On the Determination of the Boiling-Point of Sulphur, and on a Method of Standardising Platinum Resistance Thermometers by Reference to it. Experiments Made at the Cavendish Laboratory, Cambridge

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IV. *On the Determination of the Boiling-Point of Sulphur, and on a Method of Standardising Platinum Resistance Thermometers by reference to it.—Experiments made at the Cavendish Laboratory, Cambridge.*

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[Plates 7, 8.]

General Summary of the Work.

The results of many careful experiments by different observers in the course of the past few years have shown that electrical resistance thermometers afford the most accurate and convenient method of measuring temperature through a very wide range.

The object of the following paper is to illustrate a method of reducing the indications of such thermometers to the absolute scale of temperature by means of a single observation at some known fixed point in addition to 0° and 100° C.

The boiling-point of sulphur happens to be the most convenient to choose for this purpose. We have therefore made a very careful determination of this point by reference to the normal air thermometer, and have given a description of the method and apparatus which we have found most suitable for standardising resistance thermometers by means of it.

In a communication[*] which one of us had the honour to make to the Royal Society in June, 1887, "On the Practical Measurement of Temperature," it was shown that, if t be the temperature by normal air thermometer, and pt be the temperature by platinum-resistance thermometer, the difference between them is very closely represented from 0° to 700° C. by the formula,

$$t - pt = \delta \{\overline{t/100}^2 - t/100\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d).$$

The value of the constant δ for a particular specimen of wire was found to be 1·570

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[*] Callendar, 'Phil. Trans.,' A, 1887, p. 161.

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by direct comparison with the air thermometer, the platinum spiral used in the experiments being placed inside the bulb of the air thermometer itself.

In a recent communication* "On the Determination of some Boiling and Freezing Points by means of the Platinum Thermometer," some experiments are described in which the thermometers used were standardised by assuming the boiling points of naphthalene (218°·06 C.), benzophenone (306°·08 C.), and sulphur (448°·34 C.), as determined by CRAFTS and REGNAULT.

Curves were drawn with these data for each thermometer giving the difference, $d = t - pt$, in terms of pt. It was found that the upper portions of these curves differed materially (see Plate 8) from the parabolic formula (d) above given.

In order to compare the results thus obtained with those deduced from the δ-formula, a thermometer (L) was constructed out of a piece of the spiral used in the air thermometer experiments of 1887, for which the value of the constant δ was known to be 1·570.

Observations were taken with this thermometer in sulphur vapour in the same apparatus which had been used for standardising the other thermometers. The results gave $pt = 418{\cdot}5$ as the platinum-temperature attained by the thermometer. This gives $t = 442{\cdot}3$, assuming $\delta = 1{\cdot}570$.

The value thus found was nearly six degrees lower than that given by REGNAULT. This showed either that the value of δ was wrong, or that the thermometer did not attain the temperature of the sulphur vapour, or else that the number given by REGNAULT was too high.

But when the number thus found was used to calculate the appropriate values of δ for each of the other thermometers it appeared that the values of t for all the other boiling- and freezing-points, deduced by means of formula (d) from the observations with all the different thermometers, were in remarkably close agreement.

This suggests a very simple method of standardising such thermometers. Assuming that the (d) formula holds good, it is only necessary to observe the platinum-temperature of sulphur vapour with each thermometer, in order to find the appropriate value of δ, and to reduce all the platinum-temperatures to the air standard.

It was felt, however, that the value of δ assumed for the standard wire required verification. The wire had been very roughly treated, and used for all sorts of purposes since the experiments of 1887, and might well have altered in the interval. Two new thermometers, M_1 and M_2, were therefore constructed out of the remainder of the old spiral, and were very carefully compared with the air thermometer at a temperature very near the boiling-point of sulphur. Owing to the importance of this point, the experiments are very fully described in the following pages, Part I. The result agrees perfectly with that found in 1887, and shows that the value of the δ-coefficient has not altered appreciably in the interval.

The apparatus used for this comparison, although useful as a constant high-

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* GRIFFITHS, *supra*, p. 43.

temperature bath, was not very well suited for determining the actual temperature of the sulphur vapour. Another series of experiments was therefore undertaken in a Meyer tube, which proved to be more convenient for the purpose. The platinum thermometers, which had been standardised as above mentioned, were used for this determination with various screens and other precautions to guard against errors due either to super-heating of the vapour or to loss of heat by radiation and condensation.

The experiments with the Meyer tube are described in Part II. They show conclusively that errors due to radiation, &c., are of serious magnitude at this temperature, and that, in order to find the true boiling-point, it is not sufficient merely to insert a thermometer in the vapour, as we find has generally been the practice among previous observers.

According to our experiments with carefully screened platinum thermometers, the temperature by normal air thermometer at constant pressure, of the saturated vapour of sulphur, boiling freely under a pressure of 760 mm. of mercury at 0° C. and $g = 980{\cdot}61$ C.G.S. (sea-level in latitude 45°), is

$$t = 444^\circ{\cdot}53 \text{ C.}$$

We have taken great pains to verify all the work of reducing the observations, and have carefully tested all the apparatus employed. We believe that the above result may be relied on to the tenth of a degree.

The number given by REGNAULT is nearly four degrees higher than this. His results have been so widely quoted and adopted that we have thought it necessary to add a short criticism of his method, and to suggest an explanation of the discrepancy.

A table is also given containing the boiling- and freezing-points of several substances, reduced from the previous observations with the other thermometers.*

There can be no doubt that, even at low temperatures, the platinum thermometer is a far more accurate and sensitive instrument than the mercury thermometer. With suitable apparatus it is easy to read to 0°·001 C., and there is no trouble about shifting of zero. We have made a careful comparison of the platinum and air thermometers between 0° and 100° C. The experiments are described in Part III., and we find that the δ-formula holds accurately between these limits.

In setting up the apparatus and taking the observations, we have received great assistance from Mr. G. M. CLARK, B.A., of Sidney Sussex College. Our best thanks are due to him for many valuable suggestions.

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* GRIFFITHS, 'Phil. Trans.,' A, 1891.

PART I.

Comparison of Platinum and Air Thermometers at the Boiling-Point of Sulphur.

When we found that the preliminary experiments with thermometer L made the boiling-point of sulphur so much lower than the value given by REGNAULT, we at first endeavoured to account for it by supposing that the wire had altered in the four years' interval, or that the previous air thermometer experiments were faulty. In any case they were felt to require verification.

An iron-tube apparatus was therefore constructed, into which an air thermometer could be introduced, along with two platinum thermometers. The apparatus was so arranged that it could be kept at a steady temperature by a continuous flow of sulphur vapour for any length of time. Two new platinum thermometers, M_1 and M_2, were made out of the remainder of the wire of the old spiral, and were compared with the air thermometer in the iron-tube apparatus on two different days.

Description of the Air Thermometer.

The form of instrument employed is shown in Plate 7, fig. 1. It was similar in every respect to that described and figured in the paper* above referred to, except that the bulb B was formed of ordinary German glass, and not of hard glass.

A piece of tubing, about 2½ cm. in diameter, was taken, and cleaned in the usual way. One end was closed in the blowpipe, and the other was drawn out into a fine capillary tube, a metre long. This was passed through a small brass tube, the end of which was split into four for a length of 15 cm., and bound round the bulb with wire, to serve as a support and to protect the capillary tube. The brass tube was firmly fastened to a wooden stand carrying the volume- and pressure-gauge.

The volume of the bulb was determined by water calibration up to a marked zero-point O on the capillary tube. In using the thermometer care was taken to subject it up to the point O to the temperature to be measured. A short distance beyond this point the brass tube was cooled by winding closely round it several turns of thin lead tubing, through which water was made to circulate. The volume of the capillary tube, for some distance on either side of the point O, was only ·00225 c.c. per cm. The uncertainty of a centimetre or two in the position of the neutral point would not therefore introduce appreciable errors. As a matter of precaution a platinum wire was originally inserted in the brass tube, to take its mean temperature, but it was found that the corrections were always so small that they could be neglected.

A length of about 30 cm. of the capillary tube was bent into the form of a narrow U, shown at C. This served to give the end free play, and to protect the tube from strain.

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* 'Phil. Trans.,' A., 1887, p. 167.

The end of the capillary tube had been previously cut off, and ground flat to fit the end of the gauge-tube. A short double funnel of glass was drawn to fit them both closely, and sealing-wax was run in from either side. This form of joint was generally used by REGNAULT. It is perfectly air-tight if properly made, and is certainly quite unobjectionable in the case of a constant-pressure air thermometer.

Linear Expansion of German Glass.

The expansion of the glass forming the bulb was determined by the method described in the previous paper,* using the remainder of the piece of glass tubing from which the bulb had been drawn.

The glass tube was enclosed in two coaxial tubes of brass, separated from each other by strips of asbestos cloth, and was heated in a thick iron tube in a long gas furnace. The whole apparatus was supported on levelling-screws for focussing. The gas furnace was screened with bright tin plate, and all the precautions were taken which have been previously described.

The mean temperature of the portion heated was determined by means of a known platinum wire (the same piece as was used in thermometer L), extending down the axis of the tube, and supported at intervals by mica plates.

The ends of the tube were drawn down to 5 mm. diameter, to diminish conduction of heat, and to imitate as closely as possible the actual condition of the bulb. They projected on either side for a distance of about 15 cm. beyond the gas furnace.

A large and fairly rigid brass tube with end pieces projecting at right angles was supported, so that reference marks at either end of it could be brought into focus under the reading microscopes close to the ends of the glass tube. Its temperature, which was always very nearly that of the surrounding air, was taken by means of a delicate mercury thermometer placed inside it. Corrections were applied for the small variations in its temperature, and the changes in the length of the glass tube were determined by direct comparison with it.

Five series of observations were taken with this apparatus on different days. The highest temperature reached in each series was a little over 400° C. It was always taken first to avoid the permanent contraction. After the first series, the tube was found to have contracted by ·056 per cent. of its length; but towards the end of the experiments it appeared to reach a steady state.

The whole of the observations on the linear expansion of this glass were very closely represented by the formula

$$l/l_0 = 1 + \cdot 00000960\, t + \cdot 0000000057\, t^2.$$

This gives for the cubical expansion between 0° and 100° C. the factor

$$v_1/v_0 = 1\cdot 003051.$$

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* 'Phil. Trans.,' A., 1887, p. 206.

This factor appeared to be unusually high even for this kind of glass. By way of verification, the bulb of the air thermometer itself was used as a mercury weight thermometer, after it had been dismounted, at the conclusion of the whole series of experiments. It was very carefully and completely filled with pure mercury, and placed in melting ice for an hour and a half. It was then heated in steam at 99°·89 C., till some time after the mercury ceased to drop out. The mercury which had run out was very carefully weighed and found to be 12·0007 grms. The weight of the mercury filling the bulb at 0° up to the zero point (deducting the weight filling the known volume of the capillary tube exposed to the air temperature), reduced to *vacuo*, was found to be 809·023 grms., whence V_0, the volume of the bulb at 0° C., is 59·505 c.c., assuming that the density of mercury at 0° C. is 13·5960 grms. per c.c.

If V_0, V_1 be the volumes of the bulb at 0° and 99°·89 C., and ρ_0, ρ_1 the corresponding values of the densities of mercury, we have the following equation

$$V_1 \rho_1 + 12{\cdot}0007 = V_0 \rho_0.$$

The linear expansion experiments give

$$V_1/V_0 = 1{\cdot}0030476\,;$$

whence

$$\rho_0/\rho_1 = 1{\cdot}018154.$$

Regnault's experiments on the absolute expansion of mercury give for the expansion between 0° and 99°·89 the value $\rho_0/\rho_1 = 1{\cdot}018133$. The value found by assuming the linear expansion is too large, therefore, by one part in a thousand only. This degree of accuracy is amply sufficient for our purpose, as the whole correction for the expansion of the bulb only amounts to 11°·5 at the temperature of boiling sulphur.

Changes in the Volume of the Bulb.

The volume of the bulb was determined from time to time during the course of the experiments. It is interesting to trace the changes which it underwent.

Before mounting, the volume of the bulb was found by direct calibration to be 59·710 c.c. At the close of the experiments, after repeatedly boiling in sulphur, it was found to be 59·505 c.c. The volume at intermediate times was determined by observations in ice and steam in the following manner:—

Shortly after mounting, the bulb was heated in a gas furnace, and dried by exhaustion at a temperature of about 250° C. Observations taken with it next day in ice and steam, assuming the volume of the bulb to be $V_0 = 59{\cdot}710$, gave the value $\theta_0 = 272{\cdot}12$ as the absolute temperature of melting ice by air thermometer at constant pressure. This gives the value 1·36749* for the dilatation between 0° and 100° C., which is approximately that found by BALFOUR STEWART, CHAPPUIS, and the most careful of recent observers.

At the close of the experiments the bulb was repeatedly exhausted while in boiling sulphur, and filled afresh with dry air. Observations taken with it next day in ice and steam, before it was dismounted (assuming the volume of the bulb to be 59·505 c.c.), gave the value $\theta_0 = 272·10$, which is practically identical with that previously found.

We may, therefore, reasonably assume the same value of this constant in all cases. We can then use the observations in ice and steam to calculate the volume of the bulb on intermediate days.

This is the most accurate way in which the volume of the bulb can be determined without dismounting it. All the conditions are the same as those under which the value of the constant θ_0 is determined. Any error in the value of V_0 calculated by this method will not affect the temperatures deduced to any greater extent than an equal error of observation in determining θ_0.

In a trial experiment in the iron tube apparatus on Tuesday, September 9, in which the sulphur distilled over too fast to allow good observations to be taken, the bulb was exposed to a temperature of 450° for nearly a quarter of an hour. Next day its volume was found to have diminished from $V_0 = 59·710$ to $V_0 = 59·574$. Showing that, although it had been subjected to no stress whatever, the contraction was very rapid at first.

On Friday, September 12, the thermometer was kept in sulphur vapour for nearly two hours. The temperature appeared to rise slightly owing to the contraction of the bulb, for a short time after the other thermometers had become steady. After the experiment the volume was found to have diminished from $V_0 = 59·574$ c.c. to $V_0 = 59·518$ c.c.

On Saturday, September 13, the thermometer was again heated in sulphur vapour. Several observations were taken, which gave no indications of change. The bulb was then exhausted fifteen times, and dry air readmitted. In spite of the great stress to which it was thus subjected, at a temperature not far below its softening point, its volume was afterwards found to have diminished very little, namely, from $V_0 = 59·518$ to $V_0 = 59·505$ c.c.

This seems to indicate that the bulbs of mercury thermometers may be practically freed from rise of zero by a preliminary boiling in sulphur before filling them with mercury. The sulphur can be readily boiled for hours in a common test-tube or

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* REGNAULT gives for air at constant pressure 1·3670, for air at constant volume 1·3665. BALFOUR STEWART ('Phil. Trans.,' 1863) finds 1·36733 for air at constant volume. CHAPPUIS ('Archives des Sciences,' Genève, vol. 20, 1888, pp. 5–36) finds for nitrogen at constant pressure the value 1·36747. The two latter observers appear to have used more accurate methods and to have taken greater precautions than REGNAULT.

beaker without requiring any attention, provided that the top is covered with a piece of asbestos to prevent its catching fire. The method of boiling in mercury, which is often adopted, takes a very long time, and would probably give less perfect results, at least in the case of thermometers intended for use at temperatures above 300°.

The Volume- and Pressure-Gauge.

The gauge used with this thermometer for measuring the variations in the volume and pressure of the enclosed air, was the same as that described and figured in the paper before referred to.* The figure is reproduced for convenience in Plate 7, fig. 2. The **U**-tube FHJK represents the sulphuric acid pressure-gauge for indicating the small differences between the external pressure and the pressure of the air enclosed. The bulb A, together with the rest of the tubes and taps, represents the volume-gauge for measuring the dilatation at constant pressure.

The use of the sulphuric acid pressure-gauge is particularly advantageous in connection with a constant-pressure air thermometer. Its employment makes it possible to take a series of readings very rapidly when the temperature is varying slightly. The reading of the gauge can be instantly recorded at any desired moment, and the other observations, such as weighing the mercury and reading the barometer, may be made comparatively at leisure. These and other advantages have been already explained in the previous paper. They have since been very fully confirmed and illustrated by BOTTOMLEY† ('Phil. Mag.,' Aug., 1888, p. 149).

The gauge for measuring the variations of volume of the enclosed air consists essentially (see Plate 7, fig. 2) of a large bulb A containing mercury, and communicating with the bulb of the air thermometer by the way ED. It is surrounded by a water bath (shown in fig. 1), whose temperature can be accurately observed by means of a delicate thermometer. Mercury can be either introduced into, or withdrawn from this bulb in weighed quantities, by means of the taps T_2 and T_3, from weighed beakers of mercury, into which the tubes open at P_2, P_3. Thus, the volume, temperature, and pressure of the air in the bulb A at any moment can be accurately determined.

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* 'Phil. Trans.,' A, 1887, Plate 12.

† The reader who wishes to use an apparatus of this kind should certainly refer to his paper, as the explanations given are very full and detailed; but in our opinion the form of pressure-gauge which he describes is neither so simple nor convenient as that shown in Plate 7, fig. 2. The single three-way tap, T_1, can be made to serve all the purposes of the two taps shown in his figure (*loc. cit.*, p. 152). It can also be turned *in the middle of the acid*, so that it cannot move either way, whatever the variations of pressure. This is a most essential provision of great practical convenience, the absence of which is a serious defect in his form of gauge. The addition of the volume-gauge (Bulb A, &c., Plate 7, fig. 2), which makes it possible to use the air thermometer at constant pressure as well as at constant volume, is also a great advantage, and renders the apparatus much more complete.

Method of taking Observations.

In taking a series of observations at constant pressure with this instrument, the bulb A is first filled from the reservoir Q, till the level of the mercury stands at some point in the tube DE. The level x' is recorded by means of the scale S. The temperature t'_0 of the water-bath is also taken at the same time. These two numbers, as will presently appear, give the zero point from which the volumes are calculated. They remain the same throughout any one series of observations.

Mercury is then allowed to run out by the tap T_3 into a weighed beaker at P_3, until the sulphuric acid gauge FHJK shows that the pressure of the air in the bulb is nearly equal to that of the atmosphere. The water-bath surrounding the bulb A is well stirred; its temperature t' is recorded; and also t'' the temperature of the air. The reading x of the acid in the pressure-gauge FG, is taken at the same instant as the resistance of the platinum thermometer. The height H of the barometer is immediately observed, and the weight w of the mercury which has been allowed to run out, is taken at leisure.

The pressure-gauge FG has a range of about 7°, so that, if the temperature is varying slowly, a considerable number of observations may be taken for one weighing of the mercury.

Formulæ.

The temperature is calculated by means of the following formulæ :—

If p be the pressure of the air enclosed, V the volume of the bulb, and θ its absolute temperature, and if v be the volume of any portion of the air contained in the capillary tube, or other parts of the apparatus, at a temperature θ', the formula of the air thermometer may be stated as follows :—

$$p\,\{\mathrm{V}/\theta + \Sigma v/\theta'\} = mk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where mk is a constant depending on the mass of air enclosed, and Σ implies that the summation is extended to all parts of the apparatus which it occupies.

To find θ we deduce from formula (1),

$$\theta = p\mathrm{V}/\{mk - \Sigma pv/\theta'\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The values of the quantities included in this formula, are deduced from the quantities observed as follows :—

Reduction of the Pressure, p.

The observed height H of the barometer is expressed in centimetres of mercury at 0° C. at sea-level in latitude 45°. A correction of + ·005 cm. is added to allow for capillarity and vapour tension of mercury at 15°–20° C. The reading is also corrected for scale errors, for the error of the attached thermometer, and for any difference of level between the cistern and the air thermometer.

The barometer used is one of the Fortin pattern by CASELLA, with a scale very clearly divided in inches, and a vernier reading to ·001 inch. It was carefully compared with the Cavendish Laboratory standard metre scale, which has been verified at the Board of Trade Standards' Department. The scale errors were found to be exceedingly small, but the ivory point was set ·085 cm. too high.

To find the pressure of the air in the bulb, a small correction for the difference of level of the acid in either limb of the pressure-gauge has to be added. A preliminary experiment gave $x = 2{\cdot}50$ as the reading of the gauge when the pressure was the same on either limb. The factor for reduction to mercury was found by comparison with a mercury manometer to be 0·136. If H_0 be the corrected height of the barometer we have, therefore,

$$p = H_0 + {\cdot}136\,(x - 2{\cdot}50) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

Calculation of the Volume.

The volume V of the bulb at the temperature t is found from the equation already given,

$$V/V_0 = 1 + {\cdot}00002880\,t + {\cdot}0000000171\,t^2 \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The volume of that part of the capillary tube which was exposed to the temperature of the air, was found by mercury calibration to be 0·164 c.c.

The volume of the gauge-tubes CDE, DF, from the end of the capillary tube to the zero point of the scales at F and E, was found be 0·483 c.c.

The volume per cm. of the gauge-tube FG was 0·0232 c.c. If x be the reading of the gauge, the total volume at the air-temperature t'' is, therefore,

$$v'' = 0{\cdot}647 + {\cdot}0232\,x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

The volume of air v' in the bulb A, at the temperature t' of the water-bath, is found as follows. Let w_0 be the total weight of mercury filling the bulb A up to the zero point of the scale S, and let ρ_0 be its density at the temperature t'_0 of the bath, when the reading x' of the scale S is taken, before running out the mercury.

Let w be the weight of mercury run out, and let ρ be its density at the temperature t' of the water-bath at the time of observation. Then, if m be the coefficient of expansion of mercury, we have $\rho / \rho_0 = 1 - m\,(t' - t'_0)$.

The volume of the mercury remaining in the bulb will be $(w_0 - w) / \rho$. The volume per cm. of the tube DE is 0·0127 c.c. If the mercury stood at x' before running out, a small correction $(19 - x') \cdot 0127$ has to be added to the above expression, the point 19·0 of the scale S being the zero from which the volume of the bulb A is reckoned.

The total volume of the bulb up to the zero point is w_0 / ρ_0 at the temperature t'_0. If g be the coefficient of expansion of glass, its volume at t' will be $\{1 + g(t' - t'_0)\} w_0 / \rho_0$.

The volume v' of the air in the bulb A at the temperature t', is the difference between the volume of the glass envelope and the volume of the mercury remaining in it at the time of observation. It is given by the expression

$$\{1 + g(t' - t'_0)\} w_0 / \rho_0 - (w_0 - w) / \rho - (19 - x') \cdot 0127,$$

which reduces to

$$w / \rho - (m - g)(t' - t'_0) w_0 / \rho_0 - (19 - x') \cdot 0127 \quad . \quad . \quad . \quad . \quad (6).$$

The value of the coefficient $(m - g)$ is ·000151, so that the second term in the above expression is always very small. The volume w_0 / ρ_0 of the bulb A is approximately 48 c.c. The whole correction may be neglected, provided that the rise in temperature $(t' - t'_0)$ of the water-bath is less than a tenth of a degree. It is not, as a rule, worth while to reduce the weight of the mercury to *vacuo*, since the correction amounts to only 1 in 20,000.

Sources of Error.

The great advantage of using the air thermometer at constant pressure is that we can dispense with the mercury manometer. The apparatus it involves is generally cumbrous, the observations are slow and laborious, and it is difficult to rely on the result beyond the nearest tenth-millimetre.

In reading the barometer, on the other hand, we are measuring the height of a mercury column under much more favourable conditions. A greater degree of accuracy can be attained; a kathetometer is not required; and it is comparatively easy to verify the scale.

The operations of weighing the mercury and of reading the volume-gauge are capable of being performed with very great accuracy. An error of a decigram in the weight w would produce an error of only + 0°·004 in the resulting value of t at 50° C., and of + 0°·021 at 445° C.

The mercury thermometer used for taking the temperature of the water-bath could be relied on to at least a fiftieth of a degree, and the mean of several observations would probably be correct to 0°·01. It had been carefully compared with the platinum thermometer H,* and its readings were by this means corrected to the air standard. An error of + 0°·01 would produce an error in t of only − 0°·003 at 50° C., and of − 0°·041 at 445° C.

An error of + ·01 cm. in reading the sulphuric acid pressure-gauge would produce an error of + 0°·0086 at 50° C., and of + 0°·039 at 445° C.

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* Griffiths, 'Brit. Assoc. Report,' 1890.

The barometer readings were found to be the chief source of uncertainty, owing to the constant variations of the atmospheric pressure. An error of + 0·01 cm. in reading the barometer would give an error of + 0°·053 at 50° C., and of + 0°·24 at 445° C. The plan adopted was to read the barometer at frequent intervals, noting the time of each observation. By constructing a time-curve on a very large scale, the most probable value of the atmospheric pressure at any time could be deduced. The comparison of the platinum and air thermometers between 0° and 100° (p. 152), in which the mean deviation of the observations from the parabola is less than one-hundredth of a degree, shows that this method is capable of giving very good results.

Variations in the Constant, mk.

The observations in ice and steam give the equations

$$\left.\begin{aligned} p_1\{V_1/(\theta_0+100)+\Sigma v_1/\theta'\} &= mk. \\ p_0\{V_0/\theta_0+\Sigma v_0/\theta'\} &= mk. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

These may be used, as above explained, to calculate θ_0, if V_0 is known; or to calculate V_0, if θ_0 is known. They cannot be used to calculate both θ_0 and V_0, because the variations in *mk* may amount, under certain circumstances, to nearly one part in a thousand in the course of a few days.

The variation is generally most marked for a short period after the bulb and volume-gauge have been exhausted. If the value of *mk* is determined immediately, and again after an interval of two or three days, the value found on the second occasion is always slightly the lower, as if some of the air had been either absorbed by the sulphuric acid or by the surface of the glass, or included between the glass surface and the mercury in bulb A. It is therefore desirable to allow the whole apparatus to settle for some time, before observations are taken with it.

In the present case a whole week was allowed to elapse between the first filling and the use of the thermometer to determine the boiling-point of sulphur.

The value of *mk* observed on Thursday, September 11, the day before the first boiling in sulphur, was 17·0594. The value found on Friday, September 12, immediately after boiling in sulphur for two hours, was 17·0581. These differ by less than one part in ten thousand, and we may therefore assume that the apparatus had reached a fairly steady state.

In the series of observations between 0° and 100° given on p. 151, which were taken within a day of exhausting and refilling the air thermometer, a diminution in the value of *mk* from 17·8628 to 17·8565, amounting to one part in three thousand, was observed. In order to allow for this, it was necessary to assume that the diminution took place uniformly, and the value of *mk* at intermediate times was deduced by means of the time observations which were taken throughout the series.

Method of Calculation.

The whole set of formulæ are collected here for reference.

$$\theta = p\mathrm{V}/\{mk - \Sigma\, pv/\theta'\} \qquad (2),$$

where

$$p = \mathrm{H}_0 + \cdot 136\,(x - 2\cdot 50) \qquad (3).$$

$$\mathrm{V} = \mathrm{V}_0\,\{1 + \cdot 00002880\,t + \cdot 00000000171\,t^2\} \qquad (4).$$

$$v'' = \cdot 647 + \cdot 0232\,x, \text{ at } \theta'' = 272\cdot 10 + t'' \qquad (5).$$

$$v' = w/\rho - \cdot 0073\,(t' - t'_0) - \cdot 0127\,(19 - x'), \text{ at } \theta' = 272\cdot 10 + t' \qquad (6).$$

$$\left.\begin{aligned} mk &= p\,\{\mathrm{V}_0/\theta_0 + \Sigma\, v_0/\theta'\} \text{ in ice} \\ &= p\,\{\mathrm{V}_0/(\theta_0 + 100) + \Sigma\, v_1/\theta'\} \text{ in steam} \end{aligned}\right\} \qquad (7).$$

The values of the small correction terms were worked on a small slide-rule, with the exception of the barometer correction. The latter was taken from a large scale diagram giving the whole correction for temperature, scale errors, gravity, &c., for any height between 70 and 80 cm.

The multiplications and divisions involved in calculating $\Sigma\, pv/\theta'$ were generally performed on a FULLER's Spiral Slide-Rule, giving results correct to one part in twenty or thirty thousand.

Logarithms, as a rule, were used only in the final division.

The whole work of calculating a single observation is shown in the following table. The limit of accuracy in a single reading of the barometric pressure was about ·001 inch, corresponding to an error of 0°·01 at 50° C. The results cannot, therefore, be relied on much beyond this point, but the calculations were carried to the next figure to avoid inaccuracy in the hundredths.

TABLE I.—Showing Method of Calculation.

	Barometer.	Pressure-gauge.	Volume-gauge.	Expansion of bulb.
Quantities observed	30·271 inches at 69°·5 F.	$x = 2{\cdot}30$ cm. $t'' = 21°{\cdot}7$ C.	$x' = 17{\cdot}65$ cm., $t'_0 = 18°{\cdot}61$ C. $w = 183{\cdot}132$ gm., $t = 21°{\cdot}18$ C.	$t = 50{\cdot}3$ approximately
Corrections and reductions	= 20°·83 C.	$\theta_0 = 272°{\cdot}1$ C.	$\rho = 13{\cdot}5442$, $\theta' = 293{\cdot}28$	$t^2 = 2530$
	76·887 cm. − ·279	$\theta' = 293°{\cdot}8$ C.	$w/\rho = 13{\cdot}5203$ c.c.	$at = {\cdot}001448$
	$H_0 = 76{\cdot}608$ $q = -{\cdot}027$	$v_0 = {\cdot}647$ c.c. $v_x = {\cdot}053$ c.c.	${\cdot}0127\,(19 - x') = {\cdot}0171$ c.c. ${\cdot}0073\,(t' - t'_0) = {\cdot}0186$ c.c.	$\beta t^2 = {\cdot}000044$
	$p = 76{\cdot}581$ cm.	$v'' = {\cdot}700$ c.c.	$v' = 13{\cdot}4846$ c.c.	$gt = {\cdot}001492$
Calculation of θ	$mk = 17{\cdot}8592$ $pv''/\theta'' = {\cdot}1825$ $pv'/\theta' = 3{\cdot}5211$		$\log V_0 = 1{\cdot}7745535$ $\log(1 + gt) = {\cdot}0006475$ $\log p = 1{\cdot}8841210$	
	$mk - \Sigma = 14{\cdot}1556$		$\log(mk - \Sigma) = 1{\cdot}1509284$	
	$\log\theta = \log 322{\cdot}398 = 2{\cdot}5083936$			
Result	$t = \theta - \theta_0 = 50{\cdot}298$			

The Platinum Thermometers.

Four platinum thermometers of different patterns were used in this investigation. They are designated by the letters E, L, M_1, and M_2 respectively.

Thermometer E has been previously described.* The platinum coil was wound on calcined asbestos, and the resistance of the connections was kept constant by a flow of tap water.

Thermometer L was made on a somewhat similar pattern. The platinum wire (length 53 cm., diameter ·013 cm.) was a piece of the spiral used in the hard glass air thermometers, Nos. IV. and V., in the experiments of 1887. It was wound on calcined asbestos round a small tube of hard glass. Its ends were then soldered with silver to long electrodes of copper wire (B.W.G. 22), one of which was double. The electrodes were insulated with thin asbestos board bound round them with fine wire. The whole was calcined and slipped into a thin tube of hard glass about 30 cm. long and ·5 cm. in diameter. The tube was heated nearly red hot, and air drawn through it for a quarter of an hour to dry the asbestos thoroughly. The lower end was then

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* GRIFFITHS, *supra*, pp. 56–57.

drawn off in the blow-pipe, and the upper end was closed with sealing-wax to keep out the damp.

The ends of the three electrodes were amalgamated and dipped into ebonite mercury cups Nos. 1, 2, and 3, the single electrode being in No. 2. In taking observations the thick copper leads from the resistance box were first placed in cups 1 and 2, to measure the resistance of the platinum spiral *plus* that of the connecting wires; then in cups 1 and 3 to measure that of the connecting wires alone; and, lastly, in Nos. 2 and 3 to measure the spiral and connections again. Deducting the value found in the second observation from the mean of the first and third, we obtain the most probable value of the resistance of the spiral itself at the time corresponding to observation 2.

This form of thermometer is extremely easy to make, and gives very accurate results, provided that a good resistance-box is used.

Some preliminary experiments made with a double coil of this kind showed that, if it was kept dry, the insulation was amply sufficient up to a temperature of at least 500° C., but that it fell off beyond this point.

Thermometers M_1 and M_2 were also made from the same wire as that used for L. They were intended for use at higher temperatures with a special form of wire bridge, and were arranged and insulated in a rather different manner, as shown in Plate 7, fig. 3.

The two wires were interwound in a double screw thread, passing through holes in a thin mica plate AB, which sufficed to keep the wires from touching each other and to preserve the form of the spirals.

Each spiral was furnished with a double and single electrode symmetrically arranged. The six electrodes were insulated and kept in place by passing through holes in thin mica wads, one of which is shown at C, which were cut to fit the glass tube containing the thermometer.

In the earlier experiments in the iron tube apparatus electrodes of copper were used. These were subsequently replaced by electrodes of platinum to which the ends of the spirals were fused in the oxyhydrogen blow-pipe.

This form of thermometer is rather difficult to make, but it has the advantage of very perfect insulation even at high temperatures. Moreover, by using it with a suitable wire bridge, the resistance of the connecting wires can be automatically eliminated, and the platinum temperature can be read off on a scale of equal parts without the necessity of any calculation.

The wire bridge intended for this thermometer could not be made in time for this series of experiments. The resistances of the two spirals M_1 and M_2 were therefore observed separately with a resistance-box in the same way as that of thermometer L,

Measurement of the Resistance.

The resistance-box used in the present case was a very good Post Office box of the dial pattern made by Messrs. ELLIOTT BROS. The coils were of German silver, and had a mean temperature coefficient of ·00038 per 1° C. It was kept in a large copper water-bath to ensure steadiness and uniformity of temperature. The temperature of the coils was taken by a delicate mercury thermometer placed inside a dummy coil in the centre of the box. The resistances observed were corrected to 17° C. The temperature of the box never varied far from this point. Resistances of 10 and 1000 units were taken out in the arms of the bridge (except when determining small resistances, such as those of connections, &c., when 10 and 10,000 were used). The resistance to be measured was generally about 5–20 ohms, and it was found that this arrangement gave the best results.

A battery of two Leclanché cells* was generally used. The battery circuit connected the junction of the two lower to that of the two higher resistances. Thus the cells had to work through a resistance of about 500 ohms. The current through the thermometer was generally less than one three-hundredth of an ampère. The current-heating of the wire must therefore have been negligible.

A sensitive mirror galvanometer was used having a resistance of about 14 ohms. The sensitiveness was generally adjusted, so that one scale division corresponded to about one part in a hundred thousand of the resistance to be measured. The last two figures in each resistance measurement were determined by observing galvanometer throws and interpolating. To facilitate readings, the galvanometer was adjusted so as to be very nearly dead-beat.

A mercury commutator was used in the battery circuit, and the swings were observed by reversing the battery. This method has the advantage of doubling the sensitiveness, and of eliminating all possible errors arising from thermo-electric effects, and from the shifting of the zero of the spot of light on the scale.

The resistance of each thermometer was repeatedly observed in ice and steam. If R_0, R_1 be the corrected values of the resistances at 0° and 100° C, and R be the resistance at any other temperature, the corresponding value of the platinum temperature pt is deduced by the formula

$$pt = 100\,(R - R_0)/(R_1 - R_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

Sources of Error.

The sources of error to be avoided in using platinum resistance thermometers have been very fully discussed in a previous communication, but it will be convenient to recapitulate them briefly here.

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* In some cases (in the iron tube observations, and with thermometer H), six cells were used with 100 ohms in the battery circuit.

A good resistance-box is necessary for accurate work. The dial pattern is much to be preferred. Any change in the plug or screw contacts in the low resistance arms of the bridge must be carefully avoided. In the high resistance arms they are less material; but even here they are sometimes serious. For instance, in using a P.O. box of the ordinary pattern, it was found that the change from 499 to 500, involving a sudden change of ten in the number of plugs, produced an error of a tenth of a degree in the resulting platinum-temperature.

Thermo-electric effects are the most serious source of error. It is important to arrange the platinum-copper junctions close together. Any small residual thermo-effects in other parts of the circuit are not likely to give any trouble, and can be easily eliminated.

Variations in the resistance of the connecting wires may become a serious source of error, if not properly allowed for. In our experience, the safest method of avoiding such errors is to use double electrodes, and to measure their resistance at each observation, as above described (p. 133). The chief objection to this method is that (unless a wire bridge of special pattern is used) a complete observation of the resistance of the spiral and its connections takes two or three minutes; but this is immaterial, provided that the temperature is fairly steady.

If a resistance-box is used, and *rapidity* of observation is important, the best plan is to use connections of low resistance, as in thermometer F, the variations of which may be disregarded. The disadvantages of this method are, that a water cooler must be used to keep the upper part of the stem at constant temperature, and that the stem of the thermometer must always be immersed to nearly the same extent. Thick electrodes have also the drawback, that they increase the loss of heat by conduction along the stem, and that, unless they are similar and are symmetrically arranged, they are likely to give rise to large thermo-electric effects by unequal cooling of the junctions.

If double electrodes are used, the connections to the resistance-box must be made by mercury cups. The wires should be freshly amalgamated at frequent intervals to ensure good contacts.

Changes of Zero.

The changes of zero to which platinum thermometers are liable, when used at temperatures below 500° C., very rarely amount to so much as 1 in 10,000.

The following Table contains all the observations of the fixed points of M_1 and M_2 taken after they had been fitted with platinum electrodes. The observations were taken on different days, at different heights of the barometer, and at different temperatures of the resistance-box. We are here working up to the limit of accuracy of the resistance measurements, and it is certain that the small discrepancies shown in the Table are partly due to errors of observation.

Fortuitous errors of this kind produce the greatest effect on the platinum-temperatures deduced when they alter the value of the divisor $(R_1 - R_0)$. We have found it best, therefore, in calculating the platinum-temperatures, to take the mean value of this constant deduced from a large number of observations, and not to admit the small apparent variations from day to day.

The mean values of the constants assumed for thermometers M_1 and M_2 in reducing all the later observations were as follows :—

	R_0.	$R_1 - R_0$.	R_1 / R_0.
M_1	4·2267	1·4290	1·33805
M_2	4·1732	1·4120	1·33832

The mean deviations of the values of R_0 shown in the Table of fixed points are, for thermometer M_1, about 1 in 20,000 ; for thermometer M_2, about 1 in 30,000. The variations of the coefficient R_1 / R_0 are very much smaller.

TABLE II.—Observations on the Fixed Points of M_1 and M_2.

Date.		R_1.	R_0.	$R_1 - R_0$.	R_1 / R_0.
Saturday, Sept. 27.	M_1	5·6554	4·2268	1·4286	1·33796
	M_2	5·5848	4·1730	1·4118	1·33831
Heated red-hot for ten minutes to anneal electrodes.					
	M_1	5·6554	R_0 not observed.		
	M_2	5·5849			
Boiled in sulphur twice for an hour, and cooled rapidly.					
Tuesday, Sept. 30.	M_1	5·6556	4·2265	1·4291	1·33808
	M_2	5·5851	4·1731	1·4120	1·33834
Boiled in sulphur for an hour.					
Wednesday, Oct. 1.	M_1	5·6552	4·2262	1·4290	1·33810
	M_2	5·5849	4·1730	1·4119	1·33832
Thursday, Oct. 2	M_1	5·6554	In a hypsometer of different pattern.		
	M_2	5·5850			
Thermometers taken out of tube, and spirals re-arranged. Wire perhaps slightly strained. Boiled in mercury for one hour, and cooled very slowly.					
Saturday, Oct. 4.	M_1	5·6562	4·2270	1·4292	1·33810
	M_2	5·5853	4·1733	1·4120	1·33832
Boiled in sulphur for an hour and a half, and allowed to cool very slowly.					
Tuesday, Oct. 7.	M_1	5·6555	R_0 not observed.		
	M_2	5·5854			
Boiled in sulphur for an hour, and taken out as soon as possible.					
Wednesday, Oct. 8.	M_1	5·6555	4·2269	1·4286	1·33795
	M_2	5·5853	4·1733	1·4120	1·33832

[Note by H. L. CALLENDAR, added March, 1891.—Subsequent experiments with this thermometer make it almost certain that the small apparent changes of zero shown in the above table were due to changes in the mercury cup and screw connections or to errors of the resistance-box. I have since completed and compensated the resistance coils for the wire bridge mentioned on p. 133. With this apparatus I find it comparatively easy to read to a thousandth of a degree, and the thermometer no longer shows any changes of zero. I have made many other thermometers of this pattern with mica insulation, and I find them all remarkably constant even when used at temperatures as high as 1300° C.]

Description of the Iron Tube Apparatus.

In designing this piece of apparatus* we were chiefly guided by a study of the experiments of REGNAULT on the vapour pressures of sulphur. The difficulties which he encountered are very fully described by him in his paper in the 'Mémoires de l'Institut,' vol. 26, 1862, p. 526. A short description of the apparatus he finally adopted may not be out of place.

It consisted essentially of two coaxial cylinders of thick wrought iron, closed below, and bolted together at the top. The outer cylinder was heated in a furnace. The space between the cylinders was half filled with sulphur. The inner cylinder was open to the air. The air thermometer was made to fit the inner cylinder, and was not itself in actual contact with the sulphur vapour. A small iron tube connected the apparatus with a wider tube, in which the sulphur condensed.

REGNAULT states that he experienced great difficulties with this apparatus, owing to the super-heating of the vapour. This arose partly from the clogging of the small exit tube with viscous sulphur, but chiefly from the conduction of heat along the thick iron walls of the cylinder.

We have endeavoured to avoid these sources of error in our experiments by giving the apparatus a somewhat different form, shown in Plate 8, fig. 1.

Lengths A S, S L of two-inch gas-pipe were screwed together in the form of an inverted L by means of a four-way piece. The ends of the tubes at A and L were fitted with caps of the ordinary pattern.

The whole of the vertical limb S L was filled with sulphur up to the level S. This required about a kilogramme of sulphur, occupying, when melted, a volume of 500 c.c.

The lower cap F G was heated in a Fletcher's circular gas-furnace, shown at K, by means of a powerful blowpipe. The top of the furnace was covered with a piece of asbestos card, and the whole of the remainder of the apparatus was clothed with a double layer of asbestos board and yarn. The level of the sulphur stood at 15 cm. above the part of the tube exposed to the flame. The vapour had, therefore, to rise

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* We also received great assistance from Mr. THOMAS, of Jesus Lane, Cambridge, who personally superintended the construction of the apparatus.

through a long column of liquid before reaching the thermometers. It appeared probable that the chance of super-heating would thus be minimised.

The horizontal limb A B was about 30 cm. in length, and was provided with openings at both ends for the insertion of the platinum and air thermometers. The end B, through which the air thermometer was inserted, was closed by a split cork made by nailing together pieces of asbestos board. Some trouble and annoyance was caused at first by the escape of burning sulphur at the various joints and openings, till it was found that asbestos board, when soaked in water, formed an adhesive putty, which, if applied wet, at once stopped the escape.

With this apparatus a preliminary experiment was tried, in which the opening at H was closed with a screw-plug, and the sulphur was allowed to distil over through a tube near the end of the horizontal limb.

This arrangement, however, did not prove satisfactory. The whole of the sulphur distilled over in about a quarter of an hour, which did not suffice for the attainment of a steady and uniform temperature.

The apparatus was, therefore, reconstructed, with the addition of a condenser, as shown in Plate 8, fig. 1. The sulphur vapour was made to pass round by A and E to the condenser H G, which was fitted with a wide glass chimney a metre long, in which the condensation of the vapour could be easily observed. The condensed sulphur flowed back to the boiler by the small tube H L, which was bent in such a way as not to interfere with the insertion of the air thermometer. The tubes A E H, leading to the condenser, were of $1\frac{1}{4}$-inch bore, and so ran little risk of clogging. By way of precaution, however, a small blow-pipe flame was made to play on the joint E, until the circulation was fully established.

Observations and Results.

Observations were taken with this apparatus on two separate days with very concordant results.

Within half an hour or less of lighting the furnace on each occasion, the heavy brown sulphur vapour made its appearance in the glass tube condenser, and gradually rose with a well-defined surface until the condensation balanced the supply. The air-blast was regulated each day so as to maintain the vapour at a constant level of 40 cm. above B, thus ensuring a very uniform and steady circulation through the whole apparatus. The quantities observed, and the results of each observation, are given in Table III. The readings of the platinum and air thermometers were taken simultaneously by different observers. The fractions given in the columns headed "Resistances" represent the observed swings of the galvanometer, and show the sensitiveness of the apparatus.

TABLE III.—Comparison of Platinum and Air Thermometers in Iron tube Apparatus, at B.-P. of Sulphur.

Time.		Observed resistances.		Mercury thermometers corrected.			Barometer.		Pressure gauge.	R — connections corrected.	Results.	
		Thermometer.	Connections.	Box.	Air.	Water.	Reading.	Temp.			*pt.*	*t.*
Friday, September 12, 1890. Volume-gauge $x' = 19{\cdot}20$ cm., $t_0' = 20^\circ{\cdot}41$ C., $w = 539{\cdot}972$ grms.												
hr	min.						inches.	° F.				
4	52	M$_1$ $10{\cdot}43\frac{4}{18}$	$\cdot100\frac{20}{58}$	18·95	21·7	21·38	30·282	72·2	2·60	10·3395	420·70	444·52
5	2	M$_1$ $10{\cdot}43\frac{15}{58}$	$\cdot100\frac{3}{43}$	19·00	21·8	21·70	,,	,,	2·91	10·3403	420·75	444·90
5	6	M$_2$ $10{\cdot}35\frac{22}{23}$	$\cdot100\frac{8}{30}$	19·00	21·8	21·77	30·280	72·1	3·05	10·2642	420·63	444·68
5	18	M$_1$ $10{\cdot}43\frac{8}{32}$	..	19·00	21·8	21·93	,,	,,	3·23	10·3401	420·74	444·77
5	21	M$_2$ $10{\cdot}35\frac{25}{32}$	..	19·00	21·8	21·96	30·281	72·2	3·28	10·2653	420·71	444·79
5	26	M$_1$ $10{\cdot}43\frac{20}{123}$	$\cdot100\frac{10}{122}$	19·05	21·8	21·98	,,	,,	3·34	10·3392	420·68	444·94
5	30	M$_2$ $10{\cdot}35\frac{91}{123}$	$\cdot100\frac{24}{115}$	19·05	21·8	22·03	,,	,,	3·40	10·2652	420·70	444·98
Saturday, September 13, 1890. Volume-gauge $x' = 19{\cdot}0$ cm., $t_0' = 19{\cdot}07^\circ$ C., $w = 537{\cdot}739$.												
8	25	M$_1$ $10{\cdot}43\frac{9}{46}$	$\cdot100\frac{26}{44}$	18·95	21·8	19·67	30·298	67·8	1·75	10·3391	420·67	444·51
8	28	M$_2$ $10{\cdot}35\frac{40}{46}$	$\cdot100\frac{22}{43}$	18·97	21·9	19·71	30·298	67·8	1·79	10·2658	420·74	444·51
8	38	E 6·9180	..	18·98	22·0	19·94	30·300	67·7	2·00	6·9233	417·65	444·52
8	42	E 6·9180	..	19·00	22·1	20·04	30·300	67·7	2·11	6·9233	417·65	444·53
8	48	M$_1$ $10{\cdot}43\frac{81}{182}$	$\cdot101\frac{97}{292}$	19·00	22·2	20·21	30·301	67·5	2·28	10·3407	420·78	444·54
8	50	M$_2$ $10{\cdot}36\frac{16}{236}$	$\cdot101\frac{136}{287}$	19·00	22·2	20·26	30·302	67·5	2·31	10·2671	420·82	444·52
9	7	E $6{\cdot}918\frac{2}{5}$		19·00	22·3	20·57	30·304	67·5	2·62	6·9236	417·68	444·61
10	11	M$_2$ 10·3600	$\cdot101\frac{17}{40}$	19·05	..	..	30·312	68·4	..	10·2664	420·78	..

Air Thermometer Constants . . . . $V_0 = 59{\cdot}518$. $\theta_0 = 272{\cdot}10$. $mk = 17{\cdot}0581$.

Platinum Thermometer Constants . . . . . $\left\{\begin{array}{lll} M_1 & R_0 = 4{\cdot}2700. & R_1 - R_0 = 1{\cdot}4427. \\ M_2 & R_0 = 4{\cdot}2375. & R_1 - R_0 = 1{\cdot}4328. \\ E & R_0 = 3{\cdot}0618. & R_1 - R_0 = 0{\cdot}9246. \end{array}\right.$

The roll-sulphur used in these experiments was said to be prepared from H_2S. It smelt strongly of that gas when freshly crushed. It appears that sulphur prepared in this way is quite pure enough for the purpose, and that the presence of a small percentage of impurities does not materially affect the temperature of the vapour.

The sulphur used on the Friday was poured out of the apparatus before it solidified. It was found to be much discoloured, owing to the presence of various impurities due to residues of oil, red-lead, &c., used in fitting the iron tubes together. Fresh sulphur was used on the Saturday, and this, on examination, appeared to have suffered hardly any change.

The mean values of the platinum-temperatures, observed with thermometers M_1 and M_2, were :—

On Friday, $pt = 420 \cdot 70$,
On Saturday, $pt = 420 \cdot 75$.

The small difference is exactly accounted for by the difference of the barometric pressures on the two days. This would seem to show that the temperature of the vapour was practically unaffected by the impurities present in the sulphur used on the Friday.

The observations of the barometer taken during the course of the experiments on Friday, failed to show with certainty any variation amounting to more than ·001 inch. The mean value of all the readings was therefore taken and the same value was assumed in the reduction of all the observations.

It is probable that the slight apparent oscillations of the temperature, shown by the air thermometer, are partly due to real oscillations of the barometer, of which no account could be taken.

The observations of the barometer on Saturday showed a very steady and continuous rise. A time-chart was therefore constructed from which the most probable value of the barometric pressure, corresponding to the time of each observation, was deduced. The very close agreement in the values of t is certainly, in part, fortuitous; but the observations must, at least, be regarded as proving that the air thermometer had reached a very steady state, and that the volume of the bulb was not undergoing any further change. It is almost certain that the further diminution of volume from $V_0 = 59 \cdot 518$ c.c. to $V_0 = 59 \cdot 505$ c.c., took place when the bulb was subsequently exhausted while still exposed to the high temperature. The value $V_0 = 59 \cdot 518$ is therefore used in the reduction of the observations taken on Saturday, as well as of those taken on Friday.

The mean values of t deduced from the observations with the platinum thermometers M_1 and M_2, by assuming the value $\delta = 1 \cdot 570$ in formula (d), are :—

On Friday, $t = 444^\circ \cdot 78$ C.
On Saturday, $t = 444^\circ \cdot 84$ C.

The mean values of t deduced from the simultaneous observations with the air thermometer are :—

$$\text{On Friday,} \quad t = 444^\circ{\cdot}80\ \text{C.}$$
$$\text{On Saturday,} \quad t = 444^\circ{\cdot}52\ \text{C.}$$

The value found on Friday is seen to agree perfectly with that deduced from the observations with the platinum thermometers. The value of t deduced from Saturday's observations, is 0°·32 too low; but it is probable that the value of mk, used in reducing the observations taken on that day, is a little too great.

The *same values* of the air thermometer constants were used in the reduction of both sets of observations. They were determined by readings in ice and steam, taken on *Friday* evening shortly after the boiling in sulphur. It was, unfortunately, impossible to re-determine mk after the experiments on Saturday, because the thermometer had been filled with a fresh lot of air. A diminution of only 1 in 6000 in the value of mk would suffice to account for the small discrepancy observed, and it is certain, from the measurements taken on preceding days, that mk was diminishing at about this rate *per diem*. We may, therefore, conclude that these experiments, so far as they go, are a complete verification of the value of δ found in 1887, and show that the platinum wire has not altered appreciably in the interval.

Part II.

Experiments in the Meyer Tube.

The iron tube apparatus above described gave very good results as far as steadiness of temperature was concerned, but it was liable to several defects. It was cumbrous and difficult to set up, and, being very massive, it took some time to reach a steady state, and required a considerable blast to heat it.

The success of the glass-tube condenser suggested a much simpler form of apparatus. A wide glass tube, AB (Plate 7, fig. 4), was used, having a diameter of about 4 cm., and a spherical bulb at the lower end. Tubes of this kind are commonly employed to heat Victor Meyer's vapour-density apparatus. For the sake of brevity, therefore, we shall refer to this piece of apparatus as a "Meyer" tube. It was cut off to a suitable length (about 40 cm.) for the insertion of the thermometers. The lower half was padded externally with asbestos. The upper half was left bare to act as a condenser, and the top was covered with a piece of asbestos card, shown at A, to prevent the sulphur catching fire.

The bulb was filled with sulphur, and made to stand in a circular hole cut in a piece of asbestos board, CD. A preliminary experiment was tried, in which the tube was heated with a blow-pipe. No difficulty was found in driving the sulphur vapour up nearly to the top of the tube, and in keeping its level steady for any length of time.

Thermometer M was inserted, and some readings of its resistance were taken with the sulphur vapour at different levels in the condenser. They showed that any increase in the blast merely sent the sulphur vapour higher up the tube till its effect was compensated by the increased area of condensation, and did not appreciably alter the temperature observed in the lower portion of the tube protected by the asbestos.

The result of the observations reduced to a pressure 760, gave $pt = 418{\cdot}60$, $t = 442{\cdot}38$; which is almost identical with the value found in the preliminary experiment with thermometer L (p. 120).

To render the observations in this series comparable with each other, all the platinum-temperatures have been reduced to a standard pressure of 760 mm. of mercury at 0° C. in lat. 45°, and the corresponding air-temperature, t, by formula-(d) is also given in each case.

The correction for pressure to be applied to the air-temperature, t, of the boiling-point of sulphur to reduce to 760, is

$$\frac{dt}{dp} = 0^{\circ}{\cdot}082 \text{ per mm.}^{*}$$

The pressure correction to be applied to the *platinum*-temperature, pt, may be deduced from the formula

$$t - pt = \delta\,\{\overline{t/100}|^{2} - t/100\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d).$$

By differentiating we obtain

$$\frac{dpt}{dp} = \frac{dpt}{dt}\cdot\frac{dt}{dp} = {\cdot}082\left\{1 - \delta\,\frac{2t-100}{10000}\right\},$$

whence, if $\delta = 1{\cdot}57$, and $t = 444^{\circ}{\cdot}5$ C., we obtain $dpt/dp = 0^{\circ}{\cdot}072$ C. per mm.

The blowpipe was soon found to be unnecessary. By padding the tube with asbestos more carefully and to a greater height, the sulphur could be made to boil quite readily with a Bunsen burner (Fletcher, No. 48). By simply adjusting the gas, the vapour could be maintained at a fixed level near the top of the tube. The arrangement finally adopted for padding and supporting the tube is shown in Plate 7, fig. 4. The bulb projects through a circular hole in a piece of asbestos board CD which fits it tightly. The tube is filled with sulphur some 3 or 4 cm. above the level of the board. The padding of asbestos wool is kept in place by an outer tube of asbestos board bound with wire. A cone of asbestos board surrounds the whole. This gives the arrangement greater stability, and diminishes the rate of cooling. The method and precautions to be observed in working the apparatus are as follows.

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[*] Deduced from REGNAULT'S observations. See GRIFFITHS, *supra*.

If the sulphur is allowed to solidify in the bulb after each experiment, it must be carefully remelted *from the top*, otherwise it would burst the bulb. When the sulphur is all melted, the apparatus is placed on a tripod stand, the thermometers and leads are adjusted, and the gas is turned full on till the level of the vapour rises halfway up the condenser. This generally takes from two to three quarters of an hour. The time depends greatly on the thinness of the glass of the bulb—the thinner the better—and on the length of condenser-tube left bare above the asbestos packing. When the level of the vapour reaches the desired point, the gas is turned down till it just suffices to maintain the level steady.

Some observations taken with thermometer E in this apparatus gave the temperature

$$\text{E.}\quad pt = 416{\cdot}19\,; \quad t = 443{\cdot}31.$$

With this arrangement there are evidently two sources of error: (1) The thermometer is cooled by conduction along the stem, so that the sulphur condenses on the upper part of the stem and runs down it, cooling the bulb slightly below the temperature of the vapour surrounding it; (2) The sulphur condensed on the sides of the upper part of the tube exposed to the air acts in a similar way, and the thermometer loses heat by radiation to the walls of the tube.

To test this some readings were taken with the spiral of thermometer M inserted to various depths in the tube, with the following results :—

With the spiral just immersed below the level of the asbestos padding, and about 3 cm. below the top of the vapour, the temperature found was

$$pt = 418{\cdot}45\,; \quad t = 442{\cdot}22.$$

With the spiral about halfway down

$$pt = 418{\cdot}67\,; \quad t = 442{\cdot}47.$$

With the spiral partly immersed in the boiling sulphur

$$pt = 419{\cdot}06\,; \quad t = 442{\cdot}91.$$

These results plainly showed that the sources of error suggested above were of serious magnitude, and that, in order to find the temperature of the vapour, it was not sufficient merely to insert a thermometer in the vapour of the liquid boiling freely in a glass tube, even if the tube were very carefully protected by thick asbestos wrappings.

The difficulties above described were overcome in the following manner.

To protect the thermometer from the condensed sulphur which ran down the stem, and to shield it from radiation to the upper parts of the tube, an asbestos umbrella E, Plate 7, fig. 4, was made to fit the stem, and was bound on to it with wire a short distance above the spiral.

To protect it from cooling by radiation to the sides of the tube, a glass tube screen, FG, coaxial with the thermometer, was hung on this umbrella by three wires.

To protect it from radiation from the liquid sulphur and from the flame beneath, which might possibly tend to raise its temperature above that of the surrounding vapour, two circular screens of asbestos H were hung on to the lower end of the glass-tube screen. They fitted the outer tube very closely, and were each perforated with three holes, so arranged as to give free passage to the sulphur vapour, while not allowing any radiation to pass. The glass-tube screen was protected by the umbrella from drippings of condensed sulphur, and must have attained very nearly the temperature of the vapour. The thermometer and screens were kept in position in the centre of the tube by means of three-legged distance-pieces of wire twisted round them, some of which are indicated in the figure.

The observations indicated, as might have been expected, a slightly higher temperature than those in which the thermometer was exposed to radiation from the sides of the tube. The gas was adjusted to keep the level of the vapour near the top of the tube. The sulphur was boiling very steadily and quietly, and the thermometer did not show a variation of more than a hundredth of a degree for about half an hour.

The result found was

$$pt = 419{\cdot}81\,; \quad t = 443{\cdot}77\,;$$

showing a rise of 0°·86 C. in the value of t.

In order to test the amount of cooling produced by the condensed sulphur which ran down the stem of the thermometer, as compared with that due to radiation to the sides of the tube, a small cap of asbestos paper was fitted to the stem of thermometer E just above the spiral, to divert the drippings. The temperature observed was

$$pt_e = 416{\cdot}43\,; \quad t = 443{\cdot}59\,;$$

showing a rise of 0°·28 C.

E was then tried with the umbrella and glass-tube screen, arranged as above described. The observations gave

$$pt = 416{\cdot}86\,; \quad t = 444{\cdot}08.$$

The effect of the glass-tube screen in stopping radiation is therefore to raise the observed temperature by 0°·49 C., and the effect of diverting the dripping down the stem is to raise it by 0°·28 C. Both causes together produce a rise of 0°·77 C., which is nearly the same as the rise found in the case of thermometer M.

Seeing that the effect of radiation was so large, another experiment was tried with thermometer L, in which *two* coaxial glass-tube screens were used. It gave the result

$$pt = 420{\cdot}01\,; \quad t = 444{\cdot}00.$$

To test whether L agreed with thermometer M, an experiment was also tried with a single glass-tube screen, which gave

$$pt = 419{\cdot}83\,; \quad t = 443{\cdot}79.$$

a number practically identical with that found for M when singly screened.

The further rise caused by using the double screen seemed to indicate that *glass* tubing, though probably opaque to the radiation from the glass stem of the thermometer, might not be sufficiently opaque to the heat radiation from the platinum wire itself at this temperature. An experiment was therefore tried with thermometer M, in which the inner glass screen was replaced by a tube of brass. This was found to cause a still further rise, the result being

Thermometer M_1. $pt = 420{\cdot}36$; $t = 444{\cdot}39$.
,, M_2. $pt = 420{\cdot}34$; $t = 444{\cdot}37$.

After the experiment the brass tube was found to be rather thickly coated with sulphide. It was therefore replaced by a tube of platinum foil on glass. The naked portion of the Meyer tube at the top was cut off to a length of 3 cm., to minimise the condensation. It was felt that this arrangement would probably give the nearest approach to the actual temperature of the vapour, as a very small flame was sufficient to maintain the ebullition. All four thermometers were used, and their fixed points were re-determined after the experiment. The results found were

Thermometer E. $pt = 417{\cdot}24$. Thermometer M_1. $pt = 420{\cdot}48$.
,, L. $pt = 420{\cdot}46$. ,, M_2. $pt = 420{\cdot}48$.

Assuming $\delta = 1{\cdot}570$ for thermometers L, M_1, and M_2, we find for the corresponding air-temperature the value

$$t = \mathbf{444^{\circ}{\cdot}53}\ \text{C.}$$

We believe this to be within 0°·1 of the true temperature of the vapour of sulphur boiling freely under a pressure of 760 mm.

Results of Previous Observers.

We have not been able to find that any previous observers, with the exception of REGNAULT, have seriously attempted the accurate determination of the boiling-point of sulphur by reference to the air thermometer.

The numbers given in CARNELLEY'S tables are either deduced from REGNAULT'S observations,* or are rough experiments made to test the working of some vapour-density apparatus by comparison with his results.

Of REGNAULT'S eight observations on the pressures of sulphur vapour† at various temperatures, only two were taken in the neighbourhood of the atmospheric pressure. They are

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* *E.g.*, the number 444°·41 C. attributed to V. MEYER corresponds to a pressure of 725 mm. at Zurich, and is deduced by interpolation from two of REGNAULT'S observations. ('Berichte Deutsch. Chem. Ges.,' vol. 9, p. 1225.)

† 'Mémoires de l'Institut,' vol. 26, 1862, p. 527.

$t = 440°\cdot30$ C. $p = 679\cdot97$ mm.
$t = 447°\cdot71$ C. $p = 763\cdot04$ mm.

From the latter we obtain $t = 447°\cdot48$ C., corrected to 760 mm. at 0° in lat. 45°.

The table calculated from REGNAULT'S empirical formula by WEINHOLD[*] gives $t = 448°\cdot4$, at 760 mm. The table re-calculated and smoothed by RAMSAY[†] from REGNAULT'S observations gives $t = 448°\cdot34$. These values are nearly a degree higher than that found from the observation at 760. The reason of this discrepancy is, possibly, that the empirical formula was calculated to satisfy the observations at higher temperatures, which were more likely to be vitiated by superheating.

It was part of REGNAULT'S programme to determine the vapour-pressures of sulphur through a wide range of temperature. He was therefore compelled to work with a very strong and thick iron cylinder, heated in a charcoal furnace. The air thermometer itself was not in direct contact with the vapour, but was enclosed in a closely-fitting and massive iron tube, firmly bolted to the top of the cylinder, and coaxial with it.

REGNAULT describes, at some length, the difficulties which he experienced with this apparatus from the super-heating of the vapour, and it is plain from the language he uses that he had no great confidence in his results.[‡]

In the iron tube apparatus which we ourselves used, the possibility of super-heating was reduced to a minimum by making the vapour rise through a long column of liquid sulphur which was not directly heated. Want of space prevented the introduction of screens to guard against the cooling of the thermometers by radiation to the sides of the tube. Thus, although the temperature attained by the thermometers was steady to 0°·1 C. for more than an hour, and although it was the same (allowing for the difference of pressure) on both days, we cannot assume that it was the actual temperature of the sulphur vapour. All that we can safely assume is that since all the thermometers had glass envelopes, the loss by radiation was very nearly the same for each. The experiment may therefore be taken as affording an accurate *comparison* between the platinum and air thermometers, and a satisfactory verification of those performed in 1887.

The experiments in the Meyer-tube illustrate very forcibly the necessity of suitably screening the thermometers from loss of heat by radiation. They show that errors from this source may readily amount to 2° at 450°. In the last series of experiments, however, in which the thermometers were doubly screened and the condensation was reduced to a minimum, it is probable that the results obtained are within 0°·1 C. of the true temperature of the vapour.

We therefore propose to assume the value $t = 444\cdot53$ for standardising platinum

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[*] 'POGGENDORFF, Annalen,' vol. 149, 1873, p. 231.

[†] 'Phil. Mag.,' vol. 20, 1885, p. 524.

[‡] See also RAMSAY, 'Chem. Soc. Journ.,' vol. 49, p. 37 (1886).

thermometers. We may observe that, even if this is not the actual temperature of the vapour, it is probable that it will be the temperature *attained by the thermometer* in an apparatus similar to ours.

Any other known boiling-point, such as that of mercury, might very well be used for this purpose; but that of sulphur presents special advantages. The material is cheap, and readily procured in a state of sufficient purity. It boils at a convenient temperature, and can be kept boiling in glass vessels for any length of time without alteration. It is more suited for the purpose than mercury, because it boils more quietly and at a higher temperature. It is also less likely to crack the glass vessels, and its fumes are not poisonous.

Method of Standardising Platinum Thermometers.

The method which we recommend for standardising platinum thermometers is briefly as follows. Observe the platinum-temperature pt of sulphur vapour in an apparatus similar to that shown in Plate 7, fig. 4. Calculate the temperature t of the vapour at the observed barometric pressure, assuming t at 760 mm. to be 444°·53 C., and adding 0°·082 C. for each mm. of pressure above the standard. The value of the constant δ may then be found by substituting the observed value of the difference $(t - pt)$ in formula (d).

For instance, the observed difference in the case of thermometer E is $t - pt = 27°{\cdot}29$ C. at 444°·53 C. This gives $\delta = 1{\cdot}783$. The value of the ratio R_1/R_0 for this thermometer is 1·3024.

Another thermometer, which was made in a similar way to L, with double electrodes, but of different wire, having a coefficient $R_1/R_0 = 1{\cdot}3253$, gave the value $pt = 415{\cdot}73$ at t 442·38, whence $\delta = 1{\cdot}760$.

The value of R_1/R_0 for each of these thermometers is much lower than in the case of L, M_1, and M_2. It appears, generally, that the lower the value of R_1/R_0, the higher the value of δ.

Another wire (used in air thermometers 2 and 3, 'Phil. Trans.' A, 1887) gives the values $R_1/R_0 = 1{\cdot}3460$, $\delta = 1{\cdot}46$.

For many purposes an accuracy of the order of 1° C. at 450° is sufficient. In this case, the trouble of making a special experiment with sulphur to find δ, may be spared. It appears likely that for values of R_1/R_0 in the neighbourhood of 1·340 the value of δ may be assumed to be 1·60 without much risk of making an error of more than half a degree at 450° C., and that for thermometers of the L type the value of δ may be approximately found from the empirical formula

$$\delta = 1{\cdot}57 + 15\,(1{\cdot}3383 - R_1/R_0).$$

Boiling-Point of Mercury.

A determination of the boiling-point of mercury was also made in a similar apparatus with thermometers L, M_1, and M_2. The result found was $t = 356°·60$ C. The result deduced from previous experiments with thermometer E, in a different apparatus, is $t = 356°·76$ C. The closeness of the agreement is an indirect verification of the δ-formula. The agreement would probably have been closer, but the Meyer-tube cracked near the bottom in the course of the experiments, so that we have reason to believe that the result found with L and M is a small fraction of a degree too low.

Regnault gives seven observations on the boiling-point of mercury at atmospheric pressure. They range from 358°·8 to 354°·7. The mean is 356°·9, which agrees as closely as could be expected with the number found above.

Boiling- and Freezing-Points of some other Substances.

The results of an investigation into certain boiling- and freezing-points have been given in a previous paper,* which is referred to as "Paper (G)" throughout this Section. It was therein pointed out that the values obtained depended on the following "fixed points":—

B.-P. Naphthalene (760 mm.) = 218°·06 (Crafts)
B.-P. Benzophenone ,, = 306°·08 ,,
B.-P. Sulphur ,, = 448°·34 (Regnault)

and sufficient data for the correction of the deduced temperatures were given, in case these "fixed points" were found to be inaccurate.

The conditions under which the experiments described in Paper (G) were performed, closely resembled those prevailing in the Meyer-tube when the thermometer was unscreened. This conclusion is borne out by the numbers given on p. 120 of this Paper, where the platinum-temperature of sulphur vapour in the *same apparatus* as that used in the previous experiments was found to be 418·5, a number almost identical with that given by a specimen of the same wire when unscreened in the Meyer-tube (see p. 142).

Our experiments have shown that the temperature of the unscreened thermometer, when placed in sulphur vapour in the Meyer-tube, is too low; at the same time they enable us to apply the small correction thus rendered necessary.

The values of R_1 and R_0 in both thermometers E and G have shown signs of change in the interval which has elapsed since the spring of the year, but by assuming the old values of *pt* when in the vapour of sulphur under 760 mm. to be *equivalent* to $t = 444·53$, and calculating the values of δ for each thermometer, we shall avoid the

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* Griffiths, *supra*.

subsequent changes of zero, and it is probable that any small errors due to radiation, &c., will be eliminated, since all the determinations of boiling-points were made with similar apparatus and under similar circumstances. A small correction has first to be made in the numbers given in Paper (G), owing to a scale error in the Sidney College barometer, which had previously escaped detection. A careful comparison with the CAVENDISH Standard Barometer has shown a constant error of + 0·50 mm. The consequent correction is given in column C of Table IV. Column I. gives the corrected values of pt for each thermometer, deduced from the numbers given in Paper (G).

Applying a similar correction to the values of the platinum-temperatures of sulphur vapour in the old apparatus, we get

	pt.			δ.
E . . .	417·18	Hence the values of δ under the old conditions are	E . . .	1·786
F . . .	414·21		F . . .	1·980
G . . .	416·06		G . . .	1·859

The values of d, given in column II. of the Table of Boiling-Points, are deduced from the above values of δ.

The circumstances under which the freezing-points of the metals were determined, preclude the possibility of loss of heat by radiation, &c. In reducing these observations, therefore, the *corrected* value of the platinum-temperature of sulphur vapour under 760 mm. should be assumed, in order to obtain the value of δ.

Our experiments have shown that the difference in the platinum-temperatures given by thermometer E when unscreened and when fully protected is 1°·05 (see p. 144). We may assume, therefore, that, had all the precautions been observed which we have since found to be necessary, the values of pt would have been raised by a like amount.

The resulting values of δ are

E . . . 1·718 ; F . . . 1·912 ; G . . . 1·792 ;

and the numbers given in column II. of the Table of Freezing-Points are deduced from these values of δ.

Column III. gives the result for each thermometer, re-calculated and corrected, as above described. The close agreement of the resulting numbers is an indication of the validity of the method of reduction adopted. We believe that the results are within a tenth of a degree of the real values of t.

The vacant spaces under thermometers F and G indicate that no observations were taken with them at those points.

TABLE IV.—Boiling-Points.

Nature of experiment.	C.	Thermometer E.			Thermometer F.			Thermometer G.			Mean t by E, F, & G.	Other observers.
		I. *pt.*	II. *d.*	III. *t.*	I. *pt.*	II. *d.*	III. *t.*	I. *pt.*	II. *d.*	III. *t.*		
B.-P. Aniline (760 mm.)	—·032+·023	181·33	2·78	184·11	181·07	3·06	184·13	181·27	2·87	184·14	184·13	RAMSAY, 184·41 THORPE, 183·7
„ Naphthalene	—·038+·026	213·26	4·62	217·88	212·88	5·08	217·96	213·21	4·77	217·98	217·94	CRAFTS, 218·06
„ Methyl salicylate	—·039+·026	218·07	4·90	222·98	217·68	5·40	223·08	..	..	..	223·03	RAMSAY, 222·88 CAHOURS, 222
„ Benzophenone	—·054+·028	294·55	11·27	305·82	293·42	12·45	305·87	294·08	11·70	305·78	305·82	CRAFTS, 306·08
„ Triphenyl methane (770·3 mm.)	—·062	340·12	16·35	356·47	..	..	..	339·41	17·00	356·41	356·44	KEKULÉ, 355 (760) CRAFTS, 358 (754)
„ Mercury (760 mm.)	—·062+·033	340·37	16·37	356·74	338·70	18·12	356·82	339·69	17·02	356·71	356·76	REGNAULT, 357·25 RAMSAY, 358·2
Freezing-Points.												
Freezing-point of Sn	—·041	226·41	5·25	231·66	225·83	5·83	231·66	226·26	5·47	231·73	231·68	REIMSDYK, 228·5 KUPFFER, 230 PERSON, 232·7 CRICHTON, 238
„ „ Bi	—·048	261·34	7·84	269·18	..	..	..	261·10	8·15	269·25	269·22	PERSON, 270·5 REIMSDYK, 268·3
„ „ Cd	—·055	308·53	12·17	320·70	..	..	..	307·98	12·68	320·66	320·68	PERSON, 320·7 REIMSDYK, 320 VAN DER WYDE, 325
„ „ Pb	—·057	314·85	12·81	327·66	..	..	..	314·34	13·37	327·71	327·69	PERSON, 326·2 KUPFFER, 334 QUINCKE, 330
„ „ Zn	—·072	394·77	22·78	417·55	..	..	..	393·83	23·76	417·59	417·57	REIMSDYK, 420 WRIGHT and LUFF, 420 PERSON, 433·3 Other observers range from 342 (DANIELL) to 450 (BOUSSINGAULT)

NOTE.—The freezing-points of the metals were determined by the limit of the rise observed during surfusion.

The dotted curve (Plate 8) shows the path obtained by assuming CRAFT'S and REGNAULT'S numbers, and is a reduced copy of the one that was used in Paper (G) for reducing observations with thermometer E. The continuous line shows the path of the curve obtained from the parabola, the abscissa being $t - d = pt$, the ordinate d.

The scale on which these curves are plotted is about $\frac{1}{10}$th of the original.

It will be seen that the divergence up to a temperature of about 300° is very small, the rapid divergence above that temperature being due solely to the difference between REGNAULT'S and our determinations of the boiling-point of sulphur.

As pointed out in the previous paper, thermometers A to E* were to be regarded as trial instruments, and a summary only was given of the results obtained by means of them. Since they were of different patterns, and the spirals formed of different wires, it may be interesting to give the mean of the results obtained by applying a similar correction. Their values of (δ) range from 1·667 (Thermometer E*) to 2·158 (D). The experiments were not performed with the same care as those with thermometers E, F, and G, and their results are more irregular; in one or two cases they differ from the mean by as much as 0°·4.

The mean values of t deduced from the five thermometers are as follows :—

Aniline	184°·13	
Naphthalene	217°·82	
Methyl salicylate	222°·81	(A, B, C only)
Benzophenone	305°·85	
Mercury	356°·74	

These thermometers were not used for the determination of any freezing-points.

[Note by E. H. GRIFFITHS, March 21st, 1891.—Since the communication of the preceding paper, I have constructed and graduated another platinum thermometer.

The method of insulation and construction is similar to that described on p. 133, and shown on Plate 7, fig. 3.

The thermometer contains two coaxial spirals, the smaller one being inserted within the larger. The stem is 18 inches in length, and both ends of each spiral are fused to double platinum electrodes. The walls of the surrounding hard glass tube are of egg-shell thinness.

The resistance of the spirals can be taken separately, in series, or in parallel arc. Four resistances differing greatly in magnitude can thus be determined at any temperature. The accuracy of the resistance-box is thus exposed to a severe test. In order to reduce the stem resistance as much as possible, the stout wires forming the electrodes are, when taking observations, connected in pairs. The method adopted is as follows :—

Let R_a be the resistance of the longer spiral, and r_1, r_2 the resistances of the two arms of one of its electrodes, and r_3, r_4, the resistances of the arms of the other electrode.

A connector is first used which causes the current to pass through r_1, r_2 in parallel arc, then through R_a and leave by r_3, r_4 in parallel arc. The connector is then replaced by a second one which causes the current to pass through r_1, r_3 in parallel arc and leave in the same manner by r_2, r_4.

The resistances r_1, r_2, r_3, and r_4, being very nearly equal, both ends of the spiral will, in the second case, be at the same potential; hence the second connector gives the total external resistance.

The value of R_a can thus be determined by two observations.* Similar connectors are used to determine R_b, R_{a+b}, and R_{ab} (R_{a+b} and R_{ab} being the resistance of the two spirals when in series and parallel arc respectively).

The thermometer has been standardised in the manner described on p. 147, and all the precautions observed which our experience has shown to be necessary.

The umbrella, coaxial tubes, &c. (see Plate 7, fig. 4), were invariably attached to the thermometer when it was placed in a vapour.

I was anxious to test the accuracy of the method adopted for correcting the results of my former determinations (see Table IV., p. 150), and I have, therefore, by means of this thermometer, re-determined the boiling-points of mercury and naphthalene with great care. The results may be summarised as follows :—

Spirals.	Mercury (760 mm.).		Naphthalene† (760 mm.).	
	pt.	*t.*	*pt.*	*t.*
$a + b$	343·39	356·74	214·04	218·04
a	343·19	356·72	214·00	218·03
b	343·33	356·73	214·03	218·04]

PART III.

Comparison of Platinum and Air Thermometers between 0° and 100° C.

Thermometer H was constructed with the view of measuring temperatures between 0° and 100°. It has already been described in a paper read before the British Association.‡ A short description, however, appears to be necessary.

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* The validity of this method depends on the equality of r_1, r_2, &c. I, therefore, carefully determined their resistances separately at different temperatures. I found the limits of error to be within $\frac{3}{10000}$ths of the stem resistance, and since the stem resistance in no case exceeded $\frac{1}{25}$th of the total resistance, any inaccuracy thus introduced might be neglected.

† A fresh specimen of naphthalene gave $t = 218°{\cdot}16$ C.

‡ GRIFFITHS, "On the Comparison of Platinum and Mercury Thermometers at Low Temperatures." 'Brit. Assoc. Rep.,' 1890.

In thermometer H there is no glass contact, and the stem of the instrument, after repeated exhaustion and refilling with dry air at a temperature of three to four hundred degrees, was filled with melted anthracene. This substance (melting-point 213°) was found to be as good an insulator as paraffin at temperatures below 130°. The coil, consisting of about 56 inches of platinum wire, having a diameter of $0''\cdot005$, rests on calcined asbestos, but has no contact with the glass envelope. The spiral and asbestos are thus perfectly dry, and contained in an almost vacuous space. The leads down the stem are of silver, with a resistance of less than ·001 ohm, and approach to within one inch of the spiral, and are connected with it by moderately thick platinum wires, thus any flow of heat from the spiral to the silver is diminished. The instrument is connected with the resistance box by two leads about 6 feet long, each consisting of 50 copper wires (B. W. G. 24) enclosed in an india-rubber tube. Changes in the external resistance, caused by changes in temperature of the leads, could therefore be neglected.

The fixed points were determined at various times with the following results:—

	R_1.	R_0.
* July 26.	18·2038	13·5219
" 27.	18·2043	—
Aug. 12.	18·2038	13·5217
" 13.	18·2044	13·5219
Sept. 11.	18·2041	13·5213
" 12.	18·2042	13·5214

The first pair of observations were taken in the Sidney Laboratory, the second pair at the Cavendish, but on a different floor to the barometer, which had therefore to be corrected for difference in elevation. During the last pair of observations the barometer was placed by the hypsometer; these observations therefore are probably the most reliable. In any case the divergence of any one experiment from the mean would not affect $R_1 - R_0$ by more than 1 in 15,000.

Hence, mean $R_0 = 13\cdot5216$ and $R_1 - R_0 = 4\cdot6825$, and $R_1/R_0 = 1\cdot3463$.

The comparison of H and the air thermometer was conducted as follows. Both thermometers were placed in a nearly cubical iron tank, holding about 16 gallons of water. The air thermometer was inserted through a hole in the middle of one of the sides, the thermometer H through a hole in the centre of the lid. The two bulbs met in the centre of the tank, being in all but actual contact. The sides of the tank were covered with several wrappings of flannel, as we desired to keep the temperature nearly constant during each group of observations. The water was raised to the required temperature by a gas burner beneath the bath.

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* The first four numbers have been slightly altered since their communication to the British Association, owing to the subsequent discovery of the constant scale errors in the barometers.

A large paddle, pivoted in one corner of the lid, and driven by a water motor, proved to be the most efficient form of stirrer. It both drove the water before it, and lifted it upwards during each stroke.

The readings of the two thermometers were taken simultaneously by the two observers. Three observations were taken of the galvanometer swings for each reading of the platinum thermometer, the mean of the 1st and 3rd on the same side giving the true swing to the left at the time of taking the 2nd swing which was to the right, or *vice versâ*. The reading of the air thermometer was taken while the second swing of the galvanometer was being read.

Observations were taken about every 5° between 0° and 100°, and five observations were taken about each point. The following group of five (selected at random) will illustrate the methods of observation.

TABLE V.

Values of the constants. $V_0 = 59{\cdot}505$ c.c. ; $\theta_0 = 272^\circ{\cdot}10$; $mk = 17{\cdot}8592$.
Volume-gauge. $x' = 17{\cdot}65$ cm. ; $t'_0 = 18^\circ{\cdot}61$; $w = 183{\cdot}132$ grms.
Barometer corrected. $H_0 = 76{\cdot}608$ cm.
Pt. thermometer. $R_1 - R_0 = 4{\cdot}6825$; $R_0 = 13{\cdot}5216$.

Observed R.	Swings.	Mercury thermometers corrected.			*x*.	*pt*.	*t*.	Difference.
		Box.	Air.	Water.				
1587 1588 1587	L. 48 R. 14 L. 54	19·45	21·7	21·16	2·26	50·634	50·269	0·365
1587 1588 1587	L. 57 R. 6 L. 59	19·45	21·7	21·17	2·29	50·657	50·292	0·365
1587 1588 1587	L. 59 R. 5 L. 60	19·45	21·7	21·18	2·30	50·661	50·298	0·363
1587 1588 1587	L. 61 R. 2 L. 63	19·45	21·7	21·19	2·31	50·672	50·304	0·368
1587 1588 1587	L. 62 R. 2 L. 62	19·45	21·7	21·19	2·31	50·672	50·304	0·368
			Means			50·659	50·293	0·366

The whole work of calculating the middle observation of this group is shown in Table I., p. 132.

A single observation of the platinum-temperature with this apparatus would probably be correct to 0°·003, nearly. The indications of the air thermometer cannot be relied on much beyond 0°·01, which corresponds to the limit of accuracy attainable in a single reading of the barometer; but the last column shows that the small differences between consecutive observations, which are not affected by the uncertainty of the barometric reading, agree much more closely among themselves.

The following table gives the mean results of each group of five.

Table VI.—Comparison of Platinum Thermometer H with the Air Thermometer.

pt.	*t.*	Difference.	Calculated difference.
2·768	2·721	·047	·039
3·128	3·086	·042	·044
10·601 ?	10·499	·102	·138
16·366	16·159	·207	·200
20·599	20·370	·229	·239
25·447	25·169	·278	·278
30·209	29·910	·299	·309
35·808	35·464	·344	·337
40·573	40·215	·358	·354
45·732	45·379	·353	·365
50·659	50·293	·366	·368
56·043	55·682	·361	·364
61·169	60·815	·354	·351
65·941	65·603	·338	·333
70·632	70·323	·309	·308
75·299	75·013	·286	·276
81·092	80·856	·236	·228
85·923	85·731	·192	·189
90·200	90·090	·110	·132
95·461	95·417	·044	·064

The differences given in the last column are calculated from the formula

$$d = t - pt = 1{\cdot}474\,\{\overline{t/100}^2 - t/100\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (d).$$

Omitting the group of observations at 10°·5, where the discovery of a faulty connection led us to suspect the observations before their results were deduced, we see that the observed and calculated values in no case differ by more than 0°·012, except in the last two observations. These show an error of 0°·02, both in the same direction. In taking the two observations in question, it was unfortunately necessary to read the barometer by gaslight, when its temperature had just begun to fall. It is very likely that the temperature of the mercurial column itself would lag slightly behind that of the attached thermometer. This would account for the small discrepancy observed.

The results obtained by a comparison of H with Regnault's mercury thermometer No. 7, and with the Kew standard, are given in the communication previously referred to.* It was then pointed out that REGNAULT and Kew were in practical agreement. REGNAULT says that the differences between No. 7 and the air thermometer were so small that they could not be determined with precision.† His mercury thermometers generally showed a difference of 0°·2 to 0°·3 as compared with the air thermometer at 50°, but the observations are not consistent to 0°·1. The readings of thermometer No. 7 (which was made of ordinary glass) appear to approach the air readings more closely than is usually the case with mercury thermometers.

The comparison with the Kew standard was made by means of four thermometers, having a range of temperature from 0° to 34°, divided to 0·1 of a degree, and corrected at Kew.‡

A comparison of the (*pt* — *Kew*) difference-curve with that whose ordinates are given in the above Table, shows that the Kew standard reads 0°·10 C. lower than our air thermometer at 30° C.

CONCLUSIONS.

The experiments described in the preceding pages show conclusively that the platinum resistance thermometer is an extremely self-consistent and trustworthy instrument, and that it is remarkably free from change of zero and from secular alteration of its coefficients.

It appears certain that, by choosing some particular thermometer as the standard with which other thermometers could be directly compared, it would be possible to attain a very high degree of accuracy in the relative measurements of temperature on the arbitrary scale of the standard chosen.

We have found that, by using a good resistance-box (correct to 1 in 100,000 in the relative values of the coils), it is possible to read to 0°·003 between 0° and 100° C. By using a suitably-constructed and compensated wire bridge, a still higher degree of accuracy may be attained, and the sensitiveness of the thermometer may readily be increased so as to indicate a difference of one ten-thousandth of a degree at ordinary temperatures.

The reduction of the platinum-temperatures to the absolute scale is less certain, since it depends on the accuracy of the air thermometer experiments. But it appears probable that, by assuming the parabolic formula (*d*), and calculating the appropriate value of the constant δ for each thermometer by means of an observation at the boiling-point of sulphur, as above described (p. 147), we may attain a degree of accu-

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* GRIFFITHS, "On Comparison of Platinum and Mercury Thermometers." 'Brit. Assoc. Rep.,' 1890. Also, see the 'Electrical Review' for Sept. 26, 1890.

† 'Mém. de l'Institut,' vol. 21, 1847, p. 220.

‡ Three of these thermometers belong to the B.A. Committee on Electrical Standards; see Appendix to their Report, Brit. Assoc., 1890.

racy of the order of 0°·01 between 0° and 100° C., or of 0°·1 at 450° C., on the scale f the standard air thermometer.

We believe that thermometers standardised in this way will be found to afford the most convenient and practical method of measuring temperature in all cases where accuracy is desired.

Explanation of Plates 7 and 8.

PLATE 7.

Fig. 1. General view of the arrangement adopted for supporting the bulb of the air thermometer, and connecting it to the gauge used for determining the variations in the pressure and volume of the enclosed air.

Fig. 2. Represents the gauge on a larger scale.—A detailed explanation of the various parts will be found on p. 126.

Fig. 3. A slightly enlarged view of the spiral of the platinum thermometers M_1 and M_2, showing the method of supporting and insulating the spiral and its electrodes by means of the mica plate AB, and the mica wads shown at A and C.

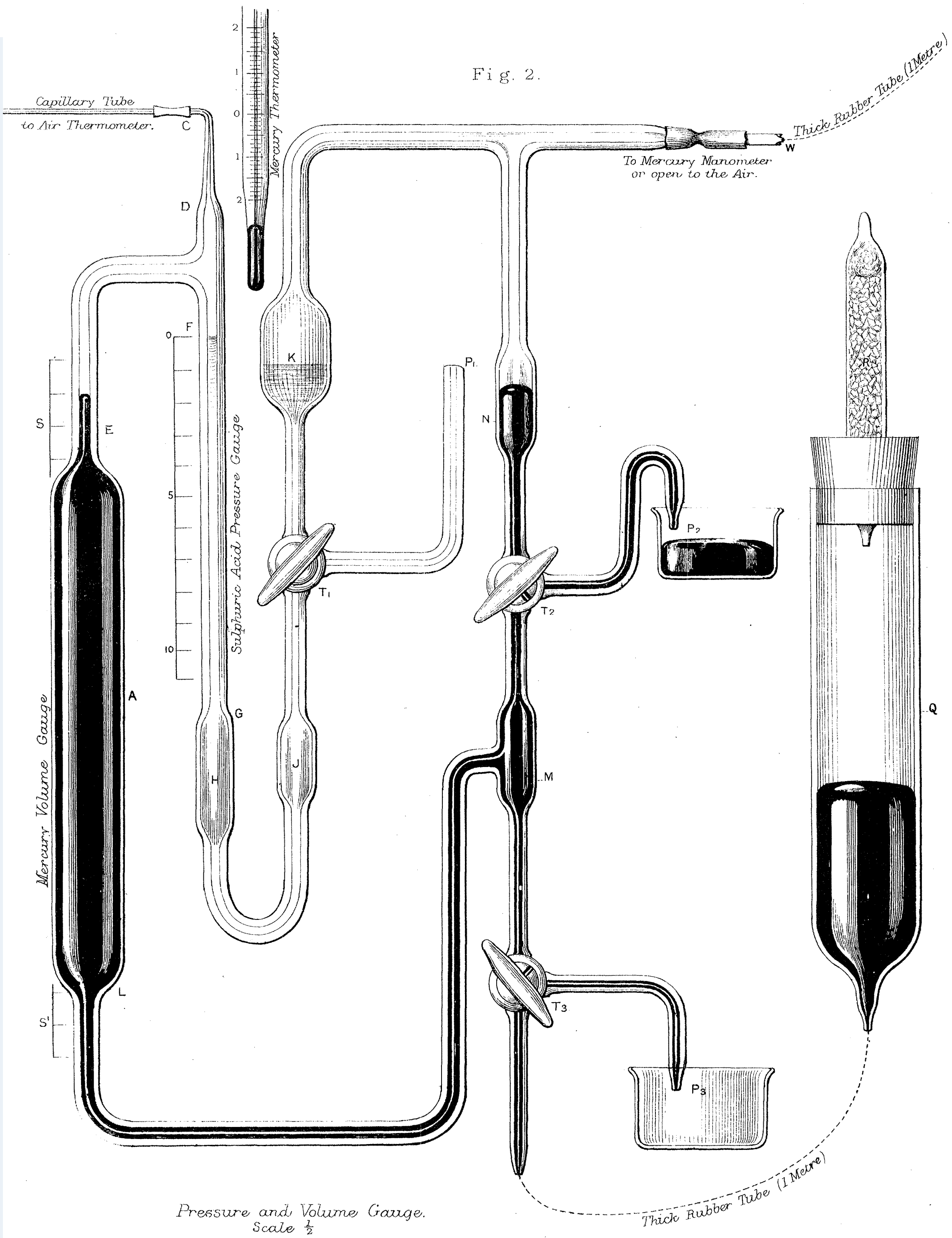
Fig. 4. Shows the method of screening the thermometer when placed in the Meyer-Tube Apparatus for determining the boiling-point of sulphur, as described in detail on pp. 142 and 143.

PLATE 8.

Fig. 1. Iron tube apparatus used in the comparison of the platinum and air thermometers at the boiling-point of sulphur. It could be maintained at a steady temperature by means of a continuous flow of sulphur vapour for any length of time. A full description of it is given on pp. 137 and 138.

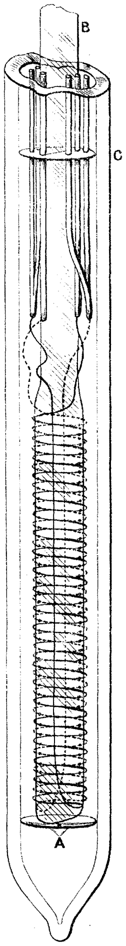
The Curves in this plate illustrate graphically the effect of using the lower value, above found, of the boiling-point of sulphur, instead of that given by Regnault. See p. 151.

Fig. 2.



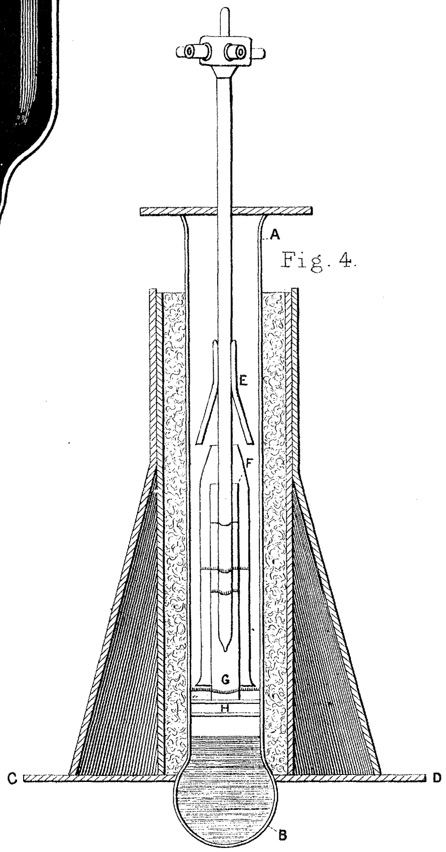
Pressure and Volume Gauge.
Scale $\frac{1}{2}$

Fig. 3.



Spiral of Thermometer M.
Enlarged by $\frac{1}{3}$.

Fig. 4.



Meyer Tube Apparatus.
Scale $\frac{1}{4}$

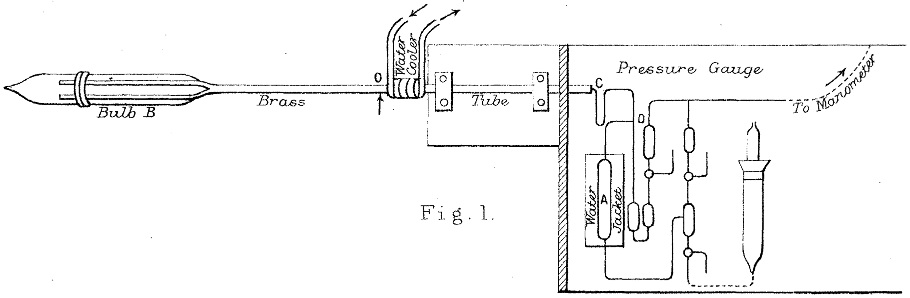


Fig. 1.

Diagram of Air Thermometer
Scale $\frac{1}{10}$th

West, Newman, lith.

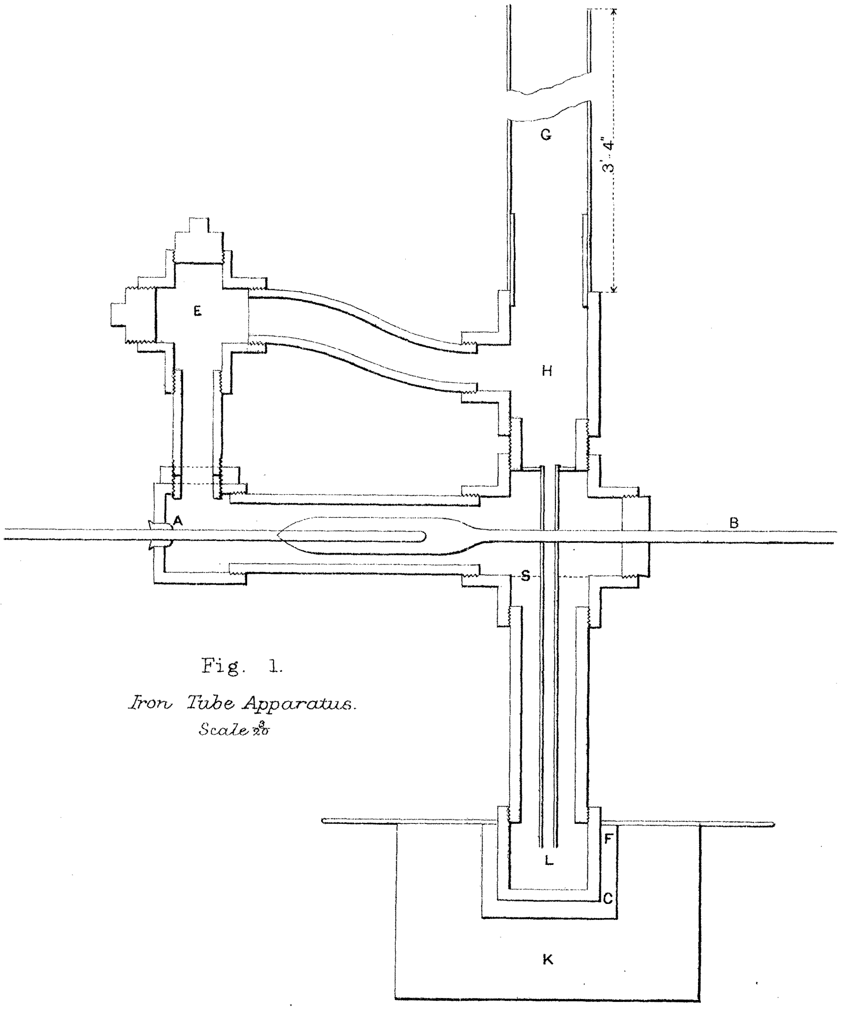
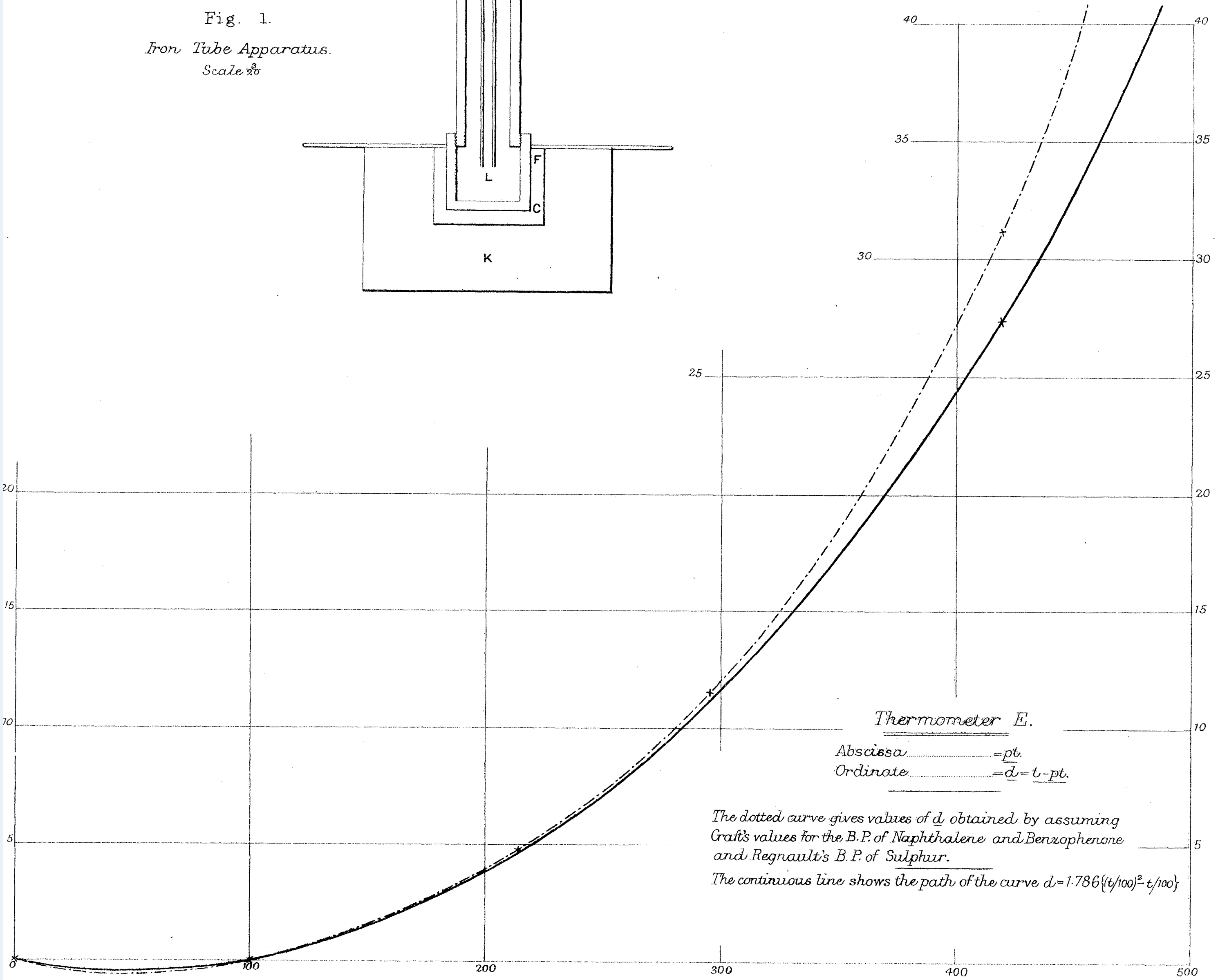


Fig. 1.

Iron Tube Apparatus.

Scale $\frac{3}{20}$



Thermometer E.

Abscissa = *pt.*

Ordinate = $d = t - pt$.

The dotted curve gives values of d obtained by assuming Crafts's values for the B.P. of Naphthalene and Benzophenone and Regnault's B.P. of Sulphur.

The continuous line shows the path of the curve $d = 1{\cdot}786\{(t/100)^2 - t/100\}$

West, Newman, lith.