

XII. *On the Expansion by Heat of Water and Mercury.* By A. MATTHIESSEN, F.R.S.

Received December 7,—Read December 21, 1865.

THE fact pointed out in my report “On the Chemical Nature of Alloys”\*, that their physical properties may in this respect be divided into two classes, namely (1) those which do not indicate their chemical nature, and (2) those which do indicate their chemical nature, has led me to investigate the property of expansion by heat, so as to find the law which regulates the expansion of alloys, as well as to determine to which of the above classes this property belongs.

To do this, it was first necessary to determine the coefficients of expansion of the metals to be employed in making the alloys; and in carrying out this research, it had to be borne in mind that bars of a sufficient length to determine the linear coefficients of expansion with accuracy would require very large quantities of the pure metals to make the alloys, in fact such quantities as it would be impracticable to prepare. A method had therefore to be devised by which the expansion of small quantities of the metals and their alloys could be determined, and at once one suggested itself, namely, that of weighing the metal or alloy in water of different temperatures. This method has been already employed for the determination of the coefficient of expansion of water by HÄLLSTRÖM and HAGEN.

To check the method (basing the calculations on KOPP’s coefficients of expansion for water), the expansion of mercury was determined. The coefficient deduced did not, however, agree with REGNAULT’S, as was expected, but, on the contrary, differed considerably; showing either an error in the method employed, or that either KOPP’S or REGNAULT’S coefficients are faulty. After carefully considering the method employed and obtaining always the same results, it then became necessary to redetermine the coefficients of expansion of water and mercury; and these redeterminations form the subject of this memoir, which will be divided into four parts:—

1. On the determination of the coefficient of linear expansion by heat of certain glass rods.
2. On the method employed for the determination of the coefficients of cubical expansion by heat of water and mercury.
3. On the redetermination of the coefficients of expansion by heat of water.
4. On the redetermination of the coefficient of expansion by heat of mercury.

\* British Association Report, 1864.

*I. On the Determination of the Coefficient of Linear Expansion by Heat of certain Glass Rods.*

I am indebted to Mr. F. OSLER for kindly interesting himself in the subject, and having had made at his manufactory two glass rods especially for these experiments. From the ends of these rods pieces were cut, ground, and polished, to be used for weighing in water at different temperatures. The approximate mixture from which the rods were made was 3 parts sand, 2 lead, and 1 alkali.

The disposition of the apparatus used for the determination of the increment in length may be seen from fig. 1 (Plate XX.), which needs some explanation.

In the long zinc trough A (fig. 1) the rod was placed, the ends of it first passing through holes in the ends of the trough; into these openings were soldered pieces of zinc tubing (fig. 2, *a, a*) of about 50 millimetres long, so as to serve both as a rest for the rod passing through them, and as a means of making the trough water-tight. As the greater part of the zinc tubing projected inwards, it was easy to draw a piece of vulcanized rubber tubing over its end, and on passing the rod through this the trough became water-tight. The few millimetres of the zinc tube projecting outwards served to keep the ends of the glass rod (about 5–10 millims.), if not quite at the same temperature of the bath, at all events very near it. Three other rests were placed in the trough to support the rod (fig. 2, *b, b, b*). The length, width, and height of the trough were 1800, 180, 150 millimetres (measured inside). The long sides and top were made double. Through an opening in the cover the thermometer T is fixed, the bulb reaching in the water the level of the rod; a smaller one (*T<sub>1</sub>*) is placed near the larger one, so as to give the mean temperature of the column of the mercury not immersed in the water; that is, its bulb is placed near the middle of the exposed column.

To give the necessary firmness to the apparatus, and to cause the expansion of the glass to be indicated in only one direction, the following arrangement was made. A hole was made in the wall so as to take the end *e* of tube B (fig. 1). Fig. 3 shows the construction of this part of the apparatus. It consists of a stout glass tube fitted into zinc caps, the ends of the tube touching the ends of the cap, so that when water enters at *d*, it is forced to flow to the end of the zinc cap to enter the tube, and to make its exit in the same manner at the other end. The zinc is connected with the glass by rubber tubing; the tube B, the end of which is cemented in the wall and supported by two bricks, to which the tube is also cemented, thereby forming a solid resistance for the one end of the rod to rest against. The communication between the other end of the rod and the measuring-apparatus is similarly constructed (fig. 4); the length of the fixed glass tube B being 300, and of the moveable one 350 millimetres. To steady the latter as much as possible, the tube passed through a larger one cemented to the brick, as shown in fig. 4. This allows the tube to move backward and forward with ease without altering otherwise its position. It was kept pressing on the end of the rod by the spring *i* (ordinary bell spring), a weight (*h*) hanging below it to serve to counteract the

upward pulling of the spring. Similar springs ( $k, k, k, k$ ) were fixed to the glass rod in the trough, to keep it pressed against the end of the fixed glass tube.

The whole of the apparatus stood on a brick floor, and so solid was the foundation, that accurate measurements could be made even when persons were moving about on it.

The measuring-apparatus\* (D, fig. 1) was a micrometer-screw, a piece of brass being fixed to the end of it, through which passed a moveable circular piece of the same alloy faced with agate. On turning the screw, this piece of brass, as soon as it touched the zinc cap, pressed against the short arm of the lever ( $l$ ), and thus indicated the point of contact. To obtain accurate readings, the screw was turned until the bent end of the long arm of the lever covered the line on the table beneath it; and to avoid parallax, the point was observed through the tube E, which has a very fine opening at the top and a magnifying glass at the bottom.

With this arrangement readings can be made with little practice (of course avoiding the back-lash of the screw), with great accuracy, in fact, easily to 0.001 millimetre.

The length-value of a turn of the micrometer-screw was found by measuring wires of known diameter. These were measured some years since in Heidelberg, in KIRCHHOFF'S laboratory, with a calibrated micrometer-screw under a microscope. I thought, however, the screw might have altered by constant use, as it had served to measure all the wires used for the electrical conducting-power experiments made in conjunction with other gentlemen. On applying to Mr. B. STEWART, he kindly placed at my disposal, at Kew, their normal measuring-screw, and on redetermining the length-value of a turn of the screw, it was found equal to 0.185 millimetre, agreeing almost absolutely with the former value, namely 0.184 millimetre. The mean of these two values was used, namely 0.1845 millimetre. The milled head was divided into 200 parts, so that each division represents about 0.001 millimetre. A small correction had to be made for the movement of the lever, as it moves bodily with the screw. The relative lengths of the arms of the lever were about as 250 : 1, so that when the screw moved backwards to allow the rod to expand, the error caused by this in the reading will be about 0.005 millimetre, for the expansion of the rod is equal to 1.3 millimetre; in other words, to bring the point of the lever to cover the line at the high temperatures, the screw would be turned too much, or the expansion would be found too small. By direct determination this correction amounts, for six turns of the screw, to 0.005 millimetre.

On carefully calibrating the screw, a part of it (consisting of eight turns) was found where the length-value of the threads was almost absolutely the same. This portion of the screw was therefore used for the experiments. The thermometers employed were correct, having been compared with a Kew Standard thermometer. Their zero-points were redetermined from time to time. The correction for the column of mercury not immersed in the water, made by using KORP'S formula,

$$\text{correction} = N(T - t) \times 0.0001545,$$

\* This apparatus was made by Mr. BECKER for the accurate measurement of the diameters of wires.

where  $N$  is equal to the number of degrees exposed,  $T$  the uncorrected temperature of the water, and  $t$  the temperature of the thermometer the bulb of which is placed in contact with the stem of the other thermometer halfway between the top of the mercury column and the middle of the cork. The number given is the apparent expansion of mercury in glass.

Having thus described the different parts of the apparatus, I will proceed to state the manner of making the determinations. The different parts having been placed together, the trough was filled with water by connecting the tap  $F$  with the water-tap; and when full the water was still allowed to enter, escaping through a waste-pipe at the top of the other end of the trough. After the water had flowed through the trough for about half an hour, it was turned off at  $F$  and connected with  $d$ , flowing through  $B$ , and thence passing through the rubber tubing from  $c$  to  $f$ . At  $f$  it enters the tube  $C$ , and escapes at  $g$  into a waste-pipe. The temperatures of the thermometers having been read off, and the position of the screw noted when touching the end of the tube  $C$ , the eighteen Bunsen burners were lighted, the screw at the same time being turned so as to allow for the expansion of the rod. When the water boiled the temperatures were read off, and the new position of the screw noted on touching the end of  $C$ . It was found necessary to continue boiling the water for about a quarter of an hour before constant readings could be obtained. To take the readings again at low temperatures, the water-tap was connected with  $F$ , and the water allowed to flow through the trough till that flowing from the waste-pipe had the same temperature as the water from the tap, when the connexion was again made with  $d$ . To obtain this temperature, it took from three to four hours. It may here be mentioned that screens were placed between the ends of the trough and the tubes  $B$  and  $C$ , to prevent their being heated by radiation from the trough whilst making the observations at high temperatures. A thermometer placed near the screw of the measuring-apparatus showed no change of temperature during the time of the experiment, the room in which the experiments were made being a very large one.

Only such observations were deemed reliable as gave concordant results on heating and cooling the rod, the slightest movement in any part of the apparatus causing large differences in these values. No good results were obtained at first, but after some practice the values found agreed well together. These are given in Table I.

Nos. 1, 2, & 3 are the observations made with Rod I., with only two springs in the trough.

Nos. 4 & 5, the observations made with Rod I., the apparatus having been taken to pieces and put together again; the rod also being turned, and four springs being used.

Nos. 6 & 7, the observations made with Rod II., with four springs.

No. 8, the observations made with Rod II., with four springs, rod turned, and apparatus readjusted.

Table II. gives some measurements which prove that the increment in length between

$0^\circ$  and  $100^\circ$  may be considered for these rods as proportional to increase of temperature.

No. 1. The observation  $T_2$ ,  $a$ , and  $b$  was taken whilst heating the trough for Experiment No. 4, Table I.

No. 2. The observation  $T_2$ ,  $a$ , and  $b$  was taken whilst heating the trough for Experiment No. 5, Table I.

No. 3. The observation  $T_2$ ,  $a$ , and  $b$  was taken whilst heating the trough for Experiment No. 7, Table I.

No. 4. The observation  $T_2$ ,  $a$ , and  $b$  was taken whilst heating the trough for Experiment No. 8, Table I.

It was not easy to obtain a constant temperature for  $T_2$ ; the values for  $T_2$  and  $a$  are therefore the mean of two or more readings.

TABLE I.

No.	$T_1$ .	$T_2$ .	$T_3$ .	$a$ .	$b$ .	$\frac{100a}{T_2-T_1}$ .	$\frac{100b}{T_2-T_3}$ .
1.	18.6	100.3	17.8	1.098	1.098	1.344	1.331
2.	17.8	100.2	18.1	1.092	1.090	1.325	1.328
3.	18.2	100.3	18.6	1.099	1.091	1.339	1.335
4.	19.2	100.0	18.6	1.073	1.078	1.328	1.324
5.	18.6	100.0	19.4	1.087	1.070	1.335	1.327
6.	18.6	100.6	18.8	1.091	1.084	1.330	1.325
7.	18.4	100.4	19.0	1.091	1.090	1.330	1.339
8.	20.6	100.5	19.4	1.069	1.072	1.337	1.332
Mean .....							1.331

TABLE II.

No.	$T_1$ .	$T_2$ .	$T_3$ .	$a$ .	$b$ .	$\frac{100a}{T_2-T_1}$ .	$\frac{100b}{T_3-T_2}$ .
1.	19.2	60.7	100.0	0.549	0.524	1.323	1.333
2.	18.6	63.4	100.0	0.598	0.489	1.335	1.336
3.	18.4	66.0	100.4	0.633	0.458	1.330	1.330
4.	20.6	59.2	100.5	0.512	0.557	1.326	1.349

$T_1$ ,  $T_2$ ,  $T_3$  denote the true temperature of the water.

$a$  and  $b$ , the true expansion of the rod between those temperatures, expressed in millimetres.

The last two columns give the expansion of the rods, calculated from the respective observations for  $100^\circ$ .

The length of the two rods was the same, namely 1825 millimetres, and their diameter about 20 millimetres.

The increment in length for 1 metre will be therefore between  $0^\circ$  and  $100^\circ$ ,

$$0^{\text{m}}.729;$$

or the formula for the correction of the linear expansion of the glass rods will be

$$L_t = L_0(1 + 0.00000729t),$$

and for the cubical expansion,

$$V_t = V_0(1 + 0.00002187t).$$

In carrying out the foregoing experiments an interesting observation was made; when the glass rod was heated in the morning for the first determination, the value deduced for the expansion of the rod was greater than those obtained afterwards on the same day—a result which proves that the rod, on being heated, only resumes its normal length after a certain time, and that this gradual change in length is perceptible after twelve to fifteen hours. Table III. gives a few examples of this fact.

TABLE III.

No.	T <sub>1</sub> .	T <sub>2</sub> .	T <sub>3</sub> .	a.	b.	$\frac{100a}{T_2 - T_1}$ .	$\frac{100b}{T_2 - T_3}$ .
1.	19.6	100.5	19.0	1.110	1.085	1.372	1.331
2.	17.4	100.3	18.8	1.133	1.090	1.367	1.337
3.	17.2	100.5	18.8	1.138	1.089	1.366	1.333
4.	18.2	100.0	19.0	1.126	1.087	1.376	1.342

From the above the mean expansion of the rod on first heating between 0° and 100° is

$$1.370.$$

The mean of the experiments given in Table I. is

$$1.331,$$

making a difference of about 3 per cent. on the expansion\*.

## II. *On the Method employed for the Determination of the Cubical Expansion of Water and Mercury.*

Fig. 5 shows the arrangement of the apparatus used for the determinations.

Through a small hole in the bottom of the balance and shelf a platinum wire hung from the small pan above. The diameter of the wire is about 0.5 millim. To this wire, by means of a hook, the metal was suspended by a finer wire (0.04 millim. diameter) in the water contained in the box below. The size of the box, measured inside, was 200 millims. cube. It was made of zinc, double sided, and encased in wood. The covers were cut in two to allow them to be put on or taken off without disturbing the fine wire. Through these, holes were made (fig. 6), *a*, *a* for the stirrer, *b* for the draft pipe, *c* for the fine wire, and *d* for the thermometer. The stirrer was a square piece of sheet zinc, soldered to the end of the copper wires R, R, with a hole cut in

\* The rods must have been well annealed, for they stood sudden changes of temperature remarkably well, as shown by the process employed for cooling the water in the trough.

the middle of it to make room for the cylinder  $\alpha$ . The wires R, R, as shown in fig. 5, were connected together by a stout wire and binding screws. The draft-pipe  $b$ , figs. 5, 6 (of zinc tubing soldered to the one-half of the cover joining at  $e$  with  $b$ ), served to draw off the steam formed at high temperatures, thereby preventing its condensation on the platinum wire. This was accomplished by leading the end of the pipe into a chimney and creating a draft by lighting a gas-burner in it. It was found by experiments at low temperature that creating this draft had not the slightest influence on the weighings, for those made with and without it were exactly the same.

In the middle of the box stands the silver cylinder  $\alpha$ , filled with distilled water, and in this the metal or glass was weighed. As seen in the figure, the thermometer-bulb stands in the same level as the metal. To prevent the evaporation of water by the current of air sucked in at  $e$  by the draft-pipe, as well as to hinder particles of dust falling into the water, the cylinder was covered with a platinum cover,  $f, f$  (divided in two), with two holes, the one for the fine wire, the other for the thermometer\*. The water in the box was heated by steam, the pipe surrounding the cylinder, a small screen of sheet zinc bent outwards being placed between them to prevent the steam coming in direct contact with the cylinder. The general method of observing with this apparatus was as follows:—The substance to be experimented on was cast or ground to a form somewhat like fig. 7, and suspended by means of a slip-knot made with the fine platinum wire in the cylinder filled with boiling distilled water. This being made to boil, was boiled with the substance for the space of half an hour. Another silver vessel was kept ready with boiled out and boiling water to supply the loss by evaporation. After boiling for the half hour, the cylinder was placed in the box already filled with water of the proper temperature, and the platinum covers placed on it; the box was then covered with the zinc and wooden covers, of course great care being taken to let the fine wire swing freely. Whilst experimenting at high temperatures, steam had to be passed into the box to keep a constant temperature. By means of a small boiler, heated by gas placed at some distance from the apparatus, this was easily effected. In fact, by carefully regulating the gas, any temperature between  $50^{\circ}$  and  $100^{\circ}$  may be kept constant for any time. A waste-pipe was fitted into the side of the box to allow the water when it reached a certain level to flow away; as soon as the temperature became constant, the first weighing was proceeded with; in the one pan of the balance, large weights were placed so as to make that side of the balance the heaviest; this is brought into equilibrium by placing smaller weights in the other pan, namely, the one to which the platinum wire is fixed. The balance stands in a glass case, and surrounding this is another glass case (not shown in the figure), to keep the temperature of the balance as constant as possible. It did not vary during a series of observations more than  $1^{\circ}$ . The proper weight having been found, which it was possible to do to an accuracy of 0.0001 grm. when weighing in water, it was noted,

\* To diminish the amount of air sucked in at  $e$ , and as a protection against dust, the opening at  $e$  was covered with a piece of zinc cut as shown in fig. 8, the hole in the centre having about 2 millimetres diameter.

together with the temperatures of the thermometers, the one (T) in the box, that ( $T_1$ ) reaching halfway up the exposed column, and the one in the balance-case. These thermometers were connected as already described in Part I. The thermometer (T) in the box was read off at a distance by a second observer through a telescope. All these data being noted down, a second and third weighing was made, and as the temperature only altered one- or two-tenths of a degree during the time, it was easily seen whether the weighings agreed with each other; and if this were not the case, fresh weighings were made, and often when these again did not agree, it was found that a small particle of dust had attached itself to the wire in the water; in fact this occurs very often, so that, after the weighings are finished, great care was taken to see whether any dust was hanging to the fine wire. Having finished the observations at the one temperature, the cylinder was taken out of the box, the water brought to boil, and kept boiling again for half an hour, and in the same manner as before, the weighings, &c. repeated, and so on for each different temperature.

The balance was carefully adjusted, so that 50 grms. in each pan might be changed without showing the slightest difference in weight. The weights were from time to time compared with each; the 50 grms. being correct according to the Kew Standard, any alteration found in the smaller weights was allowed for. At least once a day, and with some experiments after each observation, the barometer and thermometer placed by its side were read off for the reduction of weights to *vacuum*.

The dipping in and out of the water the fine platinum wire did not influence the weighings at all; wires of somewhat larger diameter could not be used, as with these appreciable differences were observed. As the weight of a metre of the fine platinum wire was only 0.06 gm., the error caused by the wire dipping in the water may be neglected, it being so small, as only 60 to 70 millimeters dipt in the water (forming the slip-knot, &c.). These weigh about 0.004 gm., and they would lose in water 0.0002 gm.; but as we only have to deal with the differences of loss of weight in water at different temperatures, these 0.0002 gm. will alter in volume between  $0^\circ$  and  $100^\circ$  to such an unmeasurable extent that they need not enter into the calculations. The column of mercury in the thermometer (T) not immersed in the water was corrected for as described in Part I.

### III. *On the Redetermination of the Coefficients of Expansion of Water.*

To determine the coefficients of the expansion of water, the pieces of glass cut from the ends of the rods and ground to the shape of a double wedge were weighed in water at different temperatures. The pieces were highly polished, and at one end notches were ground in to give a hold to the platinum wire.

Between each of the observations at different temperatures the water in the cylinder was reboiled to drive out any air which might have been absorbed during the time of weighing. The water employed was distilled from a copper still (tinned inside), the steam being condensed in a tin worm, and kept for use in a large glass bottle.



The results of the different weighings are contained in Tables IV., V., VI. (gramme weights, all weighings reduced to *vacuum*).

TABLE IV.—Experiments made with a piece of glass rod cut from Rod I. (Series I.)

Temperature.	Absolute loss of weight in water.	$\frac{1+at}{W_t}$ .	Volume of water at $t^\circ$ .	Calculated.	Difference.
4.00	15.4057	0.0649167	1.000000	1.000000	0.000000
6.60	15.4057	0.0649204	1.000057	1.000055	+ 0.000002
12.25	15.4005	0.0649504	1.000518	1.000525	— 0.000007
16.70	15.3917	0.0649939	1.001189	1.001177	+ 0.000012
20.45	15.3822	0.0650393	1.001888	1.001889	— 0.000001
23.10	15.3730	0.0650820	1.002546		
24.80	15.3679	0.0651060	1.002915		
27.10	15.3592	0.0651461	1.003534		
32.85	15.3353	0.0652559	1.005224		
43.25	15.2808	0.0655035	1.009039		
44.50	15.2736	0.0655362	1.009544		
48.90	15.2452	0.0656646	1.011520		
61.00	15.1588	0.0660563	1.017555		
74.50	15.0487	0.0665685	1.025443		
85.10	14.9584	0.0670216	1.032424		
98.70	14.8126	0.0676558	1.042194		

TABLE V.—Experiments made with a second piece of glass rod cut from Rod I. (Series II.)

Temperature.	Absolute loss of weight in water.	$\frac{1+at}{W_t}$ .	Volume of water at $t^\circ$ .
5.35	15.7327	0.0635693	1.000015
8.45	15.7317	0.0635775	1.000144
19.75	15.7113	0.0636757	1.001689
30.45	15.6716	0.0638520	1.004463
50.80	15.5558	0.0643561	1.012393
73.30	15.3776	0.0651340	1.024628
86.40	15.2542	0.0656794	1.033209
94.30	15.1721	0.0660462	1.038980

TABLE VI.—Experiments made with a piece of glass rod cut from Rod II. (Series III.).

Temperature.	Absolute loss of weight in water.	$\frac{1+at}{W_t}$ .	Volume of water at $t^\circ$ .
8.90	11.3425	0.0881812	1.000192
20.90	11.3258	0.0883344	1.001929
32.35	11.2934	0.0886099	1.005055
46.40	11.2376	0.0890769	1.010352
60.40	11.1661	0.0896751	1.017136
70.35	11.1067	0.0901744	1.022799
86.80	10.9957	0.0911173	1.033495
98.40	10.9096	0.0918596	1.041926

In the first column the corrected temperatures are given; in the second the numbers express in grammes the loss of weight in water, or the difference between the weight

of the piece of glass rod *in vacuo* and in water at the different temperatures. In the third the numbers represent those proportional to the volumes of waters displaced at the different temperatures. These values were arrived at in the following manner:—

Let  $\alpha$  be the coefficient of the cubical expansion of the glass rod\*, and  $V_0$  its volume at  $0^\circ$ . Its volume at  $t^\circ$  will of course be  $V_0(1+\alpha t)$ . But this is likewise the volume of the displaced water whose weight, say  $W_t$ , is determined by experiment. Hence

$$\frac{V_0(1+\alpha t)}{W_t}$$

is the volume, at  $t^\circ$ , of the unit of weight of water; or more generally *the volume of a given weight of water is proportional to*

$$\frac{1+\alpha t}{W_t}.$$

In the fourth column the volume of water is taken at  $4^\circ$  equal to  $1^\circ$  (Table IV.); and to reduce the values in Tables V. and VI. to the same unit, a formula was calculated from the first five observations in Series I. Table IV. to express the expansion of water between  $4^\circ$  and  $20^\circ\cdot4$ .

The formula from which the calculated values (Table IV.) were obtained was

$$V_t = 1 + 0\cdot0000084465(t-4)^2 - 0\cdot00000008900(t-4)^3,$$

and calculating from this formula the volumes at  $5^\circ\cdot35$  and  $8^\circ\cdot90$ , and taking them equal to the values found for the numbers proportional to the volumes of water at the same temperatures in Series II. and III. (Tables V. and VI.), we reduce these volumes of water at different temperatures to the same unit.

Table VII. contains the values thus obtained for the expansion of water from the three series.

\*  $\alpha = 0\cdot00002187$ . The coefficient here used must naturally be that obtained for the glass rods after having been heated, for the pieces were boiled with the water before the weighings were made.

TABLE VII.

Series.	Temperature = $t$ .	Observed volume of water at $t^\circ = V_t$ .	Calculated volume of water.	Difference.
1	4.00	1.000000	1.000000	0.000000
2	5.35	1.000015	1.000012	+0.000003
1	6.60	1.000057	1.000049	+0.000008
2	8.45	1.000144	1.000149	-0.000005
3	8.90	1.000192	1.000181	+0.000011
1	12.25	1.000518	1.000510	+0.000008
1	16.70	1.001189	1.001175	+0.000014
2	19.75	1.001689	1.001762	-0.000073
1	20.45	1.001888	1.001911	-0.000023
3	20.90	1.001929	1.002007	-0.000078
1	23.10	1.002546	1.002512	+0.000034
1	24.80	1.002915	1.002932	-0.000017
1	27.10	1.003534	1.003534	0.000000
2	30.45	1.004463	1.004475	-0.000012
3	32.35	1.005055	1.005041	+0.000014
1	32.85	1.005224	1.005201	+0.000023
1	43.25	1.009039	1.009020	+0.000019
1	40.50	1.009544	1.009540	+0.000004
3	46.40	1.010352	1.010352	0.000000
1	48.90	1.011520	1.011464	+0.000056
2	50.80	1.012393	1.012342	+0.000051
3	60.40	1.017136	1.017178	-0.000042
1	61.00	1.017555	1.017502	+0.000053
3	70.35	1.022799	1.022858	-0.000059
2	73.30	1.024628	1.024662	-0.000034
1	74.50	1.025443	1.025413	+0.000030
1	85.10	1.032424	1.032387	+0.000037
2	86.40	1.033209	1.033284	-0.000075
3	86.80	1.033495	1.033561	-0.000066
2	94.30	1.038980	1.038917	+0.000063
3	98.40	1.041926	1.041964	-0.000038
1	98.70	1.042194	1.042179	+0.000015

To express the volumes in one formula would require too many terms, as it was found by calculation that the following formulæ did not express the results with sufficient accuracy between  $4^\circ$  and  $100^\circ$ ,

$$V_t = a + bt + ct^2 + dt^3,$$

$$V_t = 1 + a(t-4) + b(t-4)^2 + c(t-4)^3 + d(t-4)^4.$$

I therefore employed two formulæ to express the expansion of water between  $4^\circ$  and  $100^\circ$ , the first for temperatures between  $4^\circ$  and  $32^\circ$ , being

$$V_t = 1 - 0.0000025300(t-4) + 0.00000083890(t-4)^2 - 0.00000007173(t-4)^3,$$

the second for temperatures between  $32^\circ$  and  $100^\circ$ ,

$$V_t = 0.999695 + 0.0000054724t^2 - 0.000000011260t^3.$$

In calculating the first formula, the observations at  $19^\circ.75$  and  $20^\circ.90$  were omitted, as by previous calculations they were found to be faulty. To prove that the impurities contained in the water used for the foregoing experiments have no influence on the results, a short series was made with common water. I do not, however, intend to convey the idea that the water was not pure in the ordinary acceptance of the word,

as it was carefully distilled, but those who have tried to prepare absolutely chemically pure water know how difficult it is to prepare it in such a state, that it does not on evaporation leave a slight residue.

From KREMER'S experiments on the expansion of solutions of salts in water, it appears that even large percentages have only a slight influence on the coefficients of expansion of the water in which they are dissolved. Table VIII. contains some examples.

TABLE VIII.

T.	Volume.	T.	Volume.	T.	Volume.	T.	Volume.	T.	Volume.	T.	Volume.
(1) 19.5 100	1.00000 1.04135	(2) 19.5 100	1.00000 1.04144	(3) 19.5 100	1.00000 1.04179	(4) 19.5 100.0	1.00000 1.04217	(5) 19.5 100.0	1.00000 1.04135	(6) 19.5 100.0	1.00000 1.04138

(1) Expansion of water between 19°·5 and 100°\*.<sup>1</sup>

(2) Expansion of water containing in 100 parts 5.2 parts of chloride of potassium†.

(3) " " " " 4.7 " chloride of sodium†.

(4) " " " " 7.5 " sulphate of sodium\*.

(5) " " " " 5.1 " sulphate of potassium\*.

(6) Expansion of water, calculated from the above formulæ, taking the volume at 19.5, equal to 1.00000.

For the series contained in Table IX. common water was used. Water from the laboratory tap was well boiled to precipitate the carbonates held in solution by the free carbonic acid, filtered and mixed with 25 per cent. of distilled water, to prevent any precipitation of salt on boiling to drive out the absorbed air; in fact these 25 per cent. were added to replace the loss by evaporation. The determinations with this water were carried out in the usual manner; the piece of glass employed was the same as that used for Series 3.

TABLE IX.

T.	Absolute loss of weight in water.	$\frac{1+at}{W_t}$	Volumes of water at	Calculated volumes of water.	Difference.
20.70	11.3259	0.0883333	1.001964	1.001964	
55.65	11.1916	0.0894614	1.014759	1.014703	+0.000056
95.90	10.9292	0.0916900	1.040040	1.040992	-0.000052

The calculated volumes have been deduced from the above formulæ; the observed value in the second column at 20°·7 being taken equal the calculated one in order to compare the other two values with those obtained from the experiments made with pure water.

For the convenience of experimenters, I give in Table X. the volume occupied by water from degree to degree, taking that at 4°=1.000000, as well as the differences for each degree.

\* Pogg. Ann. cxiv. 41.

† *Ibid.* c. 394.

The temperature  $32^{\circ}$  used as the point of junction between the two formulæ was found by solving the equation

$$1 - 0.0000025300(t-4) + 0.00000083890(t-4)^2 - 0.00000007173(t-4)^3 \\ = 0.999695 + 0.0000054724t^2 - 0.000000011260t^3,$$

whence  $t = 32^{\circ}$ .

By the first the volume at  $32^{\circ} = 1.004932$ .

By the second the volume at  $32^{\circ} = 1.004930$ .

The mean of these values is given in the Table.

TABLE X.

T.	Volume.	Difference per $1^{\circ}$ .	T.	Volume.	Difference per $1^{\circ}$ .
4	1.000000	0.000006	53	1.013391	0.000482
5	1.000006	22	54	1.013879	488
6	1.000028	38	55	1.014376	497
7	1.000066	53	56	1.014879	503
8	1.000119	69	57	1.015390	511
9	1.000188	83	58	1.015907	517
10	1.000271	98	59	1.016432	525
11	1.000369	110	60	1.016964	532
12	1.000479	125	61	1.017505	538
13	1.000604	138	62	1.018047	545
14	1.000742	150	63	1.018596	552
15	1.000892	162	64	1.019158	559
16	1.001054	173	65	1.019724	566
17	1.001227	185	66	1.020296	572
18	1.001412	196	67	1.020874	578
19	1.001608	206	68	1.021459	585
20	1.001814	215	69	1.022050	591
21	1.002029	225	70	1.022648	598
22	1.002254	234	71	1.023252	604
23	1.002488	243	72	1.023861	609
24	1.002731	251	73	1.024477	616
25	1.002982	259	74	1.025099	622
26	1.003241	266	75	1.025727	628
27	1.003507	273	76	1.026361	634
28	1.003780	279	77	1.027000	639
29	1.004059	286	78	1.027646	646
30	1.004345	290	79	1.028296	650
31	1.004635	296	80	1.028953	657
32	1.004931	318	81	1.029615	662
33	1.005249	329	82	1.030283	668
34	1.005578	338	83	1.030956	673
35	1.005916	345	84	1.031634	678
36	1.006261	355	85	1.032318	684
37	1.006616	363	86	1.033007	689
38	1.006979	372	87	1.033701	694
39	1.007351	379	88	1.034400	699
40	1.007730	388	89	1.035104	704
41	1.008118	396	90	1.035813	709
42	1.008514	404	91	1.036527	714
43	1.008918	413	92	1.037245	718
44	1.009331	420	93	1.037969	724
45	1.009751	428	94	1.038697	728
46	1.010179	435	95	1.039429	732
47	1.010614	445	96	1.040166	737
48	1.011059	451	97	1.040907	741
49	1.011510	459	98	1.041653	746
50	1.011969	466	99	1.042404	751
51	1.012435	0.000474	100	1.043159	0.000755
52	1.012909				

For sake of comparison I have given in Table XI. the values obtained by different experimenters for the expansion of water, taking in all cases its volume at  $4^{\circ}=1.000000$ .

TABLE XI.

	Kopp*.	Despretz†.	Pierre‡.	Hagen§.	Matthiessen.
4	1.000000	1.000000	1.000000	1.000000	1.000000
10	1.000247	1.000268	1.000271	1.000269	1.000271
15	1.000818	1.000875	1.000850	1.000849	1.000892
20	1.001690	1.001790	1.001717	1.001721	1.001814
30	1.004187	1.004330	1.004195	1.004250	1.004345
40	1.007654	1.007730	1.007636	1.007711	1.007730
50	1.011890	1.012050	1.011939	1.011994	1.011969
60	1.016715	1.016980	1.017243	1.017001	1.016964
70	1.022371	1.022550	1.023064	1.022675	1.022648
80	1.028707	1.028850	1.029486	1.028932	1.028953
90	1.035524	1.035660	1.036421	1.035715	1.035813
100	1.043114	1.043150	1.043777	1.042969	1.043159

KOPP, DESPRETZ, and PIERRE used the same methods for their determinations, namely, that of determining the expansion of water in glass vessels (dilatometers). HAGEN employed the weighing process, but at high temperatures took no special precautions to prevent his fine wire becoming slightly wetted by the steam condensing on its surface. This might account for his values at  $90^{\circ}$  and  $100^{\circ}$  falling below mine||.

As I shall have to speak of the above series after describing the experiments with mercury, I will postpone the remarks I have to make.

#### IV. *On the Redetermination of the Coefficient of Expansion of Mercury.*

The mercury employed for the following experiments was purified by treating the commercial metal with nitric acid, distilling it, again treating it with nitric acid, redistilling and keeping it till required for use under a solution of the protonitrate of mercury. When required for use it was again treated with nitric acid on a water-bath for some little time, thoroughly washed with distilled water, dried first on the water, and then heated over the naked flame.

To weigh the metal in water at different temperatures, small buckets (about 20 millims. long, 15 millims. wide) were made from the ends of thin test-tubes. Across the mouths of these a thin platinum wire was fused to serve as a handle, to which the very fine wire can be fastened.

\* Pogg. Ann. xcii. 42.

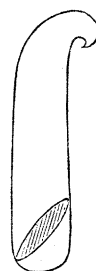
† Ann. de Chim. et de Phys. lxx. (1<sup>re</sup> série) 1.

‡ Ann. de Chim. et de Phys. xv. (3<sup>me</sup> série) 325. Calculated by FRANKENHEIM, Pogg. Ann. lxxxvi. 451.

§ Abhandlungen d. k. Akad. d. Wissensch. zu Berlin, 1855.

|| HENRICI and JOLLY's values (Bericht der k. bayer. Akad. der Wissensch. 1864, 1 Heft 11, p. 141) are not quoted in the above Table, as they compared their thermometers with an air-thermometer, and do not give the differences between them; so their results are not comparable with those in the Table. I shall refer to this point in my paper on the expansion by heat of metals and alloys.

The coefficient of expansion of this sort of glass was determined by weighing a piece of the same tubing in water at low and high temperatures. The tube was drawn out and fused as shown in the annexed figure; but before sealing to, a small piece of lead was placed in the tube to cause it to sink in water. It was weighed in water with the following results:—



Temperature.	Absolute loss of weight in water.	$W_t(1+at)$ .
11°70	7·72250	7·72595
95°20	7·44775	7·74250

The values in the third column are deduced by multiplying the observed loss of weight in water by the volume occupied by water  $(1+at)$  at the temperature at which the weighing was made (Table X.); for if the weights of water displaced be reduced to 4°, the numbers so obtained will express in cubic centimetres the volumes of glass at different temperatures.

The coefficient of expansion of the glass between 11°·7 and 95°·20 equals from the above values 0·002143, taking its volume at 11°·7=1,

or 0·002566 between 0° and 100°, taking its volume at 0°=1,

or the formula for the correction of the expansion of this sort of glass will be

$$V_t = V_0(1 + 0·00002566t).$$

In carrying out the experiments with mercury, the bucket was first weighed in air, then placed in the silver cylinder and boiled in the water for about half an hour to free it from air; the mercury during the time being dried, as already mentioned, and still hot, was poured into the bucket, just lifted out, but quite full of water. In this manner it was possible to fill the bucket with mercury without air getting between it and the glass. After filling the bucket, the boiling was continued for a quarter of an hour, and then the observation made in the ordinary manner. Table XII. contains the five series made with different specimens of mercury used. To find the weight of the mercury after the weighings had been made, it was emptied into a crucible, dried on a water-bath, and weighed.

TABLE XII.

Series I.						
Tempera- ture.	Loss of weight in water.	$W_t(1+at)$ .	Volumes of glass.	Observed volumes of mercury.	Calculated volumes of mercury.	Difference.
0.2	3.47615	3.47615	0.49900	2.97715	2.97704	+0.00011
47.3	3.46245	3.49965	0.49955	3.00010	3.00031	-0.00021
71.4	3.43280	3.51345	0.49990	3.01355	3.01333	+0.00022
95.4	3.39170	3.52640	0.50020	3.02620	3.02629	-0.00009
Series II.						
11.5	3.69250	3.69405	0.49910	3.19495	3.19497	-0.00002
41.7	3.68090	3.71180	0.49935	3.21245	3.21243	+0.00002
69.3	3.64740	3.72850	0.49985	3.22865	3.22838	+0.00027
95.3	3.60060	3.74335	0.50020	3.24315	3.24347	-0.00032
Series III.						
6.5	3.54240	3.54255	0.49905	3.04350	3.04355	-0.00005
44.6	3.53020	3.56405	0.49950	3.06455	3.06449	+0.00006
67.9	3.50235	3.57730	0.49980	3.07750	3.07730	+0.00020
94.0	3.45780	3.59160	0.50015	3.09145	3.09164	-0.00019
Series IV.						
4.7	4.54765	4.54765	0.47250	4.07515	4.07522	-0.00007
34.4	4.54395	4.56990	0.47285	4.09705	4.09702	+0.00003
63.5	4.50700	4.59210	0.47320	4.11890	4.11844	+0.00046
95.3	4.43905	4.61505	0.47360	4.14145	4.14186	-0.00041
Series V.						
6.1	4.78140	4.78155	0.47255	4.30900	4.30901	-0.00001
47.5	4.76285	4.81445	0.47305	4.34140	4.34137	+0.00003
96.6	4.66395	4.85335	0.47365	4.37970	4.37974	-0.00004

The bucket used in Series I., II., and III. was the same. Its weight *in vacuo* was =1.2523 gm., and it lost in water at 11°2, 0.4989 gm.

The bucket used in Series IV. and V. was the same. Its weight *in vacuo* was =1.750 gm., and it lost in water at 8°6, 0.4725 gm.

Deducing from these determinations the volumes at 0°, we find that of the first to be =0.49895 cub. centim., and that of second to be =0.47245 cub. centim.

The formula therefore for the correction of the expansion of the first bucket used was

$$V_t = 0.49895(1 + 0.00002566.t),$$

and that for the second

$$V_t = 0.47245(1 + 0.00002566.t).$$



The volumes of the glass were subtracted from the volumes of the water displaced, to find the volumes of the mercury for

$$W_t(1+a_1t)=U_0(1+bt)+W_0(1+at),$$

where  $U_0$  is the volume of mercury at  $0^\circ$ ,  $b$  its coefficient of expansion,  $W_t(1+a_1t)$  the volume of the water displaced, and  $W_0(1+at)$  the volume of the bucket. Calculating the relative coefficients of expansion of mercury for each series, and deducing by means of these the volumes of the mercury at  $0^\circ$ , we arrive at the following formulæ:—

For Series I.  $U_t=2.97477+0.0005400t$ .

„ II.  $U_t=3.18832+0.0003782t$ .

„ III.  $U_t=3.03998+0.0005496t$ .

„ IV.  $U_t=4.07168+0.0007364t$ .

„ V.  $U_t=4.30424+0.0007816t$ .

It will be seen that the volumes calculated by these formulæ agree closely with those observed.

The above formulæ may, however, be written as follows:—

$$\text{I. } U_t=2.97477(1+0.0001815t),$$

$$\text{II. } U_t=3.18832(1+0.0001813t),$$

$$\text{III. } U_t=3.03998(1+0.0001808t),$$

$$\text{IV. } U_t=4.07168(1+0.0001808t),$$

$$\text{V. } U_t=4.30424(1+0.0001816t),$$

where the coefficients are referred to the volumes of mercury at  $0^\circ$  equalling unity.

The mean of the coefficients is

$$0.0001812,$$

a number closely agreeing with REGNAULT'S, namely,

$$0.0001815.$$

The above five series also prove that the air absorbed by the water during the time of weighing does not influence the results; for in Series I. the water in the cylinder was boiled (to free it from air) only once during the time of the observations, the weighings being made at the highest temperature first, and then on cooling the water gradually the other weighings were taken, the water in the box not being stirred at all.

In Series II. same remarks as for Series I.

In Series III. the water was twice boiled, namely, before taking the weighings at  $94^\circ.0$  and  $44^\circ.6$ ; otherwise same remarks as for Series I.

In Series IV. the water was twice boiled, namely, before taking the weighings at  $95^\circ.3$  and  $4^\circ.7$ , and  $63^\circ.5$  and  $34^\circ.4$ ; the water in the box in which the cylinder stood being stirred during the weighings.

In Series V. the water was boiled before each observation, and the water in the box stirred during the time of weighing.

In the beginning of this paper I stated that my reason for carrying out the foregoing research was that, basing my calculations on KOPP's coefficients of expansion of water, I could not obtain a value for the coefficient of mercury which agreed with REGNAULT's.

If we deduce this value from Table XII., using KOPP's coefficients, we find, of course taking the volume of water at  $4^{\circ}=1$ , the volume

$$U_t = U_0(1 + 0.000178t).$$

The same deduced from calculations based on the values in Table X.,

$$U_t = U_0(1 + 0.0001812t).$$

REGNAULT found by direct measurement the expansion of mercury to be

$$U_t = U_0(1 + 0.0001815t).$$

On comparing the values given in Table XI., it will be seen how closely DESPRETZ's and the last series agree, whereas KOPP's and DESPRETZ's results do not agree, although obtained by the same process. Bearing these facts in mind, we must conclude that KOPP's coefficients for the expansion of water are too low, (1) as the coefficient of expansion of mercury falls below that found by REGNAULT when deduced by means of KOPP's coefficient; (2) as the said coefficients are lower than those obtained by other observers; and (3) as the coefficient of mercury when deduced by means of those obtained for water by the above-mentioned observers agrees closely with that found by REGNAULT; for had I employed DESPRETZ's coefficients instead of my own, I should have deduced very nearly the same value for the coefficient of expansion for mercury.

In conclusion I may be allowed to express my thanks to the gentlemen who have assisted in carrying out the foregoing research; to Professor HIRST for his kindness in suggesting methods of reduction and calculation, to Mr. BASSETT and Dr. MAX BEREND for the able manner in which they assisted in the experimental part, and to Dr. C. VOGT for his undertaking the greater part of the computations.

Fig 1.

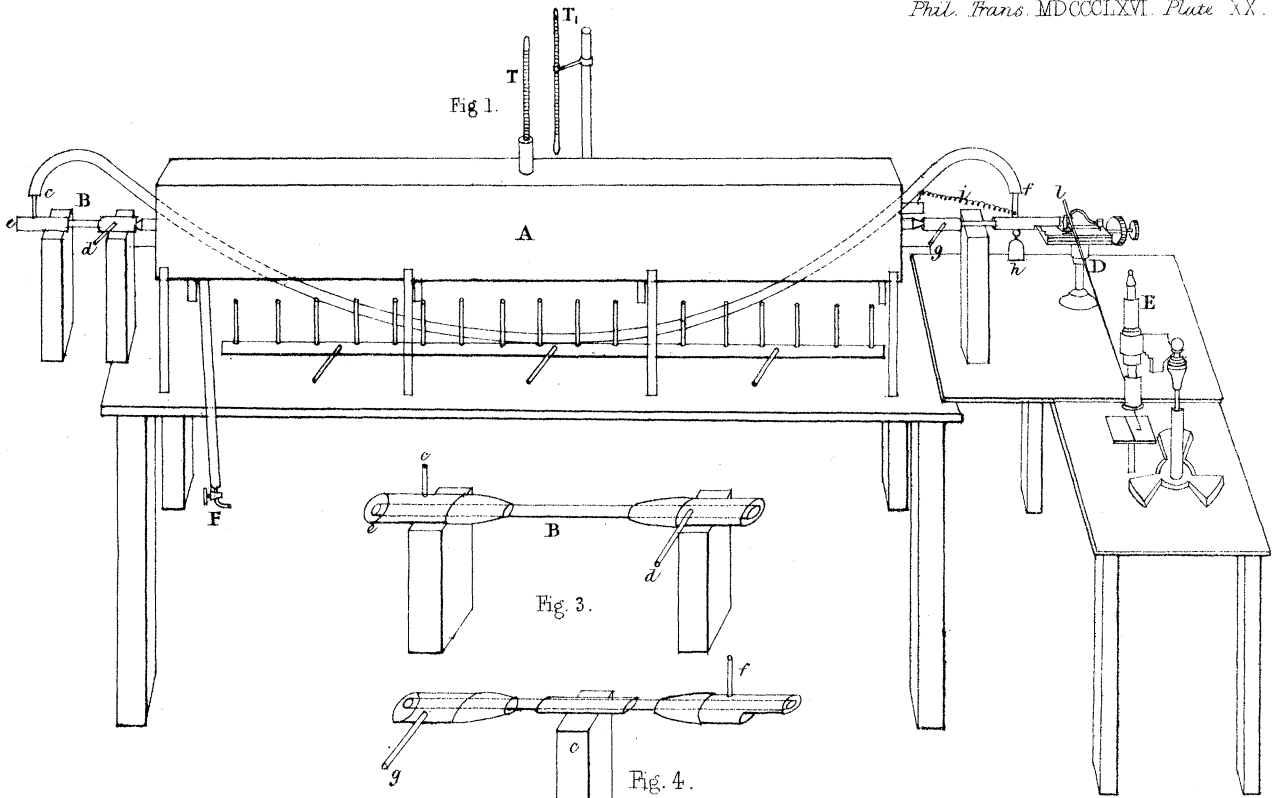


Fig. 3.

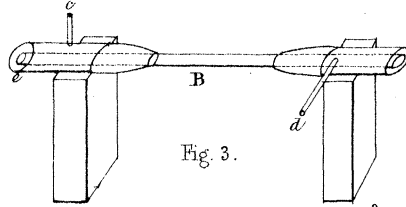


Fig. 4.

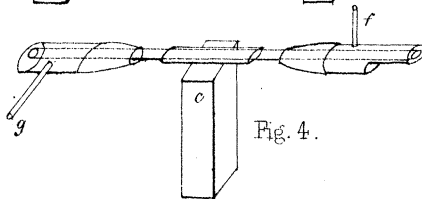


Fig 2.

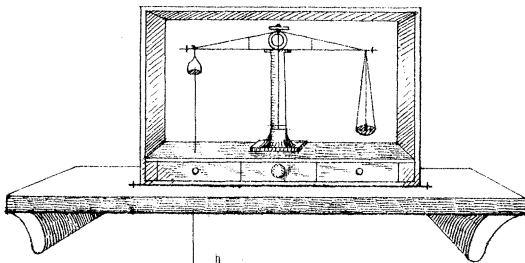
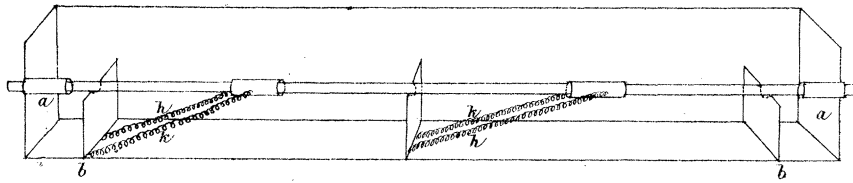


Fig. 5.

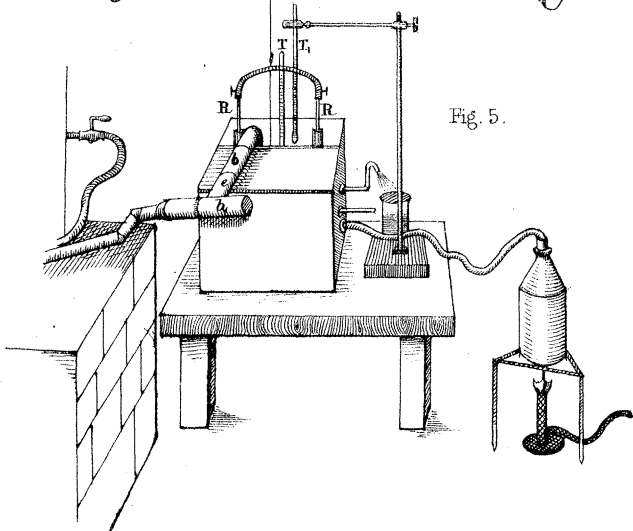


Fig. 6.

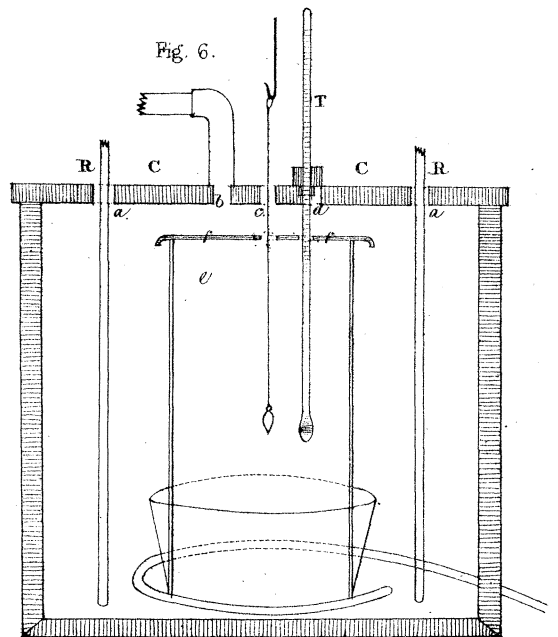


Fig. 8.

Fig. 7.