between $-10°$ and $+200°$ with even the small degree of accuracy which is found in contemporary determinations. In striving to express $F(t)$ in the simplest possible form I tried many of the expressions already proposed, but became convinced of their insufficiency [†]. As regards formula No. 1, I arrived at it from the following considerations :—

1. When I showed (see note p. 101) that the expansion of all liquids (except water) may be approximately expressed, like the expansion of gases, by the general formula

$$V_t = \left(1 + \frac{kt}{n}\right)^n,$$

where for gases $n = +1$ and for liquids $n = -1$, *i. e.* when for liquids it was possible to take

$$S_t = S_0 (1 - kt). \quad \ldots \ldots \ldots \quad (3)$$

[*] As an example I will cite one such formula, performing the multiplication by $(t-4)^2$ in order to show clearly the varying nature of the signs :

$$S_t 10^6 = 999875 + 63\cdot606\,t - 8\cdot3185\,t^2 + 0\cdot063238\,t^3$$
$$- 0\cdot00036703\,t^4 + 0\cdot0000008979\,t^5.$$

Expressions with $-At^6 + Bt^7$ can be considered as sufficient for the accuracy of contemporary determinations, but the above expression with t^5, although satisfying the greater portion of the curve, still, for ordinary temperatures ($20°$–$30°$) affords deviations which exceed the probable errors in corrected mean values.

[†] I for a long time confined my attention particularly to expressions of the form

$$\sqrt[3]{\frac{I}{S_t}} = 1 + (t-4)^2 F_1(t),$$

where the first member corresponds to the distance between the centres of the particles. I afterwards endeavoured to express the dependence of the density and of the volume of water upon its temperature by taking fractional indices (like Hagen and Rosetti) and tried the application of logarithmic (like Rankine) and catenary functions, and in general, like Hagen and Frankenheim, spent much time in endeavours to express this dependence by means of some simple algebraical formula with the least possible number of constants.

Then Thorpe and Rücker * concluded, on the bases of Van der Waals's theory, that the modulus of expansion of liquids k stands in intimate dependence on the temperature of their absolute boiling-points T_2, namely that

$$\frac{1}{k} = 2T_2 - 273. \quad \ldots \ldots \quad (4)$$

As in formula No. 2, $F(t)$ is essentially analogous in its signification to k in formula No. 3, I tried to calculate the value of $\frac{1}{F(t)}$ or $\phi(t)$ instead of $F(t)$, hoping thus to include the conception of the absolute boiling-point of water, and this led to the form of formula No. 1.

2. It was necessary for the complete expression of the expansion of water as a liquid that $F(t)$ should remain a positive fraction less than unity at all values of t, starting from a certain " critical " low temperature (below $-10°$), T_1, at which water solidifies under any condition (of pressure, electrical state, &c.), up to the higher " critical " temperature or absolute boiling-point T_2, at which water passes into vapour under any condition ; because it is only between these two limits T_2 and T_1 that the specific gravity of liquid water can be observed. Outside these limits $F(t)$ may acquire an imaginary value, or become greater than unity, or negative in sign. The form of formula No. 1 answers to these requirements for $F(t)$, because according to it

$$F(t) = \frac{1}{(A+t)(B-t)C} = \frac{1}{\phi(t)}.$$

3. It is known that if certain conditions be observed water may be cooled to $-10°$, and even much lower, without being converted into ice, and therefore A must be greater than 10. On the other hand, Dewar † showed that the absolute boiling-point of water does not lie below $+370°$, therefore B must be greater than 370 ; and as $2T_2$ enters into formula No. 4, we may suppose that B will express a quantity greater than $2T_2$, and that the value of it will be greater than $2T_1$.

4. These considerations of a theoretical character led me to conclude that the value of $\phi(t)$ should be found for various temperatures, and if these considerations were correct, that $(t-4)^2/(1-S_t)$ or $\phi(t)$ should be expressible by the parabola

$$\phi(t) = a + bt + ct^2,$$

* Thorpe and Rücker, Journal of the Chem. Soc., April 1884, xlv. p. 135.
† Dewar, Phil. Mag. 1884, (5) xviii. p. 210.

where a and b are positive and c negative; for then $ABC=a$, $(B-A)C=b$, and $-C=c$, for

$$(A+t)(B-t)C=ABC+(B-A)Ct-Ct^2.$$

Besides, under the above conditions $1/\phi(t)$ or $F(t)$ should expand in terms of t into a convergent series with changing signs, as is obtained in reality.

By taking from the most trustworthy determinations the values of $\phi(t)$ corrected as far as possible for temperatures $20°$, $30°$, $40°$, $50°$, $60°$, $70°$, and $80°$, and employing the method of least squares *, I obtained:—

$$\phi(t)=125780+1158\,t-1{\cdot}90\,t^2, \quad . \quad . \quad . \quad (5)$$

and the mean quadratic error of calculation proved to be far less than the possible error of experimental results. As a final verification of the formula obtained, the values of S_t were extrapolated by means of the expression No. 5 throughout the range of temperatures from $-10°$ to $200°$, and it was found that the difference between the values obtained by experiment and calculation in no case exceeded the errors which must be recognized as existing in the determinations of the density of water. The figures thus obtained are given in Table III.

5. As the extrapolation was extended beyond the range of my calculations (from $20°$ to $80°$, $=60°$) up to limiting temperatures exceeding more than three times the one adopted (from $-10°$ to $200°$, $=210°$), and as formula No. 1 justified itself by a possible concordance with experimental results, and since the accuracy of existent determinations is very dissimilar and generally speaking small, I considered it useless, pending the publication of more accurate determinations, to search for a more trustworthy value of $\phi(t)$ or through it of the value of S , taking the aggregate of all contemporary data; and this all the more, seeing that for ordinary temperatures (from $0°$ to $40°$) the values $\phi(t)$ and S found from formula No. 5 were entirely satisfactory. Taking into consideration the fact that in the expression

$$y=a+bt+ct^2$$

the values of the parabolic coefficients, a, b and c, deduced from experimental data by the method of least squares, are greatly

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* In all my calculations, when it was necessary to adopt the method of least squares I used the process of computation based upon P. L. Tchebysheff's method, which is fully explained in my work upon " The Compounds of Alcohol and Water," 1865, p. 89.

affected * by the existence of errors in the fundamental quantities, it appears useless at present to expect values of any accuracy for the constants A, B, and C in formula No. 1. According to the numbers of formula No. 5, we find that

$$A = 94 \cdot 10, \quad B = 703 \cdot 51, \quad C = 1 \cdot 90. \quad . \quad . \quad . \quad (6)$$

These figures satisfy the conditions $A > 10$ and $B > 370$, and also that they should be all positive and greater than unity, so that $F(t) > 0$ and < 1 ; but the true values of A, B, and C can only be found after fresh and more accurate determinations. As a first approximation, especially for ordinary temperatures †, the above values will suffice, justified as they are by a comparison of the calculated results with the aggregate of already known data (see Tables I., II., III.).

Previous to revising the extant information concerning the expansion of water, it will be well to examine the corrections and errors relating to the data of the subject. On this head special attention must be paid to the influence of pressure, the coefficients of expansion of solid bodies, and the methods employed for determining the temperatures.

Influence of Pressure.—Taking the aggregate of results from previous sources (Regnault, Wertheim, Grassi, Amaury, and others) of information about the compressibility of water, it appears that the magnitude μ (the coefficient of compressibility corresponding to a rise of pressure equal to one atmosphere) decreases when the temperature rises from $0°$, whereas for all other liquids μ increases with the temperature. The researches of Pagliani and Vicentini ‡, however, show that

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* In Prof. Markoff's researches (Proceedings of the Imp. Acad. of Sciences, St. Petersburg, 1889), the possible variations of a, b, & c in the expression $y = a + bx + cx^2$ for a given limit of the variable x and a determinate error of the variable y are considered in an exhaustive manner. This question is stated and solved for a particular case in the work " Investigation of Aqueous Solutions according to their Specific Gravity," 1887, p. 289, by the present Author.

† If we had to deal with a small range of temperature, for instance from $0°$–$40°$, then the rectilinear expression of $\phi(t)$ would amply suffice within the limits of possible errors (see Tables II. and III.). In that case

$$S_t = 1 - \frac{(t-4)^2}{A+B}.$$

A like expression, with the difference that in the numerator $(t-4)$ has an index of more than 2 and less than 3, appears sufficient for the entire range of expansion, but then great difficulty is experienced in the calculations and in reality three constants are introduced, the same as in formula No. 1. But an expression of the form

$$S_t = 1 - \frac{(t-4)^2}{A+Bt} t,$$

proves unsatisfactory.

‡ Pagliani and Vicentini. Unfortunately I have not read their memoir in the original, but only know it from an account published in Wiedemann's *Beiblätter*, 1884.

this decrease only extends to a temperature approaching 63°, and that beyond, for water as for other liquids, μ increases, viz. :—

	By experiment.	By formula No. 7.
0°.	$\mu\,10^6 = 50{\cdot}3$	$\mu_t 10^6 = 50{\cdot}5$
10°.	47·0	47·3
20°.	44·5	44·6
30°.	42·5	42·4
40°.	40·9	40·7
50°.	39·7	39·6
60°.	38·9	39·0
70°.	39·0	38·9
80°.	39·6	39·3
90°.	40·2	40·2
100°.	41·0	41·7

In order to be able to deal with experimental data for temperatures exceeding 100°, I have expressed the variation of μ by a parabola :—

$$\mu = 10^{-6}(50{\cdot}49 - 0{\cdot}348\,t + 0{\cdot}0026\,t^2) \quad . \quad . \quad . \quad (7)$$

Since the quantity μ represents some hundred-thousandths of the volume, it is evident that in determining the density of water (just the same as for all other liquids) it is impossible to obtain results agreeing to a millionth, even at ordinary atmospheric pressures, if (as is usually done) we neglect the influences of compressibility and pressure. Supposing, for example, that the experimenter had determined the volume for water at 100° as 1·043212, operating at a pressure of 1 atmosphere; and on another occasion with this pressure decreased by one tenth of an atmosphere, he ought to find 1·043212 × 1·0000042 or 1·043216, if his determinations attain an accuracy of a millionth. The influence of compressibility is particularly notable when determining the density or volume of water beyond 100°, because at such temperatures the pressures are unavoidably considerable. In this respect the first, so to speak, reconnoitring determinations were made by Sorby *

* Sorby (Phil. Mag. 1859, xviii. p. 81) made his determinations in a cylindrical sealed tube, and compared the volumes of water and of some saline solutions. His data refer to vapour-pressures p of water at the temperature indicated.

$t = 120°$	140°	160°	180°	200°.
$p = 1{\cdot}96$	3·57	6·12	9·93	15·38 Atm.
$V = 1{\cdot}05988$	1·0796	1·10186	1·12676	1·1543.

Judging from the mode of observation, the degree of accuracy hardly exceeds $\pm 0{\cdot}005$.

In 1860, being unaware of Sorby's determinations, I made a series of determinations of the expansion, above their boiling-points, of water, ether, and alcohol (Mendeléeff, Liebig's *Ann.* cxix. p. 1). My experiments,

and myself, and showed that beyond 100° the expansion of water increases just the same as at lower temperatures. Later on Hirn * accurately determined the variation of a volume of water heated from 100° to 200°, allowing it to remain all the time under a pressure of about 15 atmospheres. Taking the volume at 4° to be unity and taking, according to Despretz, $V_t = 1.04315$ for 100°, it appeared that, for

	120°	140°	160°	180°	200°
$V_t =$	1.05992	1.07949	1.10149	1.12678	1.15777

In order to render these figures comparable with the other data for a pressure of one atmosphere, it is necessary to multiply them by $(1 + \mu_t 14)$, since the volumes were observed under a pressure of 15 atmospheres †. This reduction necessitates the knowledge of μ_t between 100° and 200° inclusive. Up to the present time direct determinations of this kind do not exist, so that it becomes necessary to extrapolate by means of formula No. 7. This gives for the above temperatures :—

$$10^6 \mu_t = 46.17, \quad 52.73, \quad 61.37, \quad 73.09, \quad 84.89.$$

Therefore Hirn's figures for the volumes of water when reduced to a pressure of one atmosphere become :—

$$V_t = 1.06060, \quad 1.08029, \quad 1.10244, \quad 1.12793, \quad 1.15914.$$

Determining from these the density under a pressure of one atmosphere, we have

$$S_t = 0.94286, \quad 0.92568, \quad 0.90708, \quad 0.88658, \quad 0.86271.$$

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like Sorby's, were only intended to give a preliminary acquaintance with the phenomenon, and my error is still greater than Sorby's, namely about ± 0.01. For water a determination was made for three temperatures, and gave the following results:—

	$t = 120°$	140°	160°.
	$V = 1.07$	1.09	1.11.

The volumes were reduced to a pressure of 1 atm. Sorby's and my results are incomparably less accurate than those made by Hirn, and as such have not met with any further attention. This was a first reconnaissance into the region of the unknown.

* Hirn, 1867, *Ann. de Chimie et Phys.* (4) x. p. 32. The method of determination and the dimensions of the vessels adopted guarantee considerable accuracy to Hirn's results, which, however, judging from the mode of computing the corrections, especially for the coefficient of expansion of the vessel, contain an error hardly less than ± 0.0005.

† Hirn states in his memoir (*l. c.*) on p. 39, that the height of the mercury in the open column was 11.25 metres; but on p. 48 he says that the mean pressure was equal to 11.5 metres. Taking the first statement and adding the atmospheric pressure, we obtain 15.8 atm., but if we take the height 11.5 metres to express the total pressure we obtain 15.1 atm.

However well the results of Hirn's repeated experiments may agree with one another, still they must contain errors which it is impossible to avoid, but which should not be lost sight of. Thus, for instance, Hirn determined the expansion of his copper vessel between 22° and 101·78°, using water and the figures representing its variation in volume given by Despretz (Table I.). We know that these results, although derived from one of the best determinations, are somewhat in error, especially at about 20° (Table I.), and therefore, on their basis, the true coefficient of expansion of the copper vessel cannot be obtained *. According to Hirn 0·0000·5024 was determined to be the coefficient of cubical expansion, and this value was adopted in his calculation. But Fizeau gives for copper 0·00005034 at 40° and 0·00005094 at 50°, showing a rapid increase with the temperature. This also follows from the determinations of Dulong and Petit, who demonstrated that the linear expansion from 0° to 100° is 0·00001718 and 0·00001883 from 0° to 300°; whence it may be supposed that if the mean coefficient of cubical expansion of copper from 0° to 100° is 0·000051, then from 100° to 200° it will be 0·000056. In general the coefficient of expansion of copper increases with the temperature. Hirn took this quantity as constant, and thus introduced an error amounting to 0·000005, which in temperatures ranging from 100° to 200° involves an error of not less than 0·0005 in the volumes of water. Since, then, the reduction from 15 atmospheres to 1 atmosphere was made by us on the basis of extrapolation, and very probably the true compressibility of water between 100° and 200° is

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* Water, however, is the most convenient liquid for determining the coefficient of expansion of vessels; and if the data for the expansion of water be complete we may prefer it to all other liquids, especially for the determination of the expansion of glass vessels at moderate temperatures, because in this case water varies in volume very slightly. The following simple method, which I have practised for a long time, gives very rapid and concordant results for the coefficient of expansion of glass at temperatures near 0°. The vessel is filled with water at 0°, up to a mark, and then carefully heated; at first the level falls, but then at a certain temperature t it again returns to the former level. The determination of t gives k. Evidently the volume of the vessel at 0° and at t is equal to the volume of water V_0 and V_t at these temperatures; and hence the ratio

$$\frac{V}{V_0} = 1 + kt.$$

In this manner the expansion of vessels can be rapidly determined by means of a corrected thermometer, and the relative results obtained are very precise. This method may be of especial use in the study of areometers.

much greater than that adopted by us *, and since this reduction affected the third decimal in the volumes, it may be presumed that the above-determined densities of water contain an error at least in the fourth, or perhaps even in the third decimal place.

Having made this reservation, it will be possible to compare the densities found by experiment with those calculated from formula No. 1, adopting the above-mentioned values for the constants A, B, and C.   Thus:—

	120°.	140°.	160°.	180°.	200°.
From Hirn's experiments, S_t =	0·9429	0·9257	0·9071	0·8866	0·8627
By calculation, formula No. 1=	0·9433	0·9262	0·9073	0·8864	0·8635
Difference	−0·0004	−0·0005	−0·0002	+0·0002	−0·0008

The difference, therefore, between the results obtained by experiment and by calculation, for temperatures ranging from 100° to 200°, does not exceed the possible error in the determinations made by Hirn, which are distinguished by the highest degree of accuracy yet attained in this province.

With respect to the influence of pressure on the density of water, we must, *inter alia*, make the following remarks :—

(1) A most important addition to the study of the properties of water will be introduced by determining with the greatest possible accuracy its compressibility between $-10°$ and $+200°$.

(2) In accurate determinations of the density of water (and of other liquids) the pressure must be determined and a correction introduced for it.

(3) The normal density of liquids (also of gases) must be reckoned at the normal pressure of 760 mm. of mercury (at lat. $= 45°$).

(4) For the theory of the subject it would be highly important to make a series of determinations of the density of water from 0° to 100° and upwards at some fixed and considerable pressure, in order to judge of the manner in which S and V are dependent on t and p (pressure). At present, whilst we are ignorant of the true nature of this dependence, we may take

$$S_{t,p} = \left[1 - \frac{(t-4)^2}{\phi(t)}\right]\left[1 + \mu_t(p-1)\right],$$

if $\phi(t)$ be found for $p=1$ atmosphere.   From the theory of

* Pagliani showed that with the majority of investigated liquids μ increases very rapidly with the temperature; for instance, with normal propyl alcohol, at 0°, $\mu=0·0000086$, and at 100° $\mu=0·0000158$. Judging from the variation of the properties of water, there is reason for thinking that at 200° its coefficient of compressibility will be, for example, twice as great as at 100°.

heat (Thomson, Van der Waals, Tait, and others) we know of the existence of a sort of relation between the pressure and melting-points of ice and the maximum density of water; also that with respect to this last property Amagat demonstrated a lowering of the temperature of the maximum density as the pressure rises *; but the fact of a change of density being dependent upon an alteration of pressure at different temperatures, although theoretically admissible, still requires experimental investigations, confirming those general laws which govern the volumes of gases and liquids in relation to changes of temperature and pressure.

The Influence of the Expansion of Solids.—For water as yet we have no determinations of expansion made independently of a change of volume in other bodies (for instance, the containing vessel or solids in general), because the process of determining the height of columns of water at different temperatures presents practical difficulties which I consider it out of place to take into account here, but which I desire to overcome if it be at all possible. The true volume of water, V_t, is determined from the apparent (observed) volume W_t by multiplying it † by the changed volume v_t of the solid envelope; hence it is evident that however accurate the measuring of the apparent volume be, the resulting V_t will include the entire error contained in the expansion of the envelope. As regards the expansion of envelopes, in spite of numerous investigations, there is a great deal of confusion and doubt and more or less improper application.

1. Very frequently‡, in order to obtain the true volume V_t,

* By using formula No. 7, it is easily seen that, as the pressure rises, the temperature of the maximum density falls, and that, at a pressure of 1000 atm., it will be far below $+4^\circ$. Hence it is necessary to consider the pressure when treating of questions relating to the temperature of the maximum density of water. I may here remark that the *solution* in water of alcohol, sulphuric acid, salt, &c., also lowers the temperature of the maximum density (and also that of the formation of ice); that is, it acts *the same as compression*.

† Regnault (*Relation des expér.* i. p. 225) remarked long ago that the addition of the apparent volume to the increase of volume of the vessels involves an incidental error, because the true expansion is equal to the apparent multiplied by the volume of the vessel.

‡ As an example I may cite the determinations of Weidner (Pogg. *Ann.* 1866, lxxix. p. 300). He was, however, fully justified in having recourse to a simplified method for determining the true volume of water, because his determinations were made at temperatures not differing from 0° by more than 10°, and were not distinguished for any great degree of accuracy. When the temperatures, on the other hand, lie distant from 0° and the precision of the investigation is considerable, then the usual method of finding the true volume from the apparent volume must be abandoned, as it is erroneous in principle and introduces errors which may easily be avoided.

the increment of the volume of the vessel, *i. e. kt*, is added to the apparent volume W_t, whereas V_t should be found from the product $W_t \times v_t^c$, where $v_t = 1 + kt$. An example will show how great an error is thus introduced. Supposing $V_0 = 1$, and let us assume the apparent volume of the water at 100° equal to 1·040502, and let the coefficient of expansion of glass $= 0·00002705$. According to the generally adopted method, we should conclude from this that the true volume of water at $100° = 1·040502 + 0·002705 = 1·043207$; whereas in reality it is equal to $1·040502 \times 1·002705 = 1·043316$: thus the error committed $= 0·000109$, exceeding that of observations made in the simplest manner. Even with a difference of temperature from 0° not greater than 20°, the error of the above *modus operandi* is already clearly sensible in the sixth place. This error decreases, but does not disappear, when a similar method is employed in determining the coefficient of expansion of the vessel, viz. the subtraction of the apparent expansion of mercury from the true expansion.

2. The coefficient of expansion of glass and metals adopted when determining the density of water is usually taken for a range of temperature from 0° to 100°, and the mean value of the coefficient of expansion k of the envelope being found, it is taken as constant throughout the whole of this range. It is, however, beyond doubt, in spite of statements to the contrary [*], that the coefficient of expansion of glass increases considerably (relatively more than mercury) with the temperature. Hence the readings of the mercury thermometer, on being reduced to the normal hydrogen thermometer, require a negative correction and not a positive one, as would be necessary if the variations depended upon the unequal expansion of mercury alone [†]. From Regnault's

[*] Hagen (*Abhandl. d. K. Akademie zu Berlin*, 1855, Math. i.), in a special examination of this question and taking as basis his determinations of the linear expansion of glass, states that, between 0° and 100°, the coefficient of cubical expansion of glass is without variation. Volkmann (Wiedemann's *Ann.* 1881, xiv. p. 270), in revising the determinations of Rosetti, who found k to increase with t, concludes by denying this variability, *i. e.* he considers k constant from 0° to 100°, as generally admitted by experimenters. I may here remark that in the investigation of other liquids, which have a large coefficient of expansion and offer but slight variations in it, this supposition does not play an essential part. But in water at low temperatures, the coefficient of expansion is small—for instance, between 5° and 10° it is equal to 0·0000508, *i. e.* only twice that of glass; so that in this case the determination of small variations in the coefficient of expansion of glass is of great importance for the accuracy of the final result.

[†] Let t be the true temperature (according to the hydrogen thermometer), and let us suppose, without greatly departing from the truth in the abstract, that the expansion of mercury from 0° to 100° is expressed by $V_t = 1 + 0·000180\,t + 0·00000002\,t^2$,

data we may deduce that ordinary glass between 0° and 300° undergoes a change of volume indicated by the equation

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and the linear expansion of glass by

$$v_t = 1 + 0.000027 \, t.$$

The apparent expansion of mercury, as observed in the glass thermometer, will be $\dfrac{V_t}{vt}$, and at 100° it will equal 1·015459. Every degree of the mercury thermometer will correspond to a volume of 0·00015459, and 50° of the mercury thermometer will answer to an apparent volume of 1·0077295. The question then arises, What will be the true temperature t, above or below 50°? When $t = 50°$, the apparent volume equals $\frac{1 \cdot 009050}{1 \cdot 001350} = 1·0076896$: hence the difference between this volume and that at which the mercury thermometer shows 50° is equal to 0·0000399, corresponding to 0°·258 nearly. Therefore, if the variation of the volume of the glass were expressed lineally (*i. e.* if the coefficient of expansion of glass were constant), then, when the mercury thermometer showed 50°, the true temperature would be 50°·258 and the correction for the readings of the mercury thermometer would be positive. This correction would remain positive so long as the variation in the coefficient of expansion of glass were less than that of mercury; for which latter the value of b in the parabola $V = 1 + at + bt^2$ is 9000 times less than a. But when this relation grows greater for glass, then the correction will become negative. Let us illustrate this by an example, taking the same expansion for mercury as above, and for glass

$$v_t = 1 + 0.000025 \, t + 0.00000002 \, t^2 \, ;$$

i. e. let us suppose that its coefficient of expansion changes more rapidly with the temperature than mercury. The apparent expansion of mercury up to 100° will be as before, since the volume of the envelope will be 1·0027 at 100°; therefore one degree will again correspond to 0·0001546 of the volume and a reading of 50° on the mercury thermometer will be obtained, when the apparent volume equals 1·0077295. But at the true temperature $t = 50°$, the apparent volume will be $\frac{1 \cdot 009050}{1 \cdot 001350} = 1·0077391$. Hence when the mercury thermometer shows 50°, then the true temperature will be 49°·938, and the correction for the readings of the mercury thermometer at 50° will then be negative. All the investigations which have been made on the corrections for mercury thermometers by comparing them with the hydrogen thermometer, show (as mentioned in a subsequent note) that the correction for readings, verified in every other respect, of mercury thermometers is negative; *i. e.* the true temperature is *lower* than that shown by a mercury thermometer which has been corrected for zero, calibre, &c. throughout the entire range from 0° to 100°. Hence it is clear that (1) the variation of the volume of glass does not proceed according to a linear function of the temperature, which is the same in the case of the expansion of mercury (the latter follows from Regnault's determinations of the true expansion of mercury); and (2) the coefficient of expansion of glass increases relatively more rapidly than that of mercury.

I thought it well to demonstrate the last two propositions for three reasons:—(1) I have nowhere met with a simple, objective treatment of this subject; (2) generally the proportionality of the expansion of glass to the temperature is adopted without further discussion, or else the absence of this proportionality is considered as not proved, Hagen, Matthiessen, and others being cited; and (3) in the question of the expansion of water, true data for the expansion of glass are of very great importance.

$$v_t = 1 + (25 \cdot 3 + 0 \cdot 0062\, t)\, 10^{-6}\, t.$$

Now the true expansion of mercury through the same range of t is expressed by the formula

$$V_t = 1 + (179 \cdot 97 + 0 \cdot 0208\, t)\, 10^{-6}\, t.$$

Thus the coefficient of cubical expansion of glass is seven times less than that of mercury, while its thermal increment is only three times less. The conclusion arrived at by Benoit [*] is still more convincing. He found that between $0°$ and $40°$ the variation in volume of ordinary glass is expressed by

$$v_t = 1 + (21 \cdot 552 + 0 \cdot 0241\, t)10^{-6}\, t;$$

while, according to Broch, the expansion of mercury through this range of temperature is

$$V_t = 1 + (181 \cdot 652 + 0 \cdot 004845\, t)\, 10^{-6}\, t.$$

Here the increment of the coefficient of expansion of glass is absolutely greater than that of mercury, although at $0°$ the coefficient itself is more than $7\frac{1}{2}$ times less. From this it is evident that by taking the coefficient of expansion of glass as constant, an error is introduced which affects the result very palpably. Thus, for instance, if the true expansion of glass between $0°$ and $100°$ be expressed by the parabola

$$\frac{v_t}{v_0} = 1 + (25 + 0 \cdot 02\, t)10^{-6}t,$$

then the volume at $100°$ will be $1 \cdot 0027$ and the mean coefficient of expansion will equal $0 \cdot 000027$; whence it may be supposed, for instance, that at $20°$ the volume of the vessel should be $1 \cdot 000540$, whereas in reality it is $1 \cdot 000508$, giving a difference

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[*] Deductions from the observations of Benoit and Broch, taken from the work by Guillaume, *Traité pratique de la thermométrie de précision*, 1889, p. 336, which forms one of the fruits of the labours of the International Bureau of Weights and Measures. As regards the above-cited consequence of Regnault's determinations (*Relation des expér.* t. i. p. 225), I calculated as follows:—From observation, it appeared that the apparent expansion of mercury is expressed by the equation

$$W_t = 1 + (154 \cdot 28 + 0 \cdot 00987\, t)10^{-6}\, t;$$

and from determinations of the true expansion of mercury, I had previously calculated (Journal of the Russian Physico-Chemical Soc., Physical Section, 1875, p. 75) that it is expressed, for the same limits of temperature, in the manner given in the text, and hence the expression given above for the volumes of glass. From these data it would have been possible to deduce the variation of the coefficient of expansion of glass, if experiment had not shown that the amount of this variation is very dissimilar for different kinds of glass.

(0·000032) in the volumes which exceeds the possible errors of reading (gravimetric or volumetric). Still up to now our information respecting the variation in the coefficient of expansion of vessels with rise of temperature is not sufficiently clear to allow of its employment as the means of introducing into the existing data respecting the expansion of water corrections which would really improve our results. At present we can only say that, in determining the volume of a vessel according to the formula $v_t = v_0(1 + kt)$, and finding k for a change of t from 0° to 100°, the greatest errors are introduced between 25° and 75° and that they attain some hundred-thousandths of the volume or of the density.

3. Many observers (Hallström, Stampfer, Hagen, Matthiessen) determined the expansion of the solids adopted in the hydrostatic determination of the variation of the density of water, by measuring the linear expansion of the substance from which the body weighed in water was prepared. This method, which does not require a knowledge of the expansion of mercury, involves, firstly, three times the error accompanying the determination of the linear expansion, which error, notwithstanding all the improved methods of determination, is still sufficiently great and will scarcely give a result with an approximation of more than hundredths ; secondly, it is presumed, *à priori*, that the expansion in a transverse direction is the same as longitudinally, even for drawn-glass tubes, which fact needs demonstration, and in my opinion is very unlikely ; and, thirdly, the above-mentioned method is most often applied to glass tubes from which the body used in hydrostatic weighing is made by blowing or melting ; and it is likely that such deformation involves some change in the coefficient of expansion. In addition to this Hallström (1825) found that the cubical expansion of glass is greatly affected by a rise of temperature :

$$v_t = 1 + (5{\cdot}88 + 0{\cdot}315t)10^{-6}\,t \; ;$$

whereas Hagen (in 1855) found hardly any variation in the coefficient of expansion in the glass he used (through a range of 1·6°–81°), and gave the value :

$$v_t = 1 + 27{\cdot}69\,t\,10^{-6}.$$

According to the first formula, the volume at 70° = 1·001955, and from the second we obtain 1·001938—results nearly the same ; but at other temperatures these values vary considerably, for instance at 30° the first formula gives V = 1·000460, against 1·000831 according to the second.

Neither of these contradictory results can be considered as correct or depending only on the properties of glass, and

probably the conflicting evidence of the observers has its source in the errors accompanying the determination of the linear expansion of solids by the method of comparison.

4. No less doubtful are the determinations of the expansion of glass, carried out between 0° and 100°, by means of mercury, because the true *mean* coefficient of expansion of mercury adopted by different observers varies greatly, and it is impossible to say at present to what extent the actual value differs from those taken *. After the determinations of Dulong and Petit, this mean coefficient of expansion of mercury was taken as $\frac{1}{5550} = 0{\cdot}00018018$; Regnault deduced the value $0{\cdot}00018153$ from his classical researches. By applying different methods of interpolation to the determinations of Regnault (expressing the result multiplied by 10^5), Bosscha (1874) found 18241; Galton (1873), 18181; Wüllner (1874), 18252; Mendeléeff (1875), 18210 ± 7 †; Levy (1881), 18207; and Broch (1885), 18216. The chief cause of this discrepancy in the results lies in the circumstance that Regnault, out of 135 determinations, only made 32 for temperatures below 100°; his cold column of mercury during the experiments was not at 0°, but had a temperature from $+10$ to $+18°$, and separate experiments present differences amounting to the discrepancies above stated. Without fresh

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* The method pursued up to now since the time of Dulong consists in determining the true expansion of mercury, then from it that of glass, and, knowing the latter, from the apparent expansion the true expansion of water and of other liquids. The great difference (7-fold) between the coefficients of expansion of glass and mercury constitutes the weak point of this method, because the expansion of mercury must be ascertained with a degree of precision scarcely attainable in experiments. But the most perceptible want in this method lies in the fact that the classical researches of Regnault afford very little material for an accurate judgment of the expansion of mercury between 0° and 100°, where questions of expansion are mainly concentrated and where observations are most within reach. The great necessity for new determinations of the true expansion of mercury from 0° to 100° has already repeatedly been made manifest. I unite my voice to that of many others; but I will add that when we have reliable figures expressing the expansion of water it will then be easier to obtain them for mercury also, for experiments with water, between 0° and 100°, are easier and more convenient than with mercury, and consequently their precision may be greater. In a word, the determination of the true expansion of water is a question urgently requiring solution.

† I think it will not be superfluous here to draw attention to the fact that in the determinations of the expansion of mercury from 0° to 100° (according to Regnault) there, without doubt, exists an error, attaining ± 7 or 8 millionths of the volume; and therefore it is necessary to recognize this possible error in the calculations and to determine it, which I have endeavoured to do. The calculations of Levy and Broch, made subsequently to mine, justified my conclusion, since the difference between their result and mine does not exceed ± 7 millionths.

determinations this question will remain doubtful for the future within the limits I indicate ($+7$ for 18210). Matthiessen (1865) having determined the coefficient of expansion of glass and water, employed them for fresh determinations of the expansion of mercury, but his results are not sufficiently accurate to elucidate the matter *. Besides this, as the mean coefficient of expansion of mercury from $0°$ to $100°$ does not give the variation of the coefficient of expansion of glass, which variation must be recognized, therefore we must allow an error, affecting the fifth decimal place, in the data for the volumes of water, which error proceeds entirely from the fact of taking the mean coefficient of mercury as a basis.

The Determination of Temperatures.—The majority of the determinations of the variation of the density of water with a rise of temperature have been made with the aid of ordinary mercury thermometers, correcting their readings relative to the position of zero and to calibration, although to the exclusion of all that sum of corrections, which the researches of Pernet, Guillaume, and other observers in the Metrical Committee † have recently elucidated. Jolly (1864), however, in his determinations, referred the temperatures to the air thermometer directly. In searching, however, for the true law of the expansion of water, it is necessary to express the temperatures by the absolute scale or by the hydrogen thermometer, because in the law of the expansion of liquids we must expect a direct connexion with the law of the expansion of gases, since there is great similarity, although no identity, between the liquid and gaseous states of matter. In order to show how great is the influence of the circumstance alluded to above, we give the values, from Chappuis' experiments, of the correction Δt which must be added to the readings of a mercury thermometer of hard glass (whose analysis is $71·5°/_0 SiO_2$, $14·5°/_0 CaO$, $11°/_0 Na_2O$, $1·3°/_0 Al_2O_3$) to convert them to the scale of the hydrogen thermometer :—

	Δt	ds/dt	ΔS
$-10°$.	$+0·073$;	$+0·000264$;	$-0·000019$
$0°$.	0	$+0·000065$	0
$20°$.	$-0·085$	$-0·000148$	$-0·000013$
$40°$.	$-0·107$	$-0·000380$	$-0·000041$
$60°$.	$-0·090$	$-0·000512$	$-0·000046$
$80°$.	$-0·050$	$-0·000621$	$-0·000031$
$100°$.	0	$-0·000718$	0

Along with the corrections Δt are given the values of the differential coefficient ds/dt or the variations in the density of

* Matthiessen, Pogg. *Ann.* 1865, cxxviii. p. 512.   † See note p. 114.

water, corresponding to one degree, and after are shown the
corrections ΔS for the specific gravity of water which must be
introduced, in order to obtain from the observed quantities
these specific gravities as referred to the hydrogen thermo-
meter.   Here also the corrections for the figures given by
the experimenters apparently affect the fifth decimal.   And
since in the constancy of the temperatures and in the readings
of the thermometers we must allow, besides, their own inevi-
table errors, and seeing that, in addition to this, these errors
differ with different observers and thermometers *, it may
be considered as demonstrated that in general in the data
existing at present for the density of water, at 20° for instance,
not only the sixth but the fifth decimal place is subject to
correction.

But what is the magnitude of possible error in perfected
determinations of the density of water, if we reckon that
insignificant and individual errors disappear on taking a
mean result, and making the figures more uniform by the
method of interpolating introduced by all observers in their
experiments, by expressing them in the form of densities
referred to entire degrees ?

I have devoted much time to the consideration of the best
answer to this question : having endeavoured to determine by
an examination of the original investigations, the measure of
the errors of each experimenter by introducing into his results
all the possible corrections, and calculating the mean quadratic

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* Many investigators on the expansion of water at various tempera-
tures have determined, if not all the possible error, at least the value of
the deviations of the formulæ expressing the expansion from their experi-
mental results.   Thus, for instance, Hagen (*l. c.*) found for his observa-
tions, that the so-called "probable error," or more precisely the measure
of the discrepancies between the experimental results and those given by
formula, may be expressed in fractions of degrees of the temperature,
which we translate into millionths of the volume.

		In degrees.	In volumes.
From 0° to	8°	$+0{\cdot}1033$	$\pm\ 0{\cdot}000002$
„ 8 „	14	$^{-}0{\cdot}1085$	11
„ 14 „	20	$0{\cdot}0479$	8
„ 20 „	30	$0{\cdot}0788$	20
„ 30 „	40	$0{\cdot}0439$	14
„ 40 „	60	$0{\cdot}0526$	24
„ 60 „	80	$0{\cdot}0592$	36
„ 80 „	100	$0{\cdot}1249$	$\pm0{\cdot}0000086$

The greater portion of the errors of this kind (accidental) are elimi-
nated in the majority of the investigations by the help of interpolation, by
the method of least squares, and therefore in the sequence I avoid dwelling
upon such errors, and pay chief attention to the constant errors in con-
nexion with the fundamental methods of research, which cannot be
removed by interpolation.

digressions of the interpolation-formulæ from the observed figures in various regions of temperature. But on comparing the results thus obtained, I have come to the conclusion that— 1, the introduction of all the possible corrections does not make the results of separate observers agree with one another ; and 2, the greatest quadratic deviations do not appear in the results of those observers whose results are apparently the least trustworthy, but in those cases where the methods adopted are described in the greatest detail and most circumstantially. For this reason, I give in Table I. the original figures of the observers without introducing any corrections whatever ; and it is only to aid their comparison that I express the results in volumes, taking the volume at 4° equal to 10^6. Further, in Table II. figures are given which have been determined at different times by various investigators, deduced from an aggregate of data corrected in all respects and considered as most trustworthy. Finally, in Tables II. and III., besides the densities and volumes of water found from formula No. 1, the magnitude of the errors, which may now be looked for in the best determinations, are given. These possible errors, inherent in contemporary data, may evidently also occur in the results given by formula No. 1, for its constants and very form could only be founded upon previous determinations.

Table I. contains the figures for the volumetric variations of water found by the following investigators :—

1. Hallström, in Abo (Pogg. *Ann.* i. p. 168). He made his determinations (in 1823) by weighing in water a glass sphere (vol. about 162 c. c.) blown out of the same material as a tube, whose linear expansion he determined in a direct manner. Hallström interpolated the specific gravities, taking that at 0° as unity, according to the formula

$$S_t = 1 + at - bt^2 + ct^3 ;$$

the constants, multiplied by 10^6, $a = 52\cdot939$, $b = 6\cdot5322$, and $c = 0\cdot01445$, were found by the method of least squares for t from 0° to 30°. The determinations made by Hallström must be taken as exemplary. Subsequently Hagen and Matthiessen adopted the same method. The chief cause why the results obtained by Hallström are all below the truth, lies in the fact that his results for the linear expansion of glass, at temperatures between 0° and 30°, were below the actual figures. Taking $k = 0\cdot000026$, we obtain results from Hallström's figures which very nearly approach the date of the best and latest determinations.

2. Muncke (*Mémoires prés. à l'Académie des Sciences de*

St. Pétersbourg, t. i. p. 249), in Heidelberg, made a determination of the expansion of numerous liquids by the volumetric or thermometric method, which was afterwards adopted by Despretz, Kopp, Pierre, and many others. Although Muncke's results were communicated to the Academy in 1828, they only appeared before the public in 1831, *i. e.* simultaneously with the investigations of Stampfer. Muncke determined the expansion of the vessel by means of mercury, taking the value given by Dulong and Petit ($\frac{1}{5550}$). Muncke's results for low temperatures (0° to 30°) are greater than the actual values, and those for higher temperatures (40° to 100°) are less. This is due to the insufficient accuracy of calibration and to the determination of the coefficient of expansion of glass. It should be observed that most of the results of Muncke's researches appear inaccurate when compared with recent researches.

3. Stampfer (Pogg. *Ann.* xxi. p. 116) in 1831, in Vienna, determined the expansion of water hydrostatically by weighing a brass cylinder, whose linear expansion was previously determined and found to be 0·001920 between 0° and 100°. The determinations were conducted between −3° and +40°, and were expressed (taking the volume at 4° as unity) by the formula $S_t = S_0 + at - bt^2 + ct^3 - dt^4$. By the method of least squares the constants were : $S_0 = 999887$, $a = 60.932$, $b = 8.4236$, $c = 0.0580$, and $d = 0.0001207$, on multiplying by 10^6. Temperatures below zero appear for the first time in Stampfer's researches. For −3° he gives the volume 1·000373 ; and since the difference of the volumes at −3° and −5° equals 0·000275, I have introduced the number 1·000648 for −5°. The coefficient of expansion for brass given by Stampfer is too large, and hence the volumes exceed the true values.

4. Despretz (*Ann. de Chemie et de Phys.* t. 70. pp. 23, 47), in Paris, 1837. His determinations made at temperatures from −9° to +15° had chiefly in view the study of the densities near 0°. Despretz made but few determinations for temperatures from 20° to 100°, and only gave them to hundred-thousandths. But even these must be considered as among the most trustworthy up to the present date. The coefficient of expansion of glass was only determined for a portion of the dilatometers by means of mercury with Dulong and Petit's figures. From 0° to 28°, for glass, $k = 0·0000255$, and from 0° to 100° k was equal to 0·0000258. For a long time Despretz's figures were in general use ; and if they have been eventually replaced by more recent ones, such a change has not really any firm foundation. Generally speaking, our

information respecting the expansion of water from $-10°$ to $100°$ has hardly made any progress since Despretz's determinations, as regards their trustworthiness.

5. Pierre, in 1847, published a series of volumetric-thermometric determinations for the expansion of water, but did not calculate the ultimate figures. A complete calculation of Pierre's results from $-10°$ to $100°$ was subsequently made by Frankenheim (Pogg, *Ann.* 1852, lxxxvi. p. 463), whose figures are given in the table.

6. Kopp (Pogg. *Ann.* lxxii. p. 1), in 1874, like Pierre, measured the expansion of many definite liquids, and amongst them of water, chiefly with a view to compare the expansion of liquids up to their boiling-points. The method adopted was a volumetric-thermometric one. The coefficient of expansion of glass was deduced from mercury, taking Dulong and Petit's number. The calculations for the volumes are given in four separate equations for various ranges of temperature from $0°$ to $100°$.

7. Plücker and Geissler (Pogg. *Ann.* 1852, lxxxvi. p. 238) adopted a method of compensation, and were the first to take Regnault's figures for the expansion of mercury. Into the thermometrical vessel, whose coefficient of expansion was determined by means of mercury between $0°$ and $100°$, as much mercury was poured as was necessary to compensate the expansion of the vessel, and hence the quantity of water subsequently introduced was considered to expand in a space whose volume remained unaffected by a rise of temperature. In these determinations too much mercury was taken, so that the apparent expansion of the water contains a certain excess (as Miller observed in 1856) ; secondly, the mean coefficient of expansion of mercury between $0°$ and $100°$ was taken to be the same as between $-5°$ and $+15°$, which is evidently inaccurate (the true expansion of mercury between $-5°$ and $+15°$ being still unknown, for Regnault's determinations start at higher temperatures) ; and thirdly, the coefficient of expansion of the envelope between $-5°$ and $+15°$ is presumed to be equal to the mean coefficient of expansion between $0°$ and $100°$, which is also inadmissible. But apart from these points, which are common to the determinations of other observers, the results given by Plücker and Geissler are distinguished for their remarkable accuracy, which shows that the method adopted by them is capable of giving admirable results, were the data of the expansion of mercury and glass fully known. These investigators expressed the results of their determinations graphically by a very well-proportioned curve, although for only a small range of temperature not far distant from $0°$.

8. Hagen (*Abhandlungen d. Akad. zu Berlin*, 1855, Math. Abth. p. 1), adopting a hydrostatic method, made *one* series of determinations of the expansion of water, which is remarkable for its completeness. As has been already mentioned, he employed his own determinations of the linear expansion of glass and expressed its cubic expansion by $1 + 0.00002754\,t$, for the material he employed. Hagen evidently injured the accuracy of his results by taking the expansion of glass as constant, although he paid due attention to determining the temperatures and weights with the greatest possible precision. Hagen expressed his determination for t, from 0° to 100°, by a formula which may be represented thus :

$$S_t = 1 - T^2 (A + BT^{1.6})^2 \ ;$$

here $T = t - 3.87$. A and B are two constants, and the index 1·6 (or the power of T) was found by a series of attempts to express the entire phenomenon of the expansion of water from 0° to 100° in the simplest form. I may here mention that on applying this formula to the aggregate of the existing data, and by changing the values of A and B, I became convinced of the impossibility of its satisfying with sufficient accuracy the data already known respecting the expansion of water between $-10°$ and 200°. Moreover, it should be observed that Hagen himself considers his figures as being nearer the truth for the lower than for the higher values of t, which fact is proved by a comparison with the results given by formula No. 1.

9 & 10. Jolly and Henrici (*Sitzgsb. d. Akad. München*, 1864, i. p. 160), being desirous of verifying the existing data for the expansion of water at temperatures above 30°, made a series of determinations by a volumetric-thermometric method (Jolly), and by weighing a known volume of water (Henrici). The temperatures were determined by thermometers compared with the air thermometer, and the coefficient of expansion of glass by the true coefficient of expansion of mercury as given by Regnault. The number of observations made below 30° was limited. Differences occur in the separate determinations of both observers to the extent of several ten thousandths.

11. Matthiessen (Journ. of the Chem. Soc. 1865, Pogg. *Ann.* cxxviii. p. 512), by applying methods similar to those used by Hallström and Hagen, obtained results which differed considerably from theirs, which shows that hydrostatic weighing and especially the determination of the linear expansion of glass do not afford that degree of accuracy which is generally expected from them. Moreover, the results of

the different series of observations often present differences to the amounts of ten-thousandths.

12. Weidner (Pogg. *Ann.* 1866, cxxix. p. 300) applied the volumetric-thermometric method for the determination of the expansion of water between 0° and −10°. He determined the coefficient of expansion of glass, by means of mercury, between 0° and 90° for vessels blown out of the same glass, and obtained very discordant results from two determinations, viz. 0·00002625 and 0·00002424. He only adopted the former, but this gave larger volumes than found by other observers, which is especially apparent at 0°.

13. Rosetti (Pogg. *Ann.* Ergänz. Band, v. p. 265), in 1869, published a fresh series of determinations for the density of water, which were made by a combination of the volumetric and gravimetric methods. He determined the coefficient of expansion of glass according to Regnault's data, and found it to increase with a rise of temperature. His observations were expressed by a formula of the form :

$$V_t = 1 + a(t-4)^2 - b(t-4)^{2·6} + c(t-4)^3,$$

or else in a formula where the last term $(t-4)$ is not raised to the cube, but to the 3·2 power. In its latter form, Rosetti's formula recalls that given by Hagen.

The figures given in Table I. are taken direct from the final results of the different observers, and without doubt contain some errors which in course of time will be capable of correction, so as to render the values for the volumes of water more accurate. Such corrections, or a revision of the mean of equally trustworthy determinations, have been undertaken more than once, and the results thus obtained are brought together in Table II. Although I consider it right to cite these results, and even myself proposed, in 1884, a similar revision for corrected averages, yet at the present moment, after having studied the subject more closely and recognizing the insufficiency of many of the corrections, I do not think it necessary to dwell especially upon this question, as, in the absence of new determinations, notably for the expansion of mercury and glass, it is impossible to hope to add to the trustworthiness of what is already known.

In Table II., in the first line, Biot's figures are given for their historical interest. He calculated them from an aggregate of the data extant at the beginning of the present century. I cite them from Gehler's *Physik. Wörterbuch* (1825, i. p. 616).

The following line is occupied by the figures calculated by Hallström in 1835 (Pogg. *Ann.* xxxiv. p. 24), when he became

TABLE I.

Direct Results of Observations made upon the Expansion of Water between −5° and +100° C. The volume at the maximum density-point is taken as 1,000,000. Pressure = 1 atm.

t =	−5°	0°	+5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°	90°	100°
1. Hallström, 1823...	...	1000108	1000005	1000220	1000733	1001549	1002648	1004025							
2. Muncke, 1828 ...	...	1000111	1000011	1000278	1000871	1001754	1002897	1004272	1007631	1011702	1016424	1021805	1027925	1034930	1043039
3. Stampfer, 1831 ...	1000648	1000113	1000012	1000289	1000906	1001822	1003005	1004418	1007813						
4. Despretz, 1837 ...	1000699	1000127	1000008	1000268	1000875	1001790	1002930	1004330	1007730	1012050	1016980	1022550	1028850	1035660	1043150
5. Pierre, 1847	1000600	1000118	1000008	1000266	1000846	1001712	1002826	1004190	1007631	1011935	1017238	1023059	1029482	1036417	1043772
6. Kopp, 1847	...	1000123	1000007	1000247	1000818	1001690	1002839	1004188	1007655	1011891	1016715	1022372	1028708	1035524	1043114
7. Plücker and Geissler, 1852.	1000661	1000115	1000012	1000287											
8. Hagen, 1855	...	1000127	1000010	1000269	1000849	1001721	1002861	1004250	1007711	1011994	1017009	1022675	1028932	1035715	1042969
9. Henrici, 1864......	...	...	...	...	...	...	...	1004225	1007728	1012068	1017091	1022597	1028897	1035917	1043231
10. Jolly, 1864.........	...	1000126	1000006	1000254	1000846	1001732	1002856	1004239	1007632	1011877	1016953	1022384	1029003	1035829	1043116
11. Matthiessen, 1865	...	...	1000006	1000271	1000892	1001814	1002982	1004345	1007730	1011969	1016964	1022648	1028953	1035813	1043159
12. Weidner, 1866 ...	1000709	1000136													
13. Rosetti, 1869	1000652	1000136	1000006	1000246	1000835	1001742	1002861	1004249	1007738	1011907	1016862	1022529	1028836	1035662	1043116

acquainted with Muncke's and Stampfer's results. But his results were but little known, since Despretz's figures (see Table I.) were published shortly after and attracted general attention. The same remark applies to Kopp and Pierre's figures, published ten years later.

Miller (Phil. Trans. 1856, p. 146), when establishing the relation of the English pound to other units of weight, examined the existing data for the density of water, and having corrected them for the expansion of mercury, he compiled them into a very simple formula, according to which the logarithm to seven places of the volume (reckoning unity at $3°·945$), equals

$$32·72 (t-3·945)^2 - 0·215 (t-3·945)^3,$$

and his tables (from $0°$ to $25°$) were long used by many investigators. He took Despretz's, Pierre's, and Kopp's data as a basis for his calculations.

Rosetti, taking Despretz's, Kopp's, Hagen's, and Matthiessen's, in addition to his own determinations, calculated the mean regulated values, which are frequently made use of at the present time.

Volkmann (Wied. *Annalen,* 1881, xiv. p. 277), adopting Levy's determination (1881) for the expansion of mercury (viz. $0·018207$ from $0°$ to $100°$), recalculated the determinations made by Kopp, Pierre, and Jolly, embracing Hagen's and Matthiessen's data, and rejecting those figures which he regarded as being very incorrect, and took an average of all, without, however, subjecting them to any regularization and preferring to remain as near as possible to the empirical results.

Mendeléeff ('Messenger of Commerce,' 1884, and separate work, 'The Investigation of Aqueous Solutions according to their Specific Gravity,' 1887, p. 42), in studying (1880–84) the existing data concerning solutions, made a calculation similar to Volkmann's, taking as a basis the expansion of mercury from $0°$ to $100°$ as equal to $0·00018210 \pm 0·0000007$, which he deduced in 1875 from Regnault's determinations ; and, taking into consideration all the figures given by Despretz, Kopp, Plücker and Geissler, Hagen, Jolly, Henrici, Weidner, Matthiessen, Hirn and Rosetti, he calculated the averages, which are given in the table. The figures are, however, only given to hundred-thousandths of the density, without being referred to the hydrogen thermometer, and in the calculation for $20°$ a mistake occurred, so that this number is not included.

During the current year, Admiral Makaroff (Journal of

the Russian Physico-Chemical Society, 1891, Physical Section, p. 30), in elaborating the vast material collected by him during his voyages round the globe, relative to determinations of the density of sea-water, deduced a formula which expresses the expansion of water between $-5°$ and $+35°$, employing the compilations of his predecessors, and amongst others of Herr, made for the International Metrical Commission.

To these compilatory data I subjoin (a) the arithmetical mean of all the data of Table I.; (b) the value of $\frac{dV}{dt}$, *i. e.* the increment of the volume corresponding to an increment of temperature of one degree ; (c) the value of $\frac{dV}{dp}$, or the increment of volume corresponding to an increment of pressure of one atm. (this $= \mu_t V_t$); and lastly (d) the value of the possible error in contemporary determinations of the volumes of water.   The numbers in this line were deduced on the basis of the following considerations :—

(1) Since it is conditionally received that the volume at $4°$ equals unity (or 10^6, according to the notation adopted in this table), it follows that at $4°$ the error will be zero, and we may grant that all the errors are proportional to the difference $t-4$ *.

(2) Since the existing data are, for the most part, referred to readings of the mercury thermometer, they must contain that error which these readings include if we suppose them corrected in every other respect.   The minimum of this error for the best thermometers of hard glass is given above, but I do not think it necessary to add this error to the sum of possible errors, because, in the first place, it can now be to a great extent corrected, and, in the second place, with different thermometers the amount of this error must present a certain unavoidable variability, whose value cannot possibly be now determined.

(3) In the determination of temperatures, the observers have up till now been satisfied with hundredths of a degree, and frequently even tenths, so that, generally speaking, the error for temperatures may be taken as $\pm 0°\cdot 05$.   However, for temperatures below zero, where there are fewer observations and these more difficult, the amount of this error must

---

* Although perhaps the maximum density is not exactly at $4°$, still it undoubtedly lies between $3°\cdot 5$ and $4°\cdot 5$; and within this range the volumes of water vary so little, that practically, within the limit of existing errors, this density may be presumed to be situated at $4°$, all the more so, as all later investigators give it a temperature very near $4°$, for instance Hagen $3°\cdot 98$, Rosetti $4°\cdot 07$, Kopp $4°\cdot 08$, &c.

be increased; and thus for $-10°$, I take it as $\pm 0\cdot 1$, for $+20°$ and $100°$ as $\pm 0\cdot 05$. By multiplying these values by $\dfrac{dv}{dt}$ we get, for $-10°$ ± 26, and for $20°$ ± 10, and for $100°\pm 39$ millionths of the volume.

(4) The foregoing examination of the points generally taken as granted in determining the coefficient of expansion of glass, leads to the conclusion that the error in the volume of the vessel will attain at least $\pm 0\cdot 000001$, which introduces a possible error in the volumes of water of as much as $\pm (t-4)$ millionths of the volume, because the coefficient of expansion of the vessel enters into the value of the volume of water after being multiplied by the number of degrees.

(5) Inasmuch as, up to the present, no corrections have been made for an alteration in the volume of water due to a change of atmospheric pressure, and since these differences of pressure at various seasons of the year and in different localities may amount to $\frac{1}{10}$th of an atmosphere, I hold it necessary to add a possible error of ± 4 millionths of the volume to the differences of individual observers, for the reason indicated, and equal to $\mu\, 0\cdot 1$.

(6) Judging from the description of the methods of investigation and from a comparison of individual observations, we must recognize the existence of errors amounting to tenthousandths of a volume in the determination of volumes and weights at different temperatures. But the greater portion of possible errors of this category disappear in the majority of cases, when the final results are calculated out (often by the method of least squares). I therefore estimate such an incidental error as not exceeding ± 5 millionths of the volume in the best extant determinations.

(7) The sum of the errors enumerated above, which have been taken at the lowest possible computation, is equal to ± 49 for $-10°$, ± 35 for $+20°$, and ± 144 for $100°$, taking the volume at $4°$ as equal to 10^6. Supposing the errors proportional to $t-4$, we have, in virtue of the above figures, the following equation :

$$\text{Possible error} = \pm (t-4)\,(3\cdot 0 - 0\cdot 0469t + 0\cdot 00032\,t^2).$$

The values corresponding to this equation are given under heading (d) in Table II.

Since the constants A, B, and C, in formula No. 1 are calculated from existing data, which contain, *at the very least,* the above-mentioned errors, so these errors may also occur in the values given by this formula. However, the best experimental results differ from the numbers given by the formula

in a much less degree, as is seen from the comparison of the volumes thus obtained (last line of Table II.).

In Table III. are cited the results given by formula No. 1, which is here given in the form in which I employed it for calculation :

$$S_t = 1 - \frac{(t-4)^2}{1000\phi(t)},$$

where

$$1000\phi(t) = 1\cdot90\,(94\cdot10+t)\,(703\cdot51-t),$$

and

$$\phi t = 128\cdot78 + 1\cdot158\,t - 0\cdot0019\,t^2.$$

These figures refer to the density of water S_t, which is inversely proportional to the volumes, *i. e.* $S_t\,V_t = 1$. The density at $4°$ is taken equal to unity.

In calculating this formula, averages were taken of the determinations of many investigators (Despretz, Kopp, Jolly, Rosetti, Hagen, and Matthiessen), and those of some of them (of the first four observers) were corrected for the expansion of mercury, adopting the value $0\cdot01821$ as its variation in volume between $0°$ and $100°$; but no correction was made for the variation of the coefficient of expansion (mercury and solids) with a variation of temperature, nor for the readings of the mercury thermometer as referred to the hydrogen-scale (since such corrections cannot be considered as uniform or sufficiently investigated at present). The figures, therefore, obtained by the formula may contain the same errors as commonly occur in the existing determinations, and for this reason I have indicated the possible errors in the density in this table. For temperatures below $100°$, they are found from the errors in the volumes given in Table II., on the ground that $dS = \dfrac{dV}{V^2}$; for higher temperatures than $100°$ they are derived from the considerations set forth in examining the influence of pressure (see *antè*). But although the figures given by the formula may contain errors to the amount indicated, still it is unlikely that they attain, for ordinary temperatures ($0°$ to $40°$), $\frac{1}{3}$ or $\frac{1}{4}$ of the value given, since the difference between the results given by experiments and the formula is much less, between $0°$ and $40°$, than the amount of the possible errors. Thus, for instance, for $15°$ we obtain a density $0\cdot999152$ or a volume 100849, which differs from the mean results of Volkmann, Rosetti (Table II.), Jolly, and Hagen by less than $\frac{1}{5}$ of the error, which is admissible in the existing data on the grounds stated above. Such being the case we may take the results given by the formula between

TABLE II.

Mean Values (corrected in accordance with contemporary data) for the Expansion of Water with a Change of Temperature, from −5° to +100°, taking the volume at 4°=1,000,000 and the pressure =1 atm.

	−5°	0	+5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°	90°	100°
Biot, 1811		1000130	1000002	1000196	1000694	1001486	1002562	1003911	1007387	1011832	1017161	1023293	1030143	1037629	1045668
Hallström, 1835	…	118	015	263	838	1721	2860	4335	7615	11690	16518	22040	28193	34913	42139
Miller, 1856	…	…	008	265	854	1739	2882								
Rosetti, 1871	1000702	1000129	010	253	841	1744	2888	4250	7700	11950	16910	22560	28870	35670	43120
Volkmann, 1881	…	122	008	261	847	1731	2868	4250	7700	11970	16940	22610	28910	35740	43230
Mendeléeff, 1884	…	130	…	260	843	…	2868	4248	7700	11962	16943	22651	28893	35710	43252
Makaroff, 1891	1000688	121	008	262	846	1727	2870	4243							
(a) Mean of data in Table I.	1000662	1000122	1000008	1000263	1000847	1001733	1002871	1004248	1007700	1011933	1016915	1022513	1028849	1035719	1043180
(b) dV/dt for 1 degree	−157	−65	+15	+85	+148	+204	+254	+302	+386	+461	+530	+595	+656	+719	+781
(c) dV/dp for 1 atm.	−52	−50	−48	−47	−46	−45	−44	−43	−41	−40	−39	−40	−41	−42	−44
(d) Possible error of existing determinations	∓29	∓12	±3	±15	±26	±35	±43	±49	±59	±67	±75	±85	±98	±118	±145
Volumes calculated by Formula. No. 1, $1/S_t = V_t =$	1000676	1000127	1000008	1000262	1000849	1001731	1002880	1004276	1007725	1011967	1016926	1022549	1028811	1035692	1043194

0° and 40° to be very probable. We have already seen the remarkable concurrence of the formula with Hirn's data for temperatures above 100°; so that from both sides—for the lowest and the highest temperatures—the applicability of the formula to the reality is quite likely, and the results given by it are not less trustworthy than the averages deduced from experiments.

With respect to temperatures between 40° and 100°, the evidence of investigators is more conflicting than could be desired, and than is called for by the value of the possible errors given in Table II. For instance, at 70° the difference of the volumes observed by Jolly and Matthiessen amounts to 204 millionths, and the volumes observed by Kopp and Pierre differ by 687 millionths, whereas the possible error at 70° given in Table II. only amounts to ± 85 millionths. But the volume at 70° given by the formula (1022549) differs from the general average (1022513) by only 36 millionths, and from Rosetti's experimental result (1022529) by only 30 millionths, and occupies a position among the results given by Jolly, Matthiessen, Kopp, Pierre, Hagen, and Despretz: it is, therefore, more probable than the figures of any one of these observers, and even more likely to be true than the average result, for the very reason that the formula satisfies alike the data for 70° and for higher and lower temperatures. In other words the figure shown by the formula for, say 70°, is confirmed not only by experiments made at 70°, but also by determinations at 0° or at 200°.

Besides the specific gravity, calculated by the formula and given in the second column, and the measure of the errors, which probably will not be exceeded in more accurate fresh determinations, Table III. contains the following quantities:—

(*a*) The differential coefficient $\frac{ds}{dt}$ found from the formula.

The values of this differential coefficient are not only useful practically in calculating results for intermediate temperatures, they not only demonstrate the mode of variation of the density of water, but they also present, in my opinion, a great theoretical interest, because natural phenomena, in their differential expression, always become simplified and easier to study. It appears to me to be highly instructive that the differential coefficient $\frac{ds}{dt}$ for lower temperatures gives a line of considerable curvature, but for higher temperatures asymptotically approaches a straight line, which circumstance I propose to take advantage of hereafter, for certain deductions relative to the expansion of aqueous solutions and of various other liquids.

(*b*) The differential coefficient $\frac{ds}{dp}$, or the variation of the

density of water with an increase of pressure equal to one atm. The numbers in this column are calculated by formula No. 7, and only represent a first rough approximation on this subject, and none at all for temperatures above 100°. Nevertheless I considered it useful to cite these figures in order to point to the necessity, when making accurate determinations of the variation of the density of water, of paying attention to the pressures at which these determinations are made. If μ_t be given, then $\dfrac{ds}{dp}$ will be found by multiplying by S_t.

(c) The values of $\phi(t)$ or $\dfrac{(t-4)^2}{1-S_t}1000$, because these numbers, as explained above, served chiefly in deciding the proposed formula for expressing the expansion of water.

TABLE III.

The Variation of the Specific Gravity of Water S_t from $-10°$ to $+200°$, taking $S_t=1$ at $4°$, according to the formula

$$S_t = 1 - \frac{(t-4)^2}{1000\phi_{\cdot}(t)},$$

where $\phi(t) = 1\cdot9\,(94\cdot1 + t)(703\cdot5 - t)$ at a pressure of 1 atm.

$t°$ C.	Calculated specific gravity, S_t.	Possible error of existing determinations in millionths.	Pressure Differential Coefficient ds/dt per degree Celsius in millionths.	Temperature Differential Coefficient ds/dp per atmosphere in millionths.	Value of $\phi(t)$.	Volume, V_t.
-10	0·998281	± 49	+ 264	+54	114·01	1·001722
-5	0·999325	29	+ 157	+52	119·94	1·000676
0	0·999873	12	+ 65	+50	125·78	1·000127
+ 5	0·999992	3	− 15	+48	131·52	1·000008
10	0·999738	15	− 85	+47	137·17	1·000262
15	0·999152	26	− 148	+46	142·72	1·000849
20	0·998272	35	− 203	+45	148·18	1·001731
25	0·997128	43	− 254	+44	153·54	1·002880
30	0·995743	49	− 299	+43	158·81	1·004276
40	0·992334	53	− 380	+41	169·06	1·007725
50	0·988174	65	− 450	+40	178·93	1·011967
60	0·983356	72	− 512	+39	188·42	1·016926
70	0·977948	80	− 569	+39	197·53	1·022549
80	0·971996	92	− 621	+40	206·26	1·028811
90	0·965537	109	− 670	+41	214·61	1·035692
100	0·958595	133	− 718	+42	222·58	1·043194
120	0·943314	600	− 810	+43	237·38	1·060093
140	0·926211	650	− 901	+48	250·66	1·079667
160	0·907263	700	− 995	+55	262·42	1·102216
180	0·886393	750	−1093	+64	272·66	1·128167
200	0·863473	800	−1200	+73	281·38	1·158114

(*d*) In the last column the volumes of water, taking that at 4° as unity, are given.   These volumes, like all the numbers deduced from formula No. 1, are referred to a pressure of one atmosphere.   In order to obtain the volumes at a pressure of *p* atm., we must divide the numbers in the table by

$$1 + \mu_t(p-1),$$

just as was done previously when examining Hirn's figures.

In conclusion, I think it necessary to repeat that, whenever I am able I shall endeavour to make a series of fresh determinations, taking into consideration all the necessary conditions of the variation of the density of water with a change of temperature, because the sum of modern information on this subject has been already amassed, but suppositions have been admitted (for example, the constancy of the coefficient of expansion of glass and mercury irrespective of a change of temperature, the absence of the influence of pressure, &c.), which cannot be held to agree with our existing knowledge. And should fresh determinations, made with all possible accuracy, confirm the aspect of the formula

$$S_t = 1 - \frac{(t-4)^2}{(A+t)(B-t)C},$$

or lead to a more correct formula, then we may hope by its means to arrive at a better understanding of the true law of the expansion of all liquids, and consequently of gases also. The correct idea of the influence of heat on densities and volumes began with the study of water, and, in my opinion, we may expect, by means of investigations upon water, to make further progress in the study of matter under the influence of a rise of temperature.

St. Petersburg, April 1891.

XII. *The Densities of Sulphuric-Acid Solutions.*
By Spencer Umfreville Pickering, *F.R.S.*[*]

A SHORT time ago Mr. Lupton (Phil. Mag. xxxi. p. 424) attempted to disprove one of the changes of curvature in the figure representing my " first differential " of the densities of sulphuric-acid solutions by bridging it over by a straight line. As, however, this figure is evidently curvilinear, it was not surprising that he failed, even though he selected for the attempt that particular change which, as I had pointed out, was more doubtful than any other (that at 58 per cent.), and for the same reason it is evident that he would

* Communicated by the Author.