"Researches in Absolute Mercurial Thermometry." By the late S. A. SWORN, M.A. Communicated by H. B. DIXON, F.R.S. April 21,—Read June 15, 1899.

(Abstract, prepared at the request of the Council by ARTHUR SCHUSTER, F.R.S., December, 1899.)

The experimental portion of this work consists of the careful comparison of six thermometers, with the object of studying the effects of capillarity, and in the second place of obtaining a comparison between thermometers made of English flint glass with those of French "verre dur" or Jena normal glass, and therefore indirectly with the hydrogen scale.

The instruments employed consisted of a Tonnelot "verre dur" thermometer, to be referred to as No. 4976, an English flint glass (No. 711,179) by J. J. Hicks, two normal thermometers (Nos. 2218 and 2219) of Jena 16^{III} by Gerhardt of Bonn, and two calorimetric thermometers Nos. 2220 and 2221 of Jena 16^{III} by Gerhardt, with a range from -2° to 25° C.

The Tonnelot instrument is divided on the transparent stem into tenth degrees, and is cylindrical in the bore. The other thermometers have enamelled backs, and are divided on the stem into half millimetres. At the time the latter instruments were obtained elliptical bores were the only ones procurable, but care was taken that the bore was not unduly flattened, and was smooth in contour. The author considers the readings taken with these thermometers to be quite trustworthy. The ratio of the major to the minor axis of the bore was about 2 for the Jena glass thermometers and 3 for 711,179. In each case the bulb (without enamel) was fused to the stem. Ampoules were avoided in all the instruments.

The calibration corrections were obtained in the usual way, a micrometer being used to measure the ends of the thread. The reduction was made by the Neumann-Thiessen method.

All readings other than those for calibration were made with a telescope magnifying eighteen to twenty-four times, the eye-piece of which was provided with a micrometer scale by Zeiss. With the aid of this eye-piece, which serves to further subdivide the thermometer divisions, the readings agreed to 0·005 mm. Several readings were always taken, generally three for zero readings, six for the indications in steam, twenty-one for coefficients of external pressure, fifty-four for coefficients of internal pressure; twenty-seven of zero and fifty-four in steam for the fundamental internal correction, and ninety of comparison and eighteen of zero on each instrument during the comparisons. The

probable error of the separate results for the various constants is about 0·001° C.

The Constant of Capillary Depression K *and the Coefficient of External Pressure.*—It is usual to determine the pressure coefficient by suspending the thermometer in a tube, the pressure within which can be rapidly changed from atmospheric pressure to one of a few centimetres of mercury. A sudden diminution of pressure p causes a fall in the indications of the thermometer, and in the absence of capillary effects δ/p would measure the so-called coefficient of external pressure. But the fall of thermometer being accompanied by a change in the shape of the meniscus, the readings before and after the change of pressure are not directly comparable. If the meniscus is normal at high pressure (which can be realised in the experiment, by arranging for a slowly rising temperature), we must add to the reading at the low pressure a certain constant K, which represents the difference in the readings of a thermometer between a rising and falling thread. Hence $(\delta + \mathrm{K})/p$ will be the corrected coefficient of external pressure (β). If ten sets of observations are made, with different changes of pressure (p_1, p_2) giving different falls of the thermometer (δ_1, δ_2), we may put

$$\beta_\epsilon = \frac{\delta_1 + \mathrm{K}}{p_1} = \frac{\delta_2 + \mathrm{K}}{p_2},$$

and hence $$\mathrm{K} = \frac{p_1\delta_2 - p_2\delta_1}{p_2 - p_1}, \qquad \beta_\epsilon = \frac{\delta_2 - \delta_1}{p_2 - p_1}.$$

In the actual observations the changes of temperature which take place between the readings must, of course, be allowed for, and the equations only hold if these changes are so slow that at the low pressure the actual temperature has not overtaken the apparent temperature at the moment the reading is taken. Previous observers not being interested directly in the quantity K, have arranged their experiment so that the readings of low pressure were only taken after a time sufficient to allow the rising temperature to have its effects, so that the thread was rising in all observations. Mr. Sworn, on the other hand, wishing to determine K and β_ϵ simultaneously, had to arrange the experiment so that at low pressures the hydrostatic pressure in the bulb was the same as with a falling thread.

The following table gives an idea of the consistency of the results obtained :—

Thermometer.	Temperature.	p_2.	K.
2220 p_1 = 525 mm.	0°	654 655 636 544 445 363	0·1005 mm.
	19·5°	668 659 654 561 424	0·1243 mm.
	20·5°	669 664 574 414	0·1070 mm.

Mean K = 0·111 mm. ± 0·005.
= 0·0065° ± 0·0003.

The value of K for the various thermometers was found to be as follows:—

Thermometer.	K.
2220	0·0065° ± 0·0003
2221	0·0098° ?
2218	0·0087° ± 0·0006
2219	0·0104° ± 0·0013
4976	0·0051° ± 0·0004
711179	0·0105° ± 0·0004

Mr. Sworn concluded from his results that K is a constant not affected by a change in the rate of rise in temperature, and not appreciably different in different parts of the tube, if the average value of K over a space of several millimetres is always taken.

The Fundamental Interval and the Coefficient of Internal Pressure.—The zeros were determined by plunging the thermometer into a mixture of finely pounded ice and distilled water. Samples of ice were frequently prepared from distilled water, which had for some time been kept in a partial vacuum of 50—100 mm. Norwegian ice was also used, and within the limits of experimental error was always found to give the same results as the specially prepared ice. The purity of the ice was invariably controlled by testing for chlorides, by the Nessler test, and by evaporation to dryness in a platinum basin. In order to be sure

that the two varieties of ice would give the same results, control determinations were made with Nos. 2220 and 2221, the indications of which could be relied upon to show differences exceeding 0·001° C. The apparatus for taking the zeros did not differ materially from that generally used and described by Guillaume.

The thermometer was plunged into the ice within one or two minutes after removing it from the hypsometer, whilst the bulb was still at 40—50°. The thermometer was held vertically in the hand until the mercury had fallen sufficiently for the bulb to be immersed with safety into the ice. 5—10 mm. of the stem above 0° C. were exposed to the ice, adjustment to the vertical made, the thermometer raised so that the image of the meniscus was just clear of the ice, and the readings taken. The stem was always well tapped.

The indications of thermometers at the temperature of saturated steam were investigated in a form of rotary hypsometer which presents some slight difference from that used at the Bureau International. The difference consists in an improvement of the position and construction of the manometer which measures the pressure excess of the steam. In the Breteuil instrument the manometer keeps its vertical position while that part of the hypsometer which holds the thermometer may be placed in either a vertical or horizontal position. This construction renders it necessary for the manometer opening to be placed at some distance from the thermometer bulb, the two being separated by a narrow passage through which the steam has to pass. The manometer will, therefore, register too high a pressure. To correct for this the steam in passing into the condensers when it is at atmospheric pressure, is forced through an exactly similar passage, so that the hypsometer pressure may be assumed to be half way between the pressure indicated by the manometer and the atmospheric pressure. Mr. Sworn gave up the convenience of having the manometer in a fixed position and secured thereby greater certainty in measuring the actual steam pressure at the thermometer bulb. Arrangements had to be made, of course, for the manometer to turn so as to keep the water column vertical when the tube is placed in the horizontal position. Two manometers were used, one connected with the inner chamber holding the thermometer, and the other with the outer steam jacket, but no difference in pressure could ever be detected. In order to prevent the formation of troublesome water drops in the manometers, short and wide glass chambers were interposed between them and the steam. It was thus ascertained that the pressure excess of the steam could be kept within 0·02 mm. of mercury.

A distillation of mercury was avoided by leaving the ast two degrees of the thread unexposed until it was thought that the depressed zero had attained a constant position. Tapping was always resorted to, but the author has been unable to satisfy himself that it makes any

difference for any of the instruments. By comparing the observations of the boiling point made with the vertical and horizontal thermometers, the coefficient of *internal* pressure may be determined, as in the vertical position the hydrostatic pressure of the mercury acts on the bulb. The internal pressure correction (β_i) is connected with the external pressure correction (β_ϵ) by the relation

$$\beta_i = \beta_\epsilon + \kappa,$$

where κ is the compressibility of glass. The following table gives the comparison between the observed and calculated value of β_i; in degrees per millimetre pressure of mercury. The column headed h shows the length of the mercury column between the boiling point and the centre of the bulb.

Thermometer.	β_i (calculated).	β_i (observed).	h.	κ (assumed).
4976	0·0001229	0·0001241	63·8	0·0000154
711179	0·001159	0·001172	57·3	0·0000127
2218	0·000785	0·000804	56·7	0·0000143
2219	0·000825	0·000878	59·2	0·0000143

The observed values of β_i were obtained by dividing the differences in the observed reading (horizontal—vertical position) by the height of the mercury column above the centre of the bulb. No correction was made for the fact that when the column of mercury was raised from the horizontal to the vertical position, the thread descended, and the reading therefore corresponded to one taken with a falling temperature, while in the horizontal position the reading corresponded to one taken with rising temperature. Mr. Sworn concluded from the good agreement between the observed and calculated values of β_i that the effect of capillarity is somehow eliminated in these observations.

Direct observations were made on this point. If the hypsometer is observed at an angle θ to the horizontal, the readings should differ by the quantity K according as the thermometer is brought into its position from the horizontal, or from the vertical. The observed differences are, however, for the most part *nil*, and in any case a mere fraction of K. If, further, the thermometer is gradually raised from the horizontal position, the observed differences in the readings should be expressible in the form $h\beta_i \sin\theta - \text{K}$, where h is the total height of the mercury column, but in reality they are well expressed by leaving K out of account. The author remarked on this point:—

"The effect of capillarity on the advancing or receding columns is unquestionably liable to compensation, either by vibration or by

momentary alterations in temperature or pressure not registered by the manometers. I am personally inclined to think that we are dealing in the hypsometer with steam under what I might term oscillatory conditions of temperature and pressure, the effect of which is to reduce *all* the steam indications of the thermometer to what they would be with a receding menisous. Within narrow limits the mercury may advance along the tube, but of necessity there will subsequently be a capillary force erected which will, within the same narrow limits (viz., K), prevent its return.

Comparison of Thermometers.—The apparatus in which the comparisons were conducted consisted of a cylindrical tank surrounded, except at the top, by a jacket kept at constant temperature, by a circulation of water heated in a thermo-regulator. The capacity of the tank was 5 litres, and it could be heated or cooled independently, and its temperature set a few degrees above or below that of the jacket. The contained water would then heat or cool at a definite and constant rate. The upper part of the tank has two plate glass sides let in parallel to one another and at right angles to the reading telescope. Two series of comparisons were made. In the first the normal thermometers were compared at 20°, 40°, and 60° C. At each temperature the instruments were compared, two at a time in six pairs, the zeros being taken immediately after the second set of readings for each pair. In the second series the calorimetric thermometers, 2220 and 2221 were also utilised, the former in closed series with the normals. These comparisons were made at intervals of 5° from zero to 55° and at 80°. It is not necessary to refer further to the results obtained with the calorimetric thermometers, as it was found that the water in the comparison tank was slightly different at different levels according as the tank was at a temperature higher or lower than that of the atmosphere. The bulbs of the calorimetric thermometers being placed at different and varying levels as compared with the bulbs of the standard thermometer, the results were vitiated, but this source of error did not affect the comparison of the standards. In the reduction of observations Mr. Sworn reduced all readings to a *falling* meniscus. Assuming that the actual observations at the freezing and boiling points of water are those corresponding to a falling thread, he adds to such reading in the comparison the constant K previously determined by him. From the result of his investigations, Mr. Sworn drew the conclusion that there is no systematic difference between the indications of the *verre dur* and the Jena 16^{III} thermometers, and that the flint glass thermometers give indications which are practically identical with those of the hydrogen thermometer.

[The details of the observations are deposited in the Archives of the Society.]

Note on the above Paper. By ARTHUR SCHUSTER, F.R.S.

Received January 4, 1900.

Mr. Sworn's investigations raise some questions of importance in the behaviour of mercury thermometers. The irregularities which are observed in the behaviour of the mercury thread of a thermometer while descending have led observers to take accurate measurements only in a slowly rising temperature. To avoid inconsistencies, the standard temperatures ought also to be measured under conditions which secure the normal formation of the mercury meniscus, which is that of a rising thread. At the temperature of boiling water it is supposed that this can be done by stopping momentarily the flow of steam, so as to lower the temperature before bringing the mercury thread to its final position. At the freezing point a difficulty has always been felt about the influence of effects of capillarity, and there is no doubt that this is the weakest point at present in the accurate measurement of temperatures with mercury thermometers.

Mr. Sworn's investigations led him to conclude that if the fall of a thermometer is slow (*i.e.*, when the meniscus travels its own diameter in about one minute), the fall is regular, and not a series of disjointed steps. The difference in the readings of a falling and rising thermometer being, according to him, a constant (K), which can be determined by the method described in his paper, it should be possible to reduce readings taken with a rising meniscus to readings with a falling thermometer by simply adding K to the reading.

Mr. Sworn's contention was that this should always be done, because the freezing point is approached from above, and the boiling point also, according to him, corresponds to a measurement taken with a falling thread. His observations on the behaviour of thermometers in the hypsometer are of considerable importance, but some confirmation is required, because Guillaume describes an experiment which is not in agreement with Mr. Sworn's conclusion, that the difference in the readings between a rising and falling thermometer disappears when the instrument is suspended in steam. On the contrary, Guillaume determines the amount of the difference by observations in the hypsometer, and states it to be between 0·002 and 0·003° with the standard Tonnelot thermometers. I am inclined to think that the truth lies between the two extremes, and that the effects of capillarity are still appreciable in the steam, but decidedly smaller than at lower temperatures. I am led to this conclusion through my observations at the freezing point with Tonnelot thermometers, which have always made me think that Guillaume must have underrated the effects of capillarity. But even granting for a moment that there is no effect of capillarity in the hypsometer, I should not be inclined to accept Mr. Sworn's explanation of the fact, which is that the temperature of

the steam is slightly fluctuating, and that when it is accidentally high the temperature rises, but when it is low, stiction prevents the thread from falling, so that the ultimate effect is to make the thermometer indicate too high by an amount equal to K. There is no evidence in support of such a fluctuation. It is at least equally probable that stiction is actually of smaller importance at the higher temperature, where the distillation of mercury, which is known to take place from the free surface, must assist the formation of the normal meniscus. Mr. Sworn's method of reducing thermometric observations depending on the complete disappearance of K at the boiling point, cannot therefore be accepted without further evidence, but the matter is one well worthy of careful investigation. Mr. Sworn was perfectly right in saying that the three readings, viz., freezing point, temperature, and boiling point, ought to be taken under like conditions of the meniscus, but the proper way of accomplishing this is to alter the usual practice of fixing the zero by substituting a method similar to that of determining the freezing points of solutions. If the water is first slightly undercooled, and then brought to the proper temperature by the introduction of a few ice crystals, a great improvement in zero point determinations would be effected.

Mr. Sworn's comparisons between thermometers of different composition were carried out with great care, and may be considered reliable, as far as the instruments used are concerned, but it is not quite certain in how far different thermometers purporting to be made of the same glass may differ. Thus the majority of the Jena glass thermometers carefully studied at Berlin showed a difference of over 0·01° at 50° when compared with the French hard glass,* but one instrument agreed throughout its range with the latter, while another differed in the other direction. Marek, at Vienna, did not find any systematic difference between the French and Jena glass, and Mr. Sworn's thermometers also show a practical coincidence. Mr. Sworn's evidence that his instruments were really made of the 16^{III} Jena glass rests on the assurance of the maker (Gerhardt, of Bonn), but the anomalous behaviour of two of the Berlin thermometers leaves a doubt as to how far blowers are careful to guard against accidental mixing up of different sorts of glass. It is not possible, moreover, to compare directly the result of Mr. Sworn's comparison with that of other observers, on account of the difference in the method of reduction, but, as far as I can see, the discrepancy would have been greater if Mr. Sworn had reduced his observations in the way adopted at Sèvres and Charlottenburg. The same remark applies with greater force to Mr. Sworn's reduction of the flint glass indications to those of the hydrogen thermometer. He uses Chappuis's numbers for the relation between the French hard glass and hydro-

* 'Zeits. f. Instrumentenkunde,' vol. 15, p. 438 (1895).

gen scales. But Chappuis's numbers only apply when the glass thermometers are treated and read in the way in which he treated them in his comparisons. That is the great advantage in using the Tonnelot thermometer. It is not an absolute but an intermediate standard. It is immaterial whether Chappuis's method of treating a glass thermometer can be improved upon by adopting a different way of obtaining the zero, or by making corrections for effects of capillarity. It is sufficient to know that consistent results can be obtained if the thermometers are always treated in the same way, and whether that way is good or bad, it is the only one which can be used, if we wish to refer the temperature measurement to Chappuis's hydrogen thermometer. For this reason, and also because we have not at present any guarantee that flint glass thermometers agree sufficiently in composition to give identical results, Mr. Sworn's conclusions cannot at present be accepted as final. Mr. Chree's experience* tends in the direction of indicating differences in the behaviour of different thermometers nominally made of the same glass.

January 25, 1900.

The LORD LISTER, F.R.C.S., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "Mathematical Contributions to the Theory of Evolution.—On the Law of Reversion." By Professor KARL PEARSON, F.R.S.

II. "On the Mechanism of Gelation in Reversible Colloidal Systems." By W. B. HARDY. Communicated by F. H. NEVILLE, F.R.S.

III. "A Preliminary Investigation of the Conditions which determine the Stability of Irreversible Hydrosols." By W. B. HARDY. Communicated by F. H. NEVILLE, F.R.S.

IV. "On the Effects of Strain on the Thermo-electric Qualities of Metals. Part II." By Dr. MAGNUS MACLEAN. Communicated by LORD KELVIN, F.R.S.

V. "On the Periodicity in the Electric *Touch* of Chemical Elements. Preliminary Notice." By Professor JAGADIS CHUNDER BOSE. Communicated by LORD RAYLEIGH, F.R.S.

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* 'Phil. Mag.,' vol. 45, p. 216 (1898).