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VII. *The Cubical Expansion of Fused Silica, with Note on the Variation of the Boiling Point of Aniline with Pressure.*
By F. J. HARLOW, A.R.C.S., B.Sc., Assistant Lecturer in Physics, Sir John Cass Technical Institute.

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THE properties of fused silica have been investigated considerably of late years, and the results have shown that it can be used with advantage for many scientific purposes. In particular it seems to be a suitable substance for the envelope in both liquid and gas thermometers, as many of the disadvantages of the use of glass for this purpose do not exist in the case of fused silica.

The following is an account of measurements which have been made of the cubical expansion of fused silica by the weight-thermometer method. Hitherto all measurements of the thermal expansion have been measurements of the linear coefficient, and as the possibility of calculating the cubical coefficient of expansion of a substance in the form of a bulb from the linear coefficient, with any approach to accuracy is doubtful, the direct measurements given in the present paper should prove useful for thermometric and other purposes.

Weight Thermometers and Method of Filling.

The three types of weight thermometer used are indicated in Fig. 1. They were made of clear transparent fused silica, and varied in capacity from 70 c.c. to 140 c.c. approximately. Observations were first of all made with thermometer *a*, which was filled in the ordinary way by alternate heating and cooling with the open end under mercury. As a larger value of the apparent coefficient of expansion of mercury than was expected was obtained with this filling, it was thought necessary to fill the bulb under a vacuum, in order to exclude the possibility of the presence of any air bubbles in the bulb. This was done, but on account of the difficulty experienced in thoroughly cleaning and filling the bulb, one of a different type, Fig. 1 (*b*), having tubes at both ends, was subsequently used. Fig. 1 (*c*) shows a similar bulb having in addition a number of concentric tubes sealed inside; the use of these will be explained later.

The bulb *b* was first of all dried and any volatile matter

removed from its inner surface by heating it while a current of dry air was being aspirated through. Marks were now made upon the tubes as indicated in the figure, and the quantity of mercury filling them from their ends to the marks obtained.

FIG. 1.

The bulb was then connected by airtight rubber joints to the apparatus shown in Fig. 2. By means of this, mercury, which had been dropped through a vacuum to rid it of all traces of

FIG. 2.

air, could be made to fill the bulb after the latter had been evacuated. The apparatus was first carefully dried by repeatedly evacuating and admitting dry air through the drying

tube D, and was finally evacuated to a high degree of exhaustion. Mercury from the reservoir C was now allowed to flow into the bulb A slowly by an adjustment of the pinch cock *a*, and any air given off from it, as it fell through the vacuous space or as it was boiled in A, was pumped out. By closing the tap *b* and admitting air into A through the drying tube, the mercury was forced by way of the capillary tube *t* into the bulb. When the bulb was completely filled, the pinch cock *c* was closed and the thermometer removed. The end of the tube *d* was then plugged with a piece of iron wire sealed in with wax, and, the rubber tubing and pinch cock *c* having been removed, the thermometer was ready for observations to be made.

Observations and Results.

For convenience in taking the observations the bulb was supported at the bottom by a holder attached to a brass rod parallel to the bulb. To the top of this rod was attached an arm carrying a small removable shelf and a small weighing bottle containing mercury placed upon this caught the overflow mercury. The bottle and its contents could thus easily be removed and weighed.

Fundamental Interval.—Readings of the fundamental interval were made in the usual manner. The temperature of the exposed stem was ascertained by a mercury thermometer, so that the expansion of the known quantity of mercury contained in the stem could be allowed for. It was necessary to get the rise of temperature of the stem merely approximately, as it was found that an error of 5 deg. would produce an ultimate error of 1 in 20,000 only, the accuracy to which one attempted to work. The smallest fundamental interval was about 16 grammes, so that since it was found possible to repeat similar readings to 0.0005 gramme, the required accuracy could be obtained. The steam temperature was obtained from readings of the barometric height. Observations were made with the three types of thermometer with two or three fillings for each, the results of which are given in Tables I. and II. Table I. gives the complete set of observations taken with bulb *b*, the apparent coefficients given in the last column being calculated by dividing the overflow by the mass left in the bulb at the steam temperature and by the range of temperature. The third set of readings given in this table was obtained after the bulb had been heated in aniline, and shows good agreement with the first two sets. The ice readings at

the foot of the table were taken both before and after the steam readings in each case, and the very close agreement obtained shows that no permanent alteration of volume of the bulb had occurred through heating. This was also found to be the case when the bulb was heated to the temperature of boiling aniline.

TABLE I.

Date.	Steam temperature in degrees Centigrade.	Weight of mercury filling to marks at steam temp., in grammes.	Corrected overflow in grammes.	Apparent coefficient of expansion of mercury $\times 10^9$.	
1910.					
1st filling	May 27 ...	100.096	1,134.10	20.5555	181,076
	" ...	100.083	1,134.10	20.5523	181,071
	" ...	100.076	1,134.10	20.5490	181,055
	June 2	99.871	1,134.14	20.5086	181,064
	"	99.869	1,134.14	20.5092	181,073
	June 3	99.889	1,134.14	20.5141	181,079
	"	99.874	1,134.14	20.5113	181,081
	June 4	99.713	1,134.17	20.4754	181,052
	"	99.722	1,134.17	20.4780	181,058
June 5	99.935	1,134.13	20.5197	181,047	
"	99.898	1,134.14	20.5132	181,054	
Average 181,065					
1910.					
2nd filling	June 25 ...	99.547	1,134.16	20.4421	181,061
	June 28 ...	99.722	1,134.12	20.4787	181,064
	" ...	99.721	1,134.12	20.4777	181,065
	June 29 ...	99.748	1,134.12	20.4805	181,041
	July 6.....	99.833	1,134.12	20.4963	181,026
Average 181,051					
1911.					
3rd filling	January 27	100.492	1,134.02	20.6345	181,056
	"	100.476	1,134.02	20.6290	181,049
	January 28	100.531	1,134.01	20.6414	181,056
	"	100.522	1,134.03	20.6394	181,056
	February 1	100.776	1,133.97	20.6904	181,056
February 2	100.745	1,133.98	20.6844	181,056	
Average 181,056					
Ice Readings.—					
First filling	May 26.....	140.5004			
	June 4.....	140.4979			
	June 9.....	140.4979			
Second filling	June 25	140.0510			
	June 28	140.0505			
	July 6	140.0500			
Third filling	January 26.....	168.4622			
	February 15	168.4592			

TABLE II.

Bulb.	Date.	Filling.	Apparent coeff. of expansion of mercury $\times 10^9$.	Cubical coeff. of expansion of silica $\times S_{100}$.
<i>a</i>	{ Oct., 1909 ,, ,,	(1) Ordinary...	181,017	100.6×10^{-8}
		(2) Vacuum....	181,042	
		Mean	181,030	
<i>b</i>	{ May-June, 1910 June, 1910.... Jan.-Feb., 1911	(1) Vacuum....	181,065	97.9×10^{-8}
		(2) Vacuum....	181,051	
		(3) Vacuum....	181,056	
		Mean	181,057	
<i>c</i>	July, 1910.....	(1) Vacuum....	181,026	101.0×10^{-8}
				Mean 99.8×10^{-8}

In Table II. the fourth column gives the average values of the apparent coefficients of expansion of mercury obtained from each series of readings taken. The first filling of *a* was carried out by the ordinary method of heating and cooling; the second after evacuating by a modification of the apparatus described. The approximate agreement between the results obtained shows that the ordinary method of filling a weight thermometer is fairly satisfactory. The values of the cubical coefficients of expansion of the bulbs given in the fifth column were calculated from the means of the results for each thermometer, by the well-known formula:—

$$\alpha = \frac{m}{Mt} + \frac{M+m^*}{M} S,$$

where α = absolute coefficient of expansion of mercury.

m = overflow.

M = mass of mercury left in at the higher temperature.

t = higher temperature in degrees Centigrade.

S = coefficient of cubical expansion of the bulb.

The value of the absolute coefficient of expansion of mercury used was that given by Callendar and Moss * in their recent paper—viz., 0.000182054.

Surface Effect.—It was thought at one time during the investigation that possibly the expansion of the mercury near the surface was in some way affected by the surface, and that this might explain the discrepancies existing in the values of

* "Phil. Trans.," January, 1911.

the coefficient of expansion of mercury obtained by the weight-thermometer and absolute methods. For the purpose of testing this, the bulb *c* was used, in which the ratio of the surface to the volume was considerably increased by the concentric silica tubes sealed inside. The results with the three bulbs show that a surface effect, if it exists at all, is extremely small.

Pressure Effect.—The possibility of an error arising from the pressure on the bulb was also considered. Such an error may arise either from the change in the effect of the pressure in the bulb due to an alteration of the elastic properties of the silica with the rise of temperature, or from the change in the pressure itself due to the change in the density of the mercury. To test the first, the contraction which took place, when a pressure of an atmosphere was applied, was measured at 0°C. and at 100°C. These were found to differ by 0.004 of a gramme of mercury only, so that since the average internal pressure on the bulb was only about $\frac{1}{10}$ th of an atmosphere, the effect was quite negligible. A calculation of the effect due to the alteration in the density of the mercury showed this also to be quite negligible.

Ice-Aniline Readings.—It was thought desirable to extend the observations to a higher temperature, and for this purpose an aniline vapour bath was used. The bulb was enclosed in a large beaker containing aniline, the beaker being carefully lagged with asbestos cloth and closed at the top with sheets of tin and uralite. To prevent cooling by radiation, the bulb was surrounded by a cylinder of tin, and between the lid of the beaker and the bulb were placed two discs of tin separated by a distance of about 1 cm. In this way a vapour bath of uniform temperature was obtained. The temperature was measured by a platinum resistance thermometer of about 5 ohms fundamental interval, which enabled one to measure the temperature to $\frac{1}{100}$ th of a degree. It was thus possible to work to an accuracy of about 1 in 20,000, since the boiling point of aniline is 184°C. or thereabouts. A small coil of nickel wire surrounding the bulb was used for heating up the bulb slightly after a weighing of the overflow vessel. This was found necessary in order to join on the thread of mercury to the mercury in the vessel. The results of the observations are given in Table III., and it will be observed that a good agreement exists between them. With two sets of observations also the ice read-

ings are given. The agreement between those taken before the aniline readings and those taken after shows that here again no permanent change in the volume of the bulb took place through heating.

The value of the absolute coefficient of expansion of mercury used for the calculation of the expansion of the bulb was 0.000183705, obtained from the formula given by Callendar and Moss.

TABLE III.

Bulb.	Date.	Aniline bath temperature in degrees Centigrade.	Weight of mercury filling to marks at bath temperature, in grammes.	Corrected overflow in grammes.	Apparent coefficient of expansion of mercury $\times 10^3$.	Cubical coefficient of expansion of silica σ_{184} .
	1911.					
	March 4...	184.168	1,849.67	62.0712	182,214	
	" 6...	184.026	1,849.72	62.0212	182,203	
	" 8...	184.292	1,849.62	62.1169	182,230	
	" 9...	184.072	1,849.70	62.0374	182,207	
	" 13...	183.483	1,849.90	61.8376	182,184	
	" 16...	183.683	1,849.85	61.9034	182,184	
	" 17...	183.908	1,849.75	61.9875	182,218	
				Average	182,205	145.1×10^{-8}
b	1911.					
	July 10...	182.518	1,116.84	37.6163	182,186	
	" 10...	182.556	1,116.83	37.6242	182,187	
	" 12...	182.372	1,116.85	37.6019	182,264	
	" 12...	182.432	1,116.85	37.6124	182,253	
	" 13...	182.336	1,116.88	37.5834	182,207	
	" 13...	182.324	1,116.88	37.5835	182,221	
	" 14...	182.315	1,116.88	37.5834	182,230	
	" 14...	182.292	1,116.89	37.5742	182,205	
				Average	182,219	143.8×10^{-8}
c After alteration necessitated by breakage	1911.					
	July 19...	184.397	1,850.55	62.1699	182,190	
	" 20...	184.426	1,850.54	62.1837	182,203	
	" 20...	184.446	1,850.53	62.1926	182,210	
	" 20...	184.505	1,850.51	62.2168	182,225	
	" 25...	183.870	1,850.73	62.0001	182,196	
				Average	182,205	145.1×10^{-8}
				Mean		144.7×10^{-8}
<i>Ice Readings.—</i>						
c. First filling		{ March 3		121.3624		
		{ March 18		121.3593*		
b. "		{ July 10		152.2663		
		{ July 15		152.2660		

* A smaller weight was expected here, as a tiny drop of mercury was known to have been lost

Conclusion.

The mean results for the cubical coefficient of expansion of the three bulbs are :—

$$S_{100} = 99.8 \times 10^{-8}.$$

$${}_0S_{184} = 144.7 \times 10^{-8}.$$

The values of the various measurements of the linear coefficient of expansion of fused silica which have been made have been collected in a paper* by Kaye, of the National Physical Laboratory, and the values of the cubical coefficients of expansion calculated from the mean linear coefficients given in this paper are :—

$${}_0S_{100} = 147 \times 10^{-8}$$

$${}_0S_{184} = 154 \times 10^{-8}$$

Although the legitimacy of this calculation, as already mentioned, is doubtful, the wide discrepancy between the two values for the fundamental coefficient can scarcely be attributed to this. The result given in the present paper thus leads one to think that the observations, on which the value given in Kaye's paper,—viz., 49×10^{-8} for the linear coefficient between $0^\circ\text{C}.$ and $100^\circ\text{C}.$, depend, are too large. This seems all the more likely, since the same observations show that the coefficient changes sign at about $-80^\circ\text{C}.$ It does not, therefore, seem likely that it will attain the above value between $0^\circ\text{C}.$ and $100^\circ\text{C}.$, since this value is not very much less than the maximum value.

Most of the observations on the linear expansion at ordinary temperatures have been made by the well-known Fizeau interference method, in which specimens about 1 cm. long are used. The expansion to be measured is thus of the order of the wavelength of light only, and it seems that, although most of the observations have been carried out with great care, and fairly consistent readings obtained, the results may be inaccurate from possible systematic errors. The difficulty which was first met with in the application of the Fizeau method to the measurement of the expansion of silica was that inconsistent readings were obtained by reason of the existence of traces of air between the surfaces of contact. This difficulty was avoided eventually, as was also the very large and uncertain correction due to the change in the refractive index of the air with the temperature and pressure changes, by evacuating the

* Kaye, "Thermal Expansion of Fused Silica," "Phil. Mag.," October, 1910,

envelope containing the apparatus. As, however, it is extremely difficult to remove every trace of air from the surface of silica it seems quite probable that an appreciable error is introduced on this account, if one considers the extremely small expansion which is measured. It thus seems desirable that accurate measurements of the linear expansion should be made with longer specimens.

It is well known that the accuracy with which one can work with a mercury in glass thermometer is limited by the temporary changes of zero which occur on account of the bulb not returning quickly to its original volume after heating. The observations made above show that with fused silica this would not occur, the reason no doubt being that at ordinary temperatures it is so far removed from its melting point. On this account, then, the accuracy attainable with mercury thermometers should be considerably increased by the use of fused silica as the containing envelope.

Variation of the Boiling Point of Aniline with Pressure.

During the course of the experiments with the aniline vapour bath the barometer varied over a fairly wide range. A table (Table IV.) of boiling points at pressures ranging from 74 cm. to 78 cm. of mercury is given, as it may prove useful to other observers.

TABLE IV.

Barometric readings in centimetres of mercury.	Boiling point of aniline in degrees Centigrade.
74.0	183.09
75.0	183.58
76.0	184.07
77.0	184.56
78.0	185.05

These values were obtained from the curve in which temperature was plotted against pressure. Most of the points were found to be well on a straight line, the slope of which gave as the rate of change of temperature with pressure 0.49°C. per centimetre of mercury. Care, however, must be taken in applying these figures to the boiling liquid, since, if pure aniline is boiled for some time, partial decomposition takes place. This does not alter the temperature of the vapour at some distance from the liquid unless the aniline has decomposed considerably. The use of copper vessels should be avoided, as the copper seems in some way to accelerate decomposition

In conclusion, I desire to thank Prof. Callendar for suggesting this research, and for the help he has given me from time to time during the performance of the work, which has been carried out at the Imperial College of Science and Technology.

ABSTRACT.

The author describes experiments in which measurements of the cubical coefficient of expansion of fused silica from 0°C. to 100°C., and from 0°C. to 184°C., were made by the weight thermometer method. The values obtained were $\alpha_{100} = 99.8 \times 10^{-8}$, and $\alpha_{184} = 144.7 \times 10^{-8}$. The fundamental coefficient is considerably less than that calculated from previous linear measurements, whereas α_{184} is only slightly less. A low value of the fundamental coefficient is to be expected, since the coefficient has been shown to change sign at about -80°C. Observations of the ice-point before and after heating showed that no permanent change in the volume of the bulb occurred through heating, thus confirming the utility of fused silica for thermometric purposes.

DISCUSSION.

Dr. G. W. C. KAYE said that Mr. Harlow's results should prove useful now that mercury in silica thermometers were an accomplished fact. These bid fair to revolutionise mercurial thermometry. He pointed out that Mr. Harlow's results did not agree with the linear expansion of silica found by Chappius, Holborn and Henning or Randall and Scheel. He thought for fused silica it should be possible to deduce the linear expansion from the cubical. He would like Mr. Harlow to obtain some results at a higher temperature. Some preliminary results obtained with a silica meter bar at the National Physical Laboratory confirmed these other workers.

The PRESIDENT remarked that his own experiments on the linear expansion of a rod of silica 30 cm. long (described in a Paper read before the Physical Society on March 22, 1901) showed no appreciable change in the mean coefficient 0.00000054 from 15° to t , when t was varied between the limits 340° and 1,400°C. Recent experiments at temperatures below 0° appeared to indicate a lower value, and it was possible that the linear coefficient between 0 and 100° might be sensibly smaller. He did not, however, consider that the cubical coefficient could be deduced satisfactorily from the linear, because it was impossible to anneal a drawn specimen or bulb satisfactorily, owing to the rapid devitrification of amorphous silica at 1,000°C. If Mr. Harlow's value of the cubical coefficient between 0° and 100° were employed in the reduction of gas-thermometer observations with silica bulbs, in place of that obtained by assuming the above constant value for the linear coefficient, the temperature scale would be raised by a tenth of a degree at 445°C. A correction of this order was far from negligible at the present time.

Mr. T. BARRATT asked whether the Author had made any observations of the linear expansion of the thermometer bulbs used by him.

The AUTHOR thought it was quite possible that there might be a difference between the cubical coefficient of expansion and three times the linear. He was endeavouring to extend his results to higher temperatures. He had not made any observations on the linear expansion of his bulbs as the Fizeau method was the only practicable one.