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[PLATES 11-13.]

ON THE

PRACTICAL MEASUREMENT OF TEMPERATUR

EXPERIMENTS MADE AT THE CAVENDISH LABORATORY, CAMBRIDGE.

BY

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VI. *On the Practical Measurement of Temperature : Experiments made at the Cavendish Laboratory, Cambridge.*

By H. L. CALLENDAR, *B.A., Scholar of Trinity College, Cambridge.*

Communicated by J. J. THOMSON, F.R.S., Cavendish Professor of Experimental *Physics in the University of Cambridge,*

Keceived June 9,—Read June 10, 1886.*

[PLATES 11-13.]

General Account of the Experiments, and Discussion of the Results.

IN view of the enormous discrepancies at present existing in estimates of high temperatures, it is exceedingly desirable that strictly comparable thermometric standards should be issued by some recognised authority.

Professor J. J. THOMSON, in the course of a conversation which I had with him towards the close of 1885, suggested that such standards could be issued in the form of platinum wire, the change of electrical resistance with temperature being determined by comparison for each specimen before issuing. The object of the present investigation was to test whether, in spite of the B. A . report on the SIEMENS pyrometer (1874), pure platinum wire might not be possessed of the necessary qualifications for such a standard.

Let us first consider what qualifications are necessary.

(I.) Such a standard should always give the same indication at the same temperature, should be free from secular change of zero, and should possess the widest possible range.

(II.) It should be portable and readily copied, so that standards might be multiplied, and, if the original were lost, it might be replaced by means of its copies. The copies should be capable of accurate comparison and verification.

(III.) It would be convenient if it agreed very approximately with any standards already in use, and if, failing this, the relation between the new and pre-existing standards could be accurately ascertained.

(IY.) It would be a great additional advantage if, besides being useful as a standard, it could also be applied directly to all kinds of practical investigations.

With regard to the first point (I.); the self-consistency of the platinum thermometer

* The portions enclosed in square brackets have been added or altered subsequently, June, 1887.

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has been abundantly verified in all the experiments undertaken with it. If the wire is *pure* to start with, and care is taken not to alloy it with silicon, carbon, tin, or other impurities, and not to subject it to strain (such as increase of length), its resistance is always the same at the same temperature; at least, this was the case with the specimens of platinum wire used in these experiments. For the proof of these assertions the reader is referred to the experimental details (especially pp. 192, 205 *et passim).*

The wire used here is obtained from the well-known firm, Messrs. JOHNSON, MATTHEY, and Co., and is probably very pure and well adapted for the purpose (see p. 182).

Platinum wire evidently fulfils the conditions laid down in II., since it is essentially a standard of electrical resistance.

The method of comparing and verifying copies of the standard is of fundamental importance and requires a more detailed explanation. The great advantage of the proposed platinum standard over all others is the ease and accuracy with which this may be effected, a degree of accuracy greatly exceeding that of all other thermometric comparisons, and almost independent of the distribution of temperature. The wires are wound side by side on non-conducting material and symmetrically disposed, so that their mean temperatures are always the same and simultaneous values of their resistances are observed. Observations are also taken in melting ice and in steam at atmospheric pressure for the purpose of verification and to test for changes of zero. Details of the method and of the experimental comparison of wires of different metals are given in a subsequent section. An accuracy of 1 in 10,000 is attainable. The general conclusions from these experiments are as follows :-

[If R be the resistance of a given wire at the temperature t Cent., and R_1 , R_0 , the values of its resistance at 100° and 0° C. respectively, $(R_1/R_0 - 1)$ is the increase of resistance between 0° and 100° C., and is found to vary considerably for different specimens of commercial wire of the same metal. $(E.g.,$ for platinum, it varies from 0"25 to 0'35.) But the-curves of resistance variation are similar, so that the values of the function $(R/R_0 - 1)/(R_1/R_0 - 1)$ are nearly identical for different wires of the same metal through a range of 600° C., though they differ very widely for different metals. The variations are mainly due to slight chemical impurities, which suffice materially to reduce the temperature-coefficient and make the wire much less suited for thermometry.]

Pure platinum wire, 'when once annealed, is little liable to alteration. If it is pure, different lengths from the same bobbin do not behave differently, as some observers, perhaps using less pure wire, have stated. Its resistance is not liable to permanent change by mere heating and cooling, provided the wire is not strained or chemically altered. Different specimens of *pure* platinum wire agree very approximately throughout the scale. This is very convenient, but not essential ; for, if they did not, they could be accurately compared and the differences tabulated. It

therefore possesses in an eminent degree the qualifications necessary for a scientific standard. There seems no reason to expect that the temperature coefficient should be liable to secular change, seeing that violent treatment of these specimens for some months has not produced any measurable alteration.

III. As it is a very important question to determine the relation between temperature by platinum wire and temperature by air thermometer, considerable space is devoted to the discussion of experiments bearing on the question. The present standard of thermometry is REGNAULT's normal air thermometer; this, while possessing several advantages as an ultimate standard, is, nevertheless, so difficult to use that the discrepancies at present, existing are bewildering, and it cannot be used at all in ordinary work for most purposes ; all measurements have, therefore, to be referred to it indirectly, which is a great disadvantage. But until the thermodynamic thermometer shall have assumed a more practical form, the air thermometer gives the best approximation to absolute temperature. It happens that the platinum thermometer may be more accurately compared with this standard than any other.

The practical difficulty of all thermometric comparisons is that of maintaining an enclosure at a constant and uniform temperature. This was to a great extent avoided in the present case by enclosing the spiral of fine platinum wire inside the bulb of the air thermometer itself. There are, of course, some mechanical difficulties in the way, and it was found necessary to devise a modified form of air thermometer for the purpose. Full details of the experiments and methods are given in subsequent sections. The modified form of air thermometer is also minutely described, as it may be found useful in other and similar investigations. Various sources of error are also discussed, which may have considerable effect in experiments at high temperatures. The investigation of these is still incomplete, but does not present any difficulties which may not be overcome with the aid of the platinum thermometer. Among these we may mention surface actions between the gas and its enclosure ; the question of the possibility of eliminating the capricious changes of volume of the envelope ; and of determining the amount of dissociation to which gases are subject at high temperatures. The experiments are, therefore, necessarily incomplete ; they are published chiefly on account of the great practical importance of settling on a universal standard for the more accurate comparison of different measurements of temperature.

[The results of the comparison between the platinum and air thermometers are best represented graphically by drawing the curve of difference of temperature. If *t* stand for the temperature Centigrade by air thermometer, and *pt* for the temperature Centigrade by platinum wire, that is to say, for the function $100(R/R_0-1)/(R_1/R_0-1)$; the observations (Plate 13) are seen to agree fairly well with the parabola

$$
d = t - pt = 1.57\{(t/100)^2 - (t/100)\}.\t\t(1.100)\t\t(1.100)
$$

But the comparisons of different platinum wires show that this formula cannot be absolutely accurate.]

It is very convenient for practical purposes that the platinum thermometer agrees so closely with the absolute thermo-dynamic scale ; but, of course, such agreement does not much affect its value as a standard. We at present require a practical standard to which all measurements may be *directly* referred ; the question of its exact relation to the absolute thermo-dynamic scale may be matter for subsequent investigation, and can be best solved when we have arrived at a more accurate and extended knowledge of the phenomena of heat, of the dependence of radiation, conduction, &c., on temperature measured by a scale, which may be to some extent arbitrary, but which will have the incalculable advantage of uniformity, so that the results of different experimentalists will be accurately comparable. To show how imperfectly the air thermo meter fulfils this condition, we may refer to the article " Pyrometer" in the ' Encyclopaedia Britannica,' 9th edition, 1885.

IY. In comparing the platinum resistance thermometer with other instruments, it will be seen that it is essentially *practical.* The steam pressure thermometers advocated by Sir WILLIAM THOMSON in his article on Heat, in the 'Encyclopaedia Britannica,' are doubtless theoretically more interesting, and could be made of great utility in attaining known constant temperatures when the relation between steam pressure and temperature had once been determined for each case. But the most accurate way of comparing them with each other, and with the standard air thermometer, is by the intermediation of the platinum wire. Other instruments for measuring temperature have either a very small range or lay no claim to accuracy ; for this reason it is obviously unnecessary to discuss the mercury thermometer or the thermopile, especially as their defects are so well known, and their applicability so limited, although each possesses distinct advantages for certain purposes.

Platinum wire is well fitted for use as a temperature standard, it is still more admirably fitted for practical use in any experiments where accuracy is required. This arises chiefly from its adaptability. A length of wire is cut off and disposed in any way which may happen to be most convenient for the desired purpose. The observations are simple and rapid, the corrections small and easily applied, the sources of error less than with any other kind of thermometer and more easily avoided. For radiation experiments it may be made more sensitive than the thermopile (cf. LANGLEY'S Bolometer) ; owing to its great sensitiveness, it may be used to measure rapidly varying temperature without inaccuracy ; this is often desirable, as in calorimetry by method of cooling. There is, in fact, hardly any experimental investigation in which the measurement of temperature is necessary, which may not be more accurately and simply effected by means of a suitable platinum wire thermometer.

[The results of the investigation considered as a research on the resistancevariation of metals tend to prove the existence of minute irregularities which

cannot be well represented in an empirical formula. The simple parabolic formula (p) , $R/R_0 = 1 + at + \beta t^2$, corresponds exactly with (d) (p. 163), namely

$t - pt = \delta \{(t/100)^2 - (t/100)\},\,$

where $\delta = 10,000\beta/(a + 100\beta)$, and gives an accuracy of the $1\degree$, order through a range of 600° C. Other formulas may readily be found which give nearer approximations in special cases, and through small ranges. For instance, the exponential formula $\log R = \frac{at}{1 + \beta t}$ corresponds to the dotted line, Plate 13, fig. 11, and exactly smooths out the characteristic inequalities in the platinum-iron comparison-curve, agreeing with it far more closely than the parabola ; but in most other cases the exponential formula has the disadvantage. BENOIT and MATTHIESSEN use the parabolic formula, but MATTHIESSEN expressed his results as variations of conductivity (R_0/R) , so that his formulæ are quite inapplicable except between 0° and 100° C.]

I have endeavoured to give the fullest data in each case for the verification of my results, and to make the calculations in each case accurate within the limits of probable error, but among so large a mass of figures I can hardly hope to have escaped an occasional slip.

My most sincere thanks are due to the authorities at the Cavendish Laboratory for the facilities which they gave me for the prosecution of these experiments, and especially to Professor THOMSON for the kind interest he has taken in the subject, and for valuable suggestions and assistance.

In overcoming the mechanical difficulties which are always the most important part of an investigation like the present, I received great help from Professor THOMSON's assistant, Mr. D. S. SINCLAIR, though, owing to the many calls upon his time, he was unable actually to make much of the apparatus. I had intended to make many other experiments, but my progress has been much retarded by my own want of mechanical skill, and the necessity of making all my own apparatus.

I am at present intending to pursue these experiments to higher temperatures ; and have already worked out the experimental details of the application of the platinum thermometer to questions in the theory of heat where I consider greater accuracy may be obtained by its use.

Authorities consulted.

On the variation of the electrical resistance of metals with temperature. All experiments almost up to date are collected in the first volume of the last edition of ' Die Lehre von der Elektricität,' by G. WIEDEMANN. Original papers by BENOIT in the 'Comptes Rendus,' and MATTHIESSEN in the ' Phil. Trans.,' 1862 , are of the chief importance, but nearly everything has been collated.

In Thermometry the best general information up to date is to be found in the ' Enc. Brit.,' 9th edit., Articles "Heat" and "Pyrometers," already referred to. I have also studied with great care the whole of the classical researches of REGNAULT in the ' Mémoires de l'Institut,' vols. 21, 26, &c.

On Pyrometry there is a valuable paper by WEINHOLD in 'Poggendorff, Annalen,' 1873, who gives a fairly complete list of original memoirs, nearly all of which have been referred to.

On the air thermometer there is a most valuable paper by BALEOUR STEWART in the 'Phil. Trans.,' containing perhaps the most accurate experiments yet made on the dilatation between 0° and 100°. For high temperature experiments, papers by DEVILLE and TROOST, and E. BECQUEREL, are most important.

SIEMENS suggested the platinum pyrometer, but I cannot find any account, worth mentioning, of his experiments.

Determination of the Increase of Resistance with Temperature of the Standard Platinum Wire by comparison with the Air Thermometer.

As stated above, the direct comparison is preferable to the method adopted by BENOIT and others of heating the wire in vapour baths of substances whose boiling points have to be assumed from other experiments ; a spiral of fine bright platinum wire is a bad radiator, and is exceedingly sensitive to slight changes in the temperature of the air with which it is in contact; if, therefore, it be fixed inside the bulb of an air thermometer, the mean temperature of the spiral will be always very nearly the same as that of the air, and this is measured directly on the absolute scale.

The Air Thermometer.

Since the ordinary form of the instrument is in several ways inconvenient, it was found necessary to devise a modified form for the purposes of this investigation, a detailed description of which will be given. The sources of error, and the corrections to which it is liable, will also be incidentally considered.

The general plan of the instrument will be easily understood on reference to the accompanying diagram (Plate 11, fig. 1). [An improved form is described in the Appendix.]

A bulb A is connected by means of a capillary tube to a U-gauge of small bore (about 2 millims. diameter) containing pure sulphuric acid, which serves to confine a constant mass of air at nearly constant volume ; the gauge carries a bulb B on its other limb, which is connected by an indiarubber tube to an adjustable mercury manometer M with wide tubes. Attached to the limb of the U-gauge is a millimetre scale by which its reading can be recorded.

The volume of the bulb A is determined by calibration with water or mercury in the usual way, or with air by the method of the volumenometer.'"

The coefficient of cubical expansion of the bulb enters as a small correction, amounting to about 1 per cent. ; it is best determined at low temperatures by using the bulb as a mercury thermometer, and assuming the absolute expansion of mercury.

* ' Practical Physics,' GLAZEBROOK and SHAW, p. 160.

If the bulb itself cannot be used, a mercury thermometer is made from the same tube as the bulb.

Since, however, this method ceases to be applicable above the boiling point of mercury, and is moreover exceedingly liable to inaccuracy, except between 0° and 100° C., it was decided to measure the variations of the linear coefficient and assume that the cubical coefficient varied in the same way.

The method adopted was exceedingly simple, and is, shortly, as follows :—

Linear Expansion of Hard Glass.

A glass tube is heated in a thick iron tube in a long gas furnace, the variations of its length are observed by means of reading microscopes, and the mean temperature of the portion heated is given by observing the resistance of a standard platinum wire extending down the axis of the tube, assuming that when the temperature is steady the mean temperature of the wire is the same as that of the portion of the tube it occupies.

Experiments by this method were made on a piece of hard glass tube, the same as that used in making the air thermometers No. 3 and No. 5.

The ends of the tube were drawn down to 5 millims. diameter, to diminish the conduction of heat, and to ensure that the parts exposed should be nearly at the temperature of the atmosphere ; copper leads were fused on to the ends of a piece of the standard platinum wire, 69'6 centims. long, which was then inserted down the axis of the glass tube.

The glass tube was heated by being placed in an iron gas-pipe, 67 centims. long, in a gas furnace of the same length, supported on a board with levelling screws for focussing. The copper platinum junctions were exposed to the air temperature at equal distances, about 1 cm. beyond the ends of the iron tube, and, being screened from the heat by bright tinned plate, no appreciable thermo-electric effect was produced, as the junctions were very slightly, and nearly equally, warmed.

A length of about 63 cm. of the glass tube was left in its original state ; the drawndown ends projected about 16 cm. beyond the iron tube, and were practically at the air temperature for their whole length beyond the copper platinum junctions ; the variations in length of these portions of the tube may be neglected in comparison with other possible errors ; it is, therefore, assumed that the mean temperature of the platinum wire is the mean temperature of the part of the tube it occupies, whose length is variable. If the coefficient of expansion of glass were accurately constant, or if the temperature of the whole portion heated were uniform, this assumption would give mathematically correct results. Since both these conditions are nearly satisfied, the corrections to be applied for the variations at either end are negligible. We take, therefore, the length of the part of the glass tube, whose variations we are measuring, to be the distance between the ends of the platinum wire, and its mean temperature to be that of the platinum wire.

Crosses were made, with a writing diamond, on the extremities of the tube, at a distance of about 15 cm. from the gas furnace, and were observed with reading microscopes.

The reading microscopes were made by the Cambridge Scientific Instrument Society, and are all but perfect. The microscope is fixed in a carriage, which is moveable horizontally by means of a micrometer screw reading to '00002 of an inch.

They were mounted on solid stone blocks, resting on a thick stone slab which supported the gas furnace, so screened with bright tinned plate that the microscopes and their supports, and the stone slab, were not appreciably heated.

After the apparatus has been adjusted the microscopes are placed in position and focussed on the crosses, and are not subsequently touched, except with the micrometer screws, in taking readings.

Since the success of the method depends on the distance between the stands of the reading microscopes remaining invariable, this was verified, from time to time, by means of an auxiliary glass tube, 1 metre long, with diamond crosses, which could be adjusted in position beneath the microscopes without disturbing them. No variations of the distance could be detected, and they were probably less than "0001 of an inch. Several independent readings seem to show that the probable error of a single reading due to *all* causes is about of the magnitude of '0002 inch.

Readings were also taken of the temperature of the air, and of the air between the gas furnace and the stone slab ; the variations were usually small enough to be neglected. The crosses on the glass tube could be very accurately brought into focus beneath the microscopes by adjusting the levelling-screws on which the gas furnace was supported ; this is a most important provision, as the furnace expands with heat and puts the tube out of position.

With the above apparatus observations were taken on different occasions. The method employed was to light the gas furnace and wait until the temperature became steady, and then take several readings of resistance and of the microscopes on the plan shown in Table I.

It was soon found that the length of the glass tube was liable to permanent alteration owing to change of structure. For this reason the micrometer-screws were usually read only to the nearest $\frac{1}{10000}$ of an inch, and the other approximations were made in the calculation, which would have been inadmissible if the phenomenon observed were accurately self-consistent.

Table I. shows the irregularities produced by these structural changes. Table II., however, contains two series of observations strictly comparable with each other, the highest temperature observation being taken first to avoid the permanent contraction. For the sake of comparison, the third column gives the expansion calculated from the formula $l/l_0 = 1 + 0000068 \, pt + 27 \times 10^{-9} \, pt^2$, which very nearly represents the observations, and which gives for the cubical expansion

 $v/v_0 = 1 + 0000204 \, pt + 8.1 \times 10^{-9} \, pt^2$ *pi* being the temperature Centigrade by platinum wire.

TABLE I-G.-Showing Method of recording Observations and Progressive Contraction of Glass Tube at 500°C.

The temperature is calculated by the formula (a) , see page 195.

$$
\frac{R}{R_0} = 1 + 0.03460pt, \text{ or } pt = \frac{R - R_0}{R_1 - R_0} 100.
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Mercury thermometers were used to check changes of temperature in various parts of the apparatus ; their readings are recorded in the column headed " Thermometers." S T gives the temperature on the stone slab under the gas furnace : this, being carefully screened, was not found to rise appreciably, even after the furnace had been full on for an hour. R gives the temperature indicated by a thermometer placed inside the resistance box. The temperature of the ah' was taken because variations in the temperature of the reading microscopes or their supports would introduce small errors ; as the variations of the air temperature were very small, these errors could be neglected.

On the first occasion the permanent contraction of length which the glass tube underwent amounted to '052 per cent, of its length, and on the second to "026 per cent., although this glass does not begin to soften till about 700° C., and was subject to no strain whatever: with other materials *(e.g.,* porcelain) these changes would probably be more serious. They are a most important source of error, and place a limit to the accuracy attainable with an air thermometer at such temperatures, unless an arrangement is adopted to measure them.

The volume of the bulb is also liable to change, owing to the variation of pressure to which it is subjected. At ordinary temperatures these changes are usually less than $\frac{1}{10000}$ per atmosphere, and may be neglected; but at high temperatures near the softening point of the glass they might become sensible, and the bulb might even undergo a permanent deformation. As the phenomenon in question cannot be readily measured at high temperatures, it is best to avoid the difficulty by so adjusting the mass of air enclosed that its pressure may amount to an atmosphere at the highest temperature to be reached, and the glass may thus be entirely freed from the uncertain effects of a strain at the high temperature. Such alterations of volume are

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about twenty times as important in a mercury thermometer, where they produce notable changes of zero. One great advantage of the air thermometer is that they can usually be neglected.

The bulb is connected with the U gauge by a tube of capillary bore, part of which is heated with the bulb, and part of which is at the known atmospheric temperature, a length of about 5 centims. being at intermediate and unknown temperatures. If the bore be between three and five-tenths of a millimetre, and the capacity of the bulb 50 cub. centims, the uncertain error will be much less than $\frac{1}{10000}$ and may be neglected.

Some kinds of glass are liable to be acted on chemically by the gas at high temperatures. For instance, hydrogen or coal gas exerts a powerful reducing action on lead glass at a dull red heat, and the action proceeds more slowly at much lower temperatures. Perhaps nitrogen is, for this reason, the most suitable thermometric material. Water vapour and carbon dioxide also are well known to exert a disintegrating action, and are for other reasons also especially to be avoided.

The Sulphuric Acid Gauge.

It has usually been the custom to confine the air to constant volume in the air thermometer by a column of mercury whose level is adjusted up to a fixed mark before taking an observation. The use of mercury necessitates a very wide tube, otherwise the effects of capillarity produce large errors : the volume of the air unheated must, in consequence, be large and also variable with the shape of the meniscus. Moreover, for accurate work, it is necessary not only to thoroughly dry and clean the bulb of the air thermometer, but also the tubes and mercury of the manometer which is in direct connexion with it. This it is practically impossible to do perfectly. Again, it is in most observations exceedingly inconvenient to have a mercury manometer rigidly connected with the bulb of the air thermometer, and in such close proximity with the source of heat that the mercury becomes unequally heated. The chief advantage of mercury is that its vapour tension is so small (about \cdot 001 centim. at ordinary temperatures) that it is negligible. Pure H_2SO_4 , however, possesses this same qualification, and has none of the above disadvantages. Since it wets the tube, the correction for capillarity is quite constant. If the bore of the tube be about 0'2 centim., the capillary elevation is about 0"5 centim. With a gauge tube of this bore the correction volume may be made quite small, and may be very accurately known, the shape of the meniscus being constant. This enables us to use bulbs of smaller capacity, which are, for many purposes, more convenient, without unduly increasing the magnitude of this correction. The use of sulphuric acid in the gauge tube is also attended with several other advantages. The air thermometer is thus rendered very sensitive, the slightest change of temperature is at once indicated, and it is very easy to see when the temperature is steady. The mass of air under

observation is perfectly confined, and the same mass of air may be kept under observation for a lengthened period, and is maintained perfectly dry.

Since the bore of the H_2SO_4 gauge tube is small compared with that of the mercury manometer, a change of pressure of air in the bulb first takes effect in the small-bore U gauge, and only alters the reading of the wide tube mercury manometer very slightly : this enables the instrument to be used when the temperature is not absolutely constant, as the reading of the U gauge can be instantly recorded, and the mercury manometer read at leisure. It might be thought that errors would be introduced by capillarity and viscosity of the acid in so small a tube ; but it can be easily shown by direct experiment that this is not the case to an appreciable extent. If an open gauge be connected to a mercury manometer, the acid exactly and perfectly follows every readjustment of the manometer, and its capillarity and density may thus be easily determined in terms of mercury.

It has been suggested that the acid might have some action on the confined mass of air, either absorbing it or giving off $SO₂$: it would be difficult to prove that this is not the case. On the other hand there does not seem much reason to believe that it is.*

One great advantage of the $H_aSO₄$ gauge is that, when the instrument is at constant temperature, such as that of melting ice, by altering the adjustment of the mercury manometer, the reading of the H_2SO_4 gauge is altered consistently, and a great number of quite independent observations may be taken, which ought, of course, on reduction, to lead to almost identical results, the mean of which will be to a great extent freed from scale and personal errors.

The H_2SO_4 gauge is provided with a millimetre scale, and is carefully calibrated; it is difficult to make an error of "02 centim. in reading the scale, and all errors are divided by about 7 in the reduction to mercury, so that they may practically be neglected as far as the pressure is concerned ; they become more important in applying the volume correction, especially if the volume of the bulb be small.

The extremely simple sort of gauge shown in the diagram may be used with great advantage, but it is liable to some slight inconveniences.

Supposing the air in the bulb to be at atmospheric pressure and temperature, a variation of 1° C. in its temperature alters the reading of the H_2SO_4 gauge by nearly 2 centims. If the limb of the gauge be only 10 centims, long, it has thus a range of only about 5° without readjustment of the mercury manometer, so that, when the temperature is changing, the manometer requires to be continually readjusted.

More elaborate forms were, therefore, actually used in most of the experiments, one of which is shown in fig. 2, Plate 11.

The gauge tube carries a bulb B which is calibrated, and whose volume is about

* A very complete answer to this and other objections to the use of sulphuric acid will be found in § 18 of Sir WILLIAM THOMSON's article on "Heat," in the ninth edition, 1880, of the 'Encyclopedia Britannica,' vol. 11, p. 561.

equal to that of the bulb of the air thermometer : a little below the bulb the gauge tube widens out into a cylindrical reservoir C, from which a side tube communicates with the three-way tap T, which also serves to close the entrance to the large cylindrical bulb D. A side tube o , near the lower extremity of this limb of the ∇ gauge, serves for the introduction of the requisite sulphuric acid, and can be sealed off when required.

The bulb B serves to determine the volume of the bulb of the air thermometer at any time, on the principle of the volumenometer, and so to check any alteration in the volume of the bulb without the necessity of dismounting and filling it afresh ; it may also be used for several other purposes.

When it is desired to fill the bulb of the air thermometer with pure dry air by repeated exhaustion and re-admission at a high temperature, the whole of the acid (if the gauge is already full) is first drawn back into the bulb D, which it completely fills, and the tap T is turned thus (L) : the contained air is then exhausted, and the dry air re-admitted repeatedly by way of the tube CeT. When this has been satisfactorily effected the tap T is turned thus (T) , and the acid allowed to flow down into B, completely cutting off the mass of dry air in the bulb.

The mass of air enclosed may also be easily adjusted by means of the manometer, to give any desired pressure at any desired temperature.

The volume of the bulb B gives the necessary range to the gauge in heating or cooling ; if the tap T be turned thus (-1) , so as to put C and D in communication and cut off the manometer, the instrument may be left to itself to cool or heat through a large range.

When the air thermometer has been thus left to itself to cool or heat, it often happens that the pressure is only roughly known, so that, if communication were opened direct between the gauge and the mercury manometer, a sudden and disastrous movement of the acid in either direction might take place if the manometer did not happen to be exactly adjusted. It is convenient, therefore, to introduce the small, auxiliary piece of apparatus ST' on the way between the H_2SO_4 gauge and the mercury manometer.

The U tube S is of small bore, about 1 mm., and is used as a kind of safety indicator to show when the pressure is the same on both sides of the three-way tap T'; for this purpose it is half filled with mercury.

The pressure of the air in D is always known to within 20 cm. or so of mercury, so that the manometer can be approximately adjusted; the tap T is then turned thus **(T) ;** the tube S indicates the residual difference of pressure on either side of T'; the manometer is adjusted till this difference vanishes, and is then put into direct communication with the H_2SO_4 gauge. If these precautions were not taken, the acid might sometimes get sucked back into the bulb or the pressure tubes, either of which events would ruin the series of observations.

Comparison of the Coefficients of Expansion of Gases.

The sulphuric acid gauge is specially adapted for effecting this comparison by a differential method.

Similar thermometers, filled with different gases at approximately the same pressure, are exposed to the same source of heat and connected to the same mercury manometer, so that the external circumstances are precisely the same for both, and the difference of their pressures at any time is indicated by the sulphuric acid in the gauge.

In a comparison of air and $CO₃$ between 0° and 100° the difference amounts to about 40 mm. of acid, a very measurable quantity.

The Mercury Manometer.

In the first experiments the manometer belonging to a "JOLLY" air thermometer was used. It had a glass mirror scale of millimetres divided with considerable accuracy, but it was found that the tubes were of too small diameter, and the mercury was apt to stick appreciably.

Another manometer was therefore constructed, with wider tubes, about 1'7 cm. internal diameter, which was found to be exceedingly satisfactory ; the same mirror scale was used, and the same adjusting apparatus.

The scale is only divided to millimetres, but it is possible, with practice, to estimate with considerable accuracy to the tenth of a millimetre. It appears from the many observations made with the apparatus that the probable error of a single observation is of about this magnitude. It would have been theoretically preferable to take the readings with a kathetometer, but this would have involved great loss of time, and there was not one to spare.

To avoid errors of parallax, &c., readings were taken as follows :—The mirror scale was fixed vertically in a vertical plane, with the aid of a plumb-line. A telescope capable of sliding up and down, and being clamped at any height on a vertical axis, was levelled by focussing it on its own image in the mirror at the distance of about a metre ; this gave a magnifying power of about three diameters as compared with the naked eye at a distance of 10 inches.

To eliminate personal errors in estimating the tenths of a millimetre, a series of independent observations at different points of the scale were taken at each constant temperature. The close agreement of these shows that the apparatus performed satisfactorily.

The mirror scale was tested for scale errors by comparing it with the standard metre, with the aid of reading microscopes; the errors were found in all cases to be less than '01 cm., and are therefore neglected.

In taking observations, the reading of the top of the meniscus in each limb is recorded and the difference set down in an adjacent column ; this is then corrected for temperature and reduced to zero, allowing for the linear expansion of the glass scale.

The temperature of the mercury is repeatedly taken in the course of the observations by the aid of a delicate thermometer immersed in the mercury of the open limb. It almost always differs slightly from that of the air.

The correction for temperature is only applied to the nearest tenth-millimetre, partly because the readings are only accurate to this order, and partly because, since the temperature is varying and is not the same throughout, the correction itself is liable to a slight uncertainty. To avoid inaccuracy, the calculations were usually carried to the next figure, to which, however, but little weight can be attached.

The Barometer.

Readings of the atmospheric pressure were taken with the standard Fortin barometer. Each reading is subject to the following corrections :-

1. The most important is the correction for temperature. The scale is of brass, graduated in English inches, and is correct at a temperature of 62° Fahr. The scale errors are negligible.

The density of the mercury is normal at 0° .

Thus for a height of 76.0 cm. the correction is -0.24 cm. at 0° Cent., since the brass scale is incorrect ; and at 62° Fahr., when the brass scale is correct, the mercury correction is -228 cm., and the change in the correction is 0123 cm. per degree Centigrade.

The correction is uncertain, because it does not follow that the thermometer indicates the mean temperature of the mercury and scale.

2. The correction for capillary depression and vapour tension of mercury amounts altogether to about $+$ 005 cm. at 15° Cent.

8. The corrections for gravitation and height above sea-level need not be applied, since absolute measures of pressure are not required (except for determining the temperature of saturated steam at atmospheric pressure).

4. The level of the cistern of the barometer is at a height of 4 metres above the manometer. A constant correction of $+04$ cm, is applied to allow for this.

5. *Sources of Error.*—The atmospheric pressure varies incessantly and capriciously, so that the reading of the barometer cannot be relied on beyond the nearest tenthmillimetre[®] (REGNAULT), even if all the mechanical adjustments could be perfectly effected and the temperature correction were certain. The barometer is, therefore, read several times in the course of each series of observations, and the corrections are applied to each reading to the nearest tenth-millimetre.

6. The constant errors of the attached thermometer are sufficiently small to be negligible.

In reading the barometer, all precautions were taken to avoid inaccuracy in the mechanical adjustments, the probable error from this source being only about '001 in.

* ' Paris, Mémoires de 1'[nstitut,' torn. 21, p. 69.

*Formvlœ. **

The formulae applicable to this form of air-thermometer are, of course, very similar to those of the ordinary form. Let m be the mass of air confined. Let V_0 be the volume at 0° C. of the bulb, together with that portion of the capillary tube which is heated with it, and let *v0* be the volume of the capillary and gauge tubes from this point to the division x_0 of the gauge tube. Let p_0 be the pressure at 0° C. when the temperature of the gauge tube is θ' and the acid stands at the division x_0 of the scale. Let θ_0 be the absolute temperature corresponding to 0° C. Let v be the correction volume for the portion unheated at any other time when the temperature, pressure, and volume of the air in the bulb are *9, p,* V, respectively, and when *9"* is the temperature of the gauge tube, and *x* the scale reading thereof. Then, by the law of a perfect gas, we have the equation

$$
p\left\{\frac{\nabla}{\theta} + \frac{v}{\theta''}\right\} = mk = p_0\left\{\frac{\nabla}{\theta_0} + \frac{v_0}{\theta'}\right\}, \qquad \ldots \qquad \ldots \qquad (1)
$$

whence, to a first approximation,

$$
\theta = \frac{p\theta_0}{p_0}.
$$

Let γ be the mean cubical coefficient of expansion of the glass of the bulb between θ_0 and θ .

Then

$$
V = V_0 \{1 + \gamma(\theta - \theta_0)\}.
$$

Let u be the volume per centim, of the gauge tube. Then

Let

$$
v = v_0 + u(x - x_0).
$$

$$
\frac{v}{\nabla} = \beta \cdot \frac{v_0}{\nabla_o} = \beta_0.
$$

Making these substitutions in equation (1), and substituting for θ the first approximation in the small terms, we obtain at once

$$
\theta = p \frac{\theta_0}{p_0} \Big\{ 1 - \Big(\gamma \theta_0 + \beta_0 \frac{\theta_0}{\theta'} \Big) + \frac{p}{p_0} \Big(\gamma \theta_0 + \beta \frac{\theta_0}{\theta''} \Big) \Big\} \dots \dots \dots \dots \tag{2}
$$

If we write

$$
\gamma \theta_0 + \beta_0 \frac{\theta_0}{\theta'} = y_0
$$
 and $\gamma \theta_0 + \beta \frac{\theta_0}{\theta''} = y$,

this becomes

$$
\theta = p \frac{\theta_0}{p_0} \Big\{ 1 - y_0 + \frac{p}{p_0} y \Big\}.
$$

* For be'ter method with aid of slide-rule, see Appendix.

Let

$$
\frac{p}{p_0}y - y_0 = \delta, \text{ and write } p(1+\delta) = P.
$$

Then, finally,

$$
\theta = P \cdot \frac{\theta_0}{p_0} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (3)
$$

It is, in general, useless to proceed to a third approximation, because the uncertainty of the corrections is at least of the same order, as a rule.

The value of P, which may be called the " corrected " pressure, is obtained directly from the observations by applying the small corrections in the manner detailed below.

P is proportional to the absolute temperature. The ratio θ_0/p_0 is theoretically constant for each filling, though, as a matter of fact, it is variable with the " zeroerrors" of the air thermometer. The value of θ is calculated from P by the aid of logarithms, the logarithm of θ_0/p_0 being tabulated once for all for each series of observations. This is the only part of the reductions where logarithms are required. The correction terms being, from their very nature, uncertain, often to the extent of nearly 1 per cent., it is quite sufficient to perform all the multiplications they involve by the aid of a small slide-rule giving results correct to 1 per 1000. This method saves trouble, paper, time, and mistakes.

Reduction of the Pressure (p).

The correction of the mercury columns for temperature is most easily applied by a graphic method : by ruling two series of straight lines, giving the correction to be applied to any length of mercury column less than 1 metre for each degree of temperature Centigrade, both for the glass millimetre scale and for the English standard barometer with the brass scale. The barometer lines need not extend through the whole range, since its reading never varies far from 76 centims.

Let H be the height of the barometer, corrected for temperature, &c., as above described. Let M_B , M_L , be the readings of the right and left limbs of the mercury manometer; and let $M_B - M_L$ be corrected for temperature and added to H. Let x' be the reading of the H_aSO_a gauge when the pressure is the same on the acid in both limbs. Let *x* be the recorded reading in centims. Let

$$
\frac{(x-x') \text{ density of } H_2SO_4}{\text{density of mercury}} = q.
$$

Then *q* is the pressure due to the acid, expressed in terms of mercury : *q* is usually so small that no temperature correction need be applied. Both *x'* and the reduction factor are determined by previous experiment with the acid and gauge used.

 $MDCCCLXXXVII. \longrightarrow A.$ 2 A

Then, finally,

$$
p = H + [M_R - M_L]_0 + q.
$$

For reasons previously given, *p* is correct only to the nearest tenth of a millimetre.

Reduction of the Observations.

This is a formidable piece of arithmetic, with the formulae as usually given for the ordinary air thermometer : it would be still more formidable with the sulphuric acid gauge. However, by the aid of graphic methods and a slide rule, it may be effected with great rapidity and accuracy.

The value of $y = \gamma \theta_0 + \frac{v_0 + u(x - x_0)}{\nabla} \frac{\theta_0}{\theta}$ is calculated for any two values of x and for temperatures 15°+20° C. Two straight lines are ruled on logarithm paper joining these points, giving the value of *y* for any value of *x* at these two temperatures. A variation of one degree of temperature produces a variation of about $\frac{1}{300}$ in the value of *y,* so that the lines very nearly coincide.

Similarly the value of *q* is calculated for two values of *x,* and the ruling of a straight line gives it for all other values ; this line is ruled on the same piece of logarithmic paper, with the same abscissa scale. A correction diagram of this kind has to be constructed from the calibration and other details once for all for each thermometer. The values of *y* and *q.* corresponding to the recorded value of *x,* are taken from the correction diagram and copied into adjacent columns headed *y* and *q* ; *p* is evaluated by the simplest addition and subtraction; the multiplication $yp/p₀$ is performed in one operation on a slide-rule, and δ is found by subtracting y_0 ; the product δp is given at once by the slide-rule and added to *p,* giving P, which is proportioned to the absolute temperature θ : thus the whole of the calculation involved in finding P may be exhibited in a single line and worked out on the spot in the note-book used for recording the observations. This gives a great advantage in point of compactness, and the ease with which mistakes may be discovered and rectified. Where it is advisable, from the magnitude of the volume correction, to go to a third approximation, this may be taken as

$$
\theta = \frac{\theta_0}{p_0} p \{1 + \delta + \delta^2\} \text{ by neglecting } \gamma \delta \theta_0.
$$

 δ^2 is at once given by the slide-rule and added to δ , so that this involves very little extra trouble.

But the greatest advantage of this method of reduction is that it avoids the accumulation of superfluous and meaningless figures, and thereby escapes that fictitious accuracy which is so seductive and treacherous in all physical investigations.

Corrections to be applied to the Air Thermometer.

Air does not follow exactly the equation of elasticity of a perfect gas $pv/\theta = mk$. Since, however, it follows this law very approximately, its true equation of elasticity may be written

$$
\frac{pv}{\theta} = mk(1-\phi),
$$

where ϕ is an unknown function of the variables which must be very small. The experiments bearing on this deviation are those of REGNAULT on the compressibility of gases at different temperatures and the comparison of air thermometers ; and, in particular, the experiment of THOMSON and JOULE ('Phil. Trans.,' 1862) "On some Thermal Effects of Fluids in Motion."

From all these experiments RANKINE deduced as the approximate equation of elasticity $v = \mathcal{R}_p^{\text{2}} - \frac{1}{3}\mathcal{A}Cp\left(\frac{1}{\text{T}}\right)$

It may, of course, be written *in our notation* in the form

$$
\frac{p\sigma}{\theta} = mk(1-\phi), \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (E)
$$

in which for air

$$
\phi = +001173 \frac{p}{p_0} \cdot \left(\frac{\theta_0}{\theta}\right)^3.
$$

TABLE. Φ .

The following Table gives approximately the values of this correction at different points for the standard air-thermometer :—

* This is the form and notation given by CLAUSIUS, ' Mechanical Theory of Heat,' p. 227.

2 A 2

A somewhat similar Table is given by THOMSON and JOULE ('Phil. Trans.,' 1854), calculated from a more complicated, empirical formula, which does not represent the results of experiment nearly so well. It will be seen that the corrections are so small that it is not worth while to apply them, except in investigations of a higher degree of accuracy than any yet attempted.

They are rather larger for a $CO₉$ air thermometer, but still so small that a $CO₂$ air thermometer is practically correct up to $300^{\circ*}$ (REGNAULT); that is, the corrections are smaller than the uncertainty due to the expansion of the envelope or other causes; the magnitude of this correction varies directly as the initial pressure p_{0} .

Assuming equation (E), we ought to have for the compressibility of air at 0° C.

$$
1 - \frac{p}{p_0 v_0} = \phi - \phi_0 = 0.01173 \left(\frac{p}{p_0} - 1\right),
$$

or, at 5° O.,

$$
1 - \frac{pv}{p_0 v_0} = 0.0111 \left(\frac{p}{p_0} - 1\right)
$$
 approximately.

From REGNAULT's formula,[†] if $p=2$ metres and $p₀=1$ metre of mercury, we find, for air at 475° C., •

$$
1 - \frac{pv}{p_0 v_0} = \text{ '00109.}
$$

But the equation (E) does not agree so well with his results throughout the whole range of his experiments, because it is only a rough first approximation to the departure of air from the law of a perfect gas, and is only applicable within moderate limits of pressure and temperature. At high temperatures dissociation would occur, and the formula would no longer apply. In the case of $CO₂$ the dissociation is quite measurable, even at 1000° C.

The Sources of Error to which the Air Thermometer is liable.

The first and most important source of error, for which no correction can be applied, is impurity in the dry air. Water vapour and $CO₂$ are most to be avoided, and the bulb of the air thermometer must be very thoroughly cleaned. The apparatus used for supplying pure dry air, used in the earlier experiments, appeared perfect, but has since been proved faulty. See Appendix, p. 222.

The air thermometers were dried by repeated exhaustion and re-admission of dry air at temperatures between 300° and 500° C.

* 'Mémoires de l'Institut,' torn. 21, p. 187.

f 'Mémoires de l'Institut,' torn. 21, p, 421.

*Changes of Zero Pressure**

In spite of all precautions, slight changes of zero pressure were observed with all the air thermometers, amounting in some cases to upwards of a millimetre of mercury in a week ; these were probably due to surface condensation. In support of this it may be remarked that the vortex atom theory of gases requires the existence of an air film of swollen vortices sticking to the sides of the containing vessel ; the phenomenon is also well attested by many experiments ; in particular, we may mention that of Professor BUNSEN " on the condensation of $CO₂$ on the surface of fine-spun glass." \dagger It is still necessary, however, to determine in what way the air film varies with the temperature. I am investigating this, but the experiments are not yet completed. For the present we may assume that it exists and see what kind of error it will produce.

Let m be the mass of air enclosed in grammes; p, v, θ , its pressure, volume, and absolute temperature; k the difference of the specific heats of unit mass of air; σ the surface density of the air film in grammes per square centim. ; and. S the surface of the air thermometer in square centims. σ is a function of the pressure and temperature, and also apparently of the nature of the gas, and of the surface, of its past history, and of the time.

We shall have the equation

$$
k\mathbf{S}\sigma + \frac{pv}{\theta} = mk = k\mathbf{S}\sigma_0 + \frac{p_0v_0}{\theta_0} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \mathbf{(\Sigma)}
$$

First approximation, $\theta = \frac{\mu}{\sigma}$. Solving this to a second approximation, σ being small, *Po* we have

$$
\theta=p\frac{\theta_0}{p_0}\Big\{1+\frac{8'}{m}(\sigma-\sigma_0)\Big\},\,
$$

neglecting other corrections.

Let p_1 , p_0 , be the pressures corresponding to 100[°] and 0[°] C. respectively, then, according to REGNAULT, $\frac{1}{p_1/p_0} = 1.3665$; according to BALFOUR STEWART, § $p_j/p_0 = 1.3673$. In REGNAULT's experiments $S/m = 400$ roughly. In BALFOUR STEWART's case S/m = 1060, so that, if we assume $\sigma_1 - \sigma_0 = 000001$ gramme per square centim., we shall derive, both from REGNAULT and BALFOUR STEWART, the value $p_1/p_0 = 1.3659$, corrected for surface condensation; also, in the case where $S/m = 2400$, as in my air thermometer (No. III.), we should expect to find the value

* Similar changes were observed by REGNAULT.

t ' Phil. Mag.,' Series 5, vol. 17, p. 161.

+ Vide ' Mém. Inst.,' torn. 21.

§ Vide ' Phil. Trans.,' 1863.

of p_1/p_0 , uncorrected for surface condensation, to be 1.3693, which very nearly agrees with that actually observed (see Table Λ , III.) [For another explanation see Appendix, p. 222.]

It appears, however, that when the air film has been very completely removed by exhaustion at a high temperature it increases gradually for some time before it has recovered its normal state.

To illustrate this, the following Table gives the changes of zero pressure observed with two of my air thermometers.

Such changes of zero pressure are a most important source of uncertainty, especially if the instrument be used at high temperatures.

We have said a great deal about the air thermometer, because the chief experimental difficulties arose from it ; the other essential part of the apparatus is the platinum spiral, which we will now proceed to consider.

The Platinum Spiral.

The spirals used in this investigation were all made from the same reel of pure platinum wire supplied by Messrs. JOHNSON, MATTHEY, and Co. Its purity is attested by the following facts : (l) the high temperature coefficient of its resistance, '00346, instead of about "0030, as with ordinary platinum ; (2) it was very infusible and unalterable : after being kept for about two hours at a temperature of about 1200° C., its resistance had not altered by 1 in 5000 at 0° C.; (3) no impurities could be detected by chemical analysis.

Details of the ivire.—Diameter, about "017 centim. ; resistance, about 5 ohms per metre ; mass, "00488 gramme per centim. About 1 metre of the wire is measured off and its ends fused on to tails of thicker platinum wire (diameter, "073 centim.) in the oxy-hydrogen blowpipe. (It is less trouble to solder with copper, but the spiral cannot then be boiled with acids in the bulb of the air thermometer.) The wire is then annealed by passing it slowly through the solid BUNSEN flame of a FLETCHER

furnace ; this renders the wire very soft. (If the wire is not annealed, its resistance will be slightly diminished on the first heating, owing to a change of structure.) It is then wound on a glass tube and annealed again, to make it preserve a perfect spiral form.

Measurement of the Resistance.

If the resistance be too small, chance errors, such as change in the contacts, are unduly magnified. To make the resistance large involves either inconveniently fine wire or an awkwardly long spiral. In the actual experiments, therefore, spirals were used with resistances varying from 5 to 20 ohms. The most rapid and accurate way of measuring such a resistance is by the WHEATSTONE bridge method with an ordinary post-office box, and a sensitive THOMSON mirror galvanometer with lamp and scale. Resistances of 10 and 1000 are taken out in the arms of the balance, so that the adjustable resistance is 100 times that of the spiral when the balance is obtained. This gives the value direct to four figures, and a fifth may be obtained by accurately observing the galvanometer throws and interpolating.

The box used was a very accurate box of B.A . units by Messrs. ELLIOTT. On the extraordinary accuracy of the boxes the reader may be referred to the paper by GLAZEBROOK, " On the Determination of the Ohm in Absolute Measure " (see ' Phil. Trans.,' 1883, p. 262), whence it appears that an uncertainty of 1° C. in the temperature of the box will give an error of about '0004 in the absolute value of a resistance, but that ratios of resistances, if the temperature of the box be uniform may be determined with an error of only about '00002.

The sensitive galvanometer employed had a resistance of about $14\frac{1}{9}$ ohms, being approximately that most suited to the given arrangement of resistances. It was arranged so as to be extremely sensitive. A deflection of one scale division corresponded to a difference of '0001 ohm when the resistance to be measured was 10 ohms. It was also nearly dead-beat to facilitate the reading of deflections for interpolation.

The battery consisted of from four to six LECLANCHÉ elements in series ; as the circuit had a resistance of about 500 ohms, they worked steadily.

Sources of Error.

Thermo-electric effects were made as small as possible by careful arrangement of the junctions ; they were then completely eliminated by using a rocking mercury cup commutator in the battery circuit, for rapidly reversing the current and observing when the reversal had no effect on the galvanometer ; it is important, however, to make the thermo-electric effect small, because, if it is large and variable, it greatly interferes with accurate observation of the resistance by making the galvanometer unsteady.

There were only two screw contacts; these were between the thick copper leads

and the resistance box. They were always very tight and clean, and cannot have introduced appreciable errors. The plugs of the resistance box were very large and truly ground, and their contacts good.

It was suggested that the conductivity of the glass at high temperatures might prove a source of error in the resistance measurements. A rough experiment was therefore tried. A cubic millimetre of the hard glass at a dull red heat had a resistance of about a megohm, and about ten times less at a bright red heat. This is less than 1 in 10,000, and may be neglected. Moreover, since only one of the platinum terminals was actually fused through the glass in this case, the bad contact further diminished any possible error from this source. Current heating of the wire would produce a small and nearly constant error ; since, however, the current was never greater than '01 ampère, the effect must have been almost negligible. From experiments on the cooling by air contact of this particular kind of platinum wire, I am in a position to estimate the excess of temperature due to a current of '01 ampere at about '016° Centigrade.

Reduction of the Resistance.

There are some small corrections to be applied.

The resistance of the copper wires connecting the coil to the resistance box is generally about '01 ohm, and varies very slightly with the temperature. The whole correction amounts to about 1% , and may be measured on each occasion by means of double electrodes.

The temperature of the resistance box varies slightly. A special experiment gave '00040 as the value of the temperature coefficient. The box is correct in B.A. units at 14'2° Centigrade. The temperature is therefore taken by a mercury thermometer kept inside the box, and the observed resistance reduced to 14'2° Centigrade. This correction is also very small, and can be applied with tolerable certainty.

Finally, to render the results comparable with each other, each observed resistance of the platinum coil is reduced to what it would have been for a coil having the resistance of a unit at 0° Centigrade, by dividing by the observed value of the resistance of the coil at 0° Centigrade.

Explanation of the Tables of Comparison of Platinum and Air Thermometers.

The letters at the head of each column have the same meaning as explained in section entitled Formulæ (see page 176). The column headed Thermometers gives the observed temperatures B of the barometer, *v* of the air near the U gauge, Hg of the mercury in the right limb of the manometer, R of the air in the resistance box; *v,* Hg, R, being taken with the same mercury thermometer. * Each line contains the

* [Tliis is bad, and may introduce small errors : latterly a separate thermometer was set apart for each purpose.]

whole work of the reduction of a single complete observation. The method of observing is as follows :—When the temperature is nearly steady, the approximate resistance having been ascertained, the galvanometer circuit is closed and the moment observed when reversing the battery current with the rocking commutator does not affect the galvanometer ; the simultaneous reading *x* of the U gauge and the time are recorded, and the readings of the manometer and barometer are taken.

The column θ gives the absolute temperature corresponding to the mean corrected pressure P; t the temperature Centigrade $= \theta - \theta_0$; R *observed* the corrected value of the resistance reduced to 1 at 0° C. by dividing by the value of R_0 ; R *calculated* the value of B calculated from the empirical formulae

$$
\frac{R}{R_0} = 1 + \alpha t - \beta t^3 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (b)
$$

(see page 194), and

E = ei+(«. En

Observations.—Series I.

I constructed ajl experimental instrument in November, 1885, of lead glass at the Cavendish Laboratory. It was necessarily imperfect from want of skill in glass working, and lack of the requisite assortment of glass tubing, However, it was well suited to test the capacities of the method, and the observations taken with it agree as nearly as may be expected with subsequent and improved apparatus. Details :-- $V_0 = 32.25$ cubic centims., $\beta_0 = 0.378$, $\gamma = 0.000263$.

The observations are not all given, as they are less accurate for several reasons. Most of them were taken with the temperature varying rapidly, and the mercury manometer belonging to a "Jolly" air thermometer was used, the tubes of which were too narrow for purposes of accuracy. Nearly five centims. of the fine wire was outside the bulb, and the resistance measurements were rendered less accurate by some small thermo-electric effects and a slight uncertainty in the resistance of the connecting wires, and by neglecting to take the temperature of the resistance box.

The capillary tube was also of the same bore as the tube of the $H_aSO₄$ gauge, as there was none finer to be had on the spot ; this of course renders the volume correction more uncertain.

Table A-I. contains all the observations taken when the temperature was approximately steady. The column B *calculated* shows how very nearly they agree with the formulæ. Some of the observations, however, taken when the temperature was varying rapidly about 250° C., are nearly two degrees out.

 $MDCCCLXXXVII$, $-A$. 2 B

TABLE A-L-Containing some of the Results of Observation with the experimental Air Thermometer No. 1.

Observations.—Series II.

Owing to the success of the experimental instrument, a slightly improved form was devised and ordered of a London glass-worker about the beginning of December, 1885, for which I wound a platinum spiral of the same wire at the Cavendish Laboratory; the first spiral was broken and another sent, and other casualties intervened, so that the instrument did not arrive until February, 1886, and then, owing probably to some want of clearness in the specification, I had to alter it in some essential details before it could be used. It was cleaned and calibrated in the usual manner, and finally, on February 13, it was filled with dry air, at a temperature of about 350°, and a series of observations, recorded in Table A-II. , were taken with it in a large mercury vapour bath ; the fixed points being determined with the aid of a hypsometer and melting ice.

On February 17 another series of observations was begun, but the zero pressure had increased in four days from 34'10 cm. to 36'09 cm., owing to leakage, the platinum wires not having been fused air-tight through the glass. In an attempt to remedy this somewhat serious defect, the instrument was unfortunately broken. This was much to be regretted, as less reliance can be placed on observations taken while the temperature is varying ; all the observations are given, however, as they show how perfectly the method works. The time observations show the rate of variation of the temperature. A mercury thermometer in the same enclosure often differed from 20 to 50 degrees, in its indication, from the air thermometer.

Values of R are calculated by both formulae (*b*) and *(e)* for comparison. The agreement with the formula *(e)* is in some cases so close that it must be fortuitous to some extent; it is, however, satisfactory to see that single observations are so consistent, and give so smooth a curve.

Details of Air Thermometer No. II.

Volume of bulb $V_0=77.01$ cub. centims.

Total volume of capillary tube="0840 cub. centim.; diameter, '03 centim. The U gauge tube was of very uniform bore : $u = 0442$ cub. centim. per centimetre.

$$
x=1, v_0
$$
=-122 cc., β_0 = $\frac{v_0}{V_0}$ =-001585, y_0 =-0084
 $x=10, v$ =-520, β =-00675, y =-0133
 y = 0.133
 y = 0.133

Mean coefficient of expansion of glass between 0° and 100° Cent., $y=0000251$, by mercury weight thermometer.

From the observations in ice and steam, on February 13, we have

$$
\theta_0 = \frac{99.97.34 \cdot 102}{12.620} = 270.12. \qquad \log \frac{\theta_0}{p_0} = .89881.
$$

 θ To find the other temperatures, $\theta = \degree P$. *To*

For the platinum spiral the resistance of the connexions was, at 0° Cent., '0139 ; at 353° Cent., '0221. The value of this small correction at intermediate temperatures was found by ruling a straight line on logarithm paper with sufficient accuracy. Applying corrections, we find $R_0=5.0845$ B.A. ohms, colog $R_0=9.29375$.

As the U gauge tube had been made unnecessarily long, the q' correction was large and negative. By direct comparison with the mercury of the manometer, the ratio of the density of acid to mercury at 15° was determined to be '1382 and the capillarity '45 centim.

Thus, when $x=0$, $q=-3.12$ centims.; and, when $x=10$, $q=-1.75$ centim.

From these details the " correction diagram " is constructed which is shown in Plate XI., fig. 5, for the purpose of illustrating the method of reducing the observations. The ordinate scale, on one side, gives values of *y,* on the other, values of *q,* for the same abscissa scale of x. A difference of $+5^{\circ}$ in θ'' makes $y=0132$ instead of '0133 when $x=10$, so that variations of θ'' may almost be neglected. Only one line is therefore drawn, corresponding to $\theta'' = 15^{\circ}$ C. (The lines of the section paper are only indicated, every tenth line being reproduced in the diagram.)

[When the apparatus was cooling the lower part of the bath was some 50° hotter than the upper. The platinum spiral was hung vertically in this instrument, and was deformed by its own weight, so as to be massed chiefly in the lower and hotter portion of the bulb. The observations taken during cooling are, therefore, affected by a *constant error* amounting to two or three degrees, the mean temperature of the being higher than that of the air.]

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TABLE A-II.—Showing Comparison of Platinum and Air Thermometers.

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Observations.—Series III.

Since lead-glass begins to soften at about 450° C., it was considered advisable to make an instrument of harder glass. Air thermometer No. 3 was therefore constructed of combustion tubing. Since hard glass cannot well be joined on to other tubing, the capillary tube was formed by drawing out a piece of combustion tubing, which formed the bulb ; the platinum spiral was then inserted and the other end drawn out, and the whole cleaned and calibrated.

To avoid leakage, one of the electrodes passed out through the whole length of the capillary tube, and the fine wire itself was sealed through the glass at the other end, a length of 1 centim. being perfectly coated with glass. A capillary tube formed in this way is of course exceedingly fragile, and some delicacy of manipulation is required, but it appears that the instrument cannot be otherwise made of hard glass without a glass furnace in which a bulb can be blown.

This thermometer was suitably mounted and filled with dry air at a temperature of 470° C., and the series of observations recorded in Table A-m. were taken with it. It was heated in a thick iron tube constructed to fit it, and the temperature maintained steady by regulating the gas supply.

It showed no tendency to leak, till at the conclusion of observation (10) it was unfortunately cracked by too sudden exposure to the air after heating in the steam bath.

The chief objection to this thermometer was the small volume of the bulb, and the large volume correction, which necessitated a third approximation ; the value of $\frac{S}{m}$ (see equation Σ , p. 181) being large, all the uncertain effects of surface condensation are unduly magnified. For instance, for observation (7) we obtain for the value of the *g* temperature 397'6 or 398'3, according as we use the first or second value of $\frac{10}{10}$. The *Po* mean deviation of observations (1), (6), (7), from the curve (e) is 2° -5.

For this reason, I made a larger and better instrument on the same plan, but it was unfortunately broken just as it was completed. In spite of this accident, I hoped to make another series of experiments with a better thermometer, but a most unfortunate accident has completely disabled my right hand for the last month and put a stop to my experiments.

Details of Air Thermometer No. 3.

Volume of bulb. $V_0=15.02$ cub. centims.

*Capillary and gauge tube.—u='*0442 cub. centim. per centim.

 $x=1$ centim., $v=270$ cub. centim., $\beta=0.178$ $x=10$ centims., $v=667$ cub. centim., $\beta=0442$

By observations on linear expansion we deduce the mean cubical coefficient from 0° to t.

$$
\gamma = 0000204 + 8.1 \times 10^{-9}t.
$$

Pressure correction :—

 $x=3.12, q=0.0;$ $x=0,$ $q=-425;$ $x=7, \t q=+54.$

Two pairs of observations were taken in ice and steam to determine the fixed points.

From observations (2) and (3), taken on February 23, we have

$$
\theta_0 = \frac{100 \cdot 30 \times 37 \cdot 435}{13 \cdot 885} = 270 \cdot 42 \cdot \log \frac{\theta_0}{p_0} = 85875.
$$

From (4) and (5), taken on February 24,

$$
\theta_0 = \frac{100 \cdot 18 \times 37 \cdot 400}{13 \cdot 872} = 270 \cdot 10 \cdot \log \frac{\theta_0}{p_0} = 85864.
$$

On February 25, at the beginning and end of the series, we have at 100° -20 C., observation (6),

 $P=51.25$; and, observation (10), $P=51.22$ in steam.

For the platinum spiral the resistance of the connexions at 0° was "0501, and at 470° was -0635, only a small portion being heated.

For the platinum spiral.—Resistance at 0°, corrected,

$$
R_0 = 6.2374, \quad \log R_0 = 79500.
$$

In the values of the resistance calculated for comparison—

(6) refers to the formula

$$
\frac{\mathrm{R}}{\mathrm{R}_0} = 1 + \alpha t - \beta t^3 ;
$$

(e) to the exponential formula

$$
\frac{\mathrm{R}}{\mathrm{R}_{0}}\!\!=\!e^{\frac{\gamma 0034259t}{1+\gamma 001429t}},
$$

which last agrees best with the observations.

TABLE A-III.—Comparison of Platinum and Air Thermometers.

; Observations marked as doubtful and not included in the means.

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GENERAL Table of Results. IV. - Observations at fixed points 0° and 100°.

Resistance observed and corrected.	Reduced to 1 at 0° .	Temperature.	Date.	No. of observation.
5.0845 6:2364 6.2374 6-2373	1.0000 -99983 1.0000 1:0000	0° C. (Ice not washed) (Ice washed) After long heating	Feb. 13 Feb. 23 Feb. 24 Feb. 25	2 -11. 3 Ш Ш. 5 Ш. 12

A.— *I n melting ice.*

B.—*In hypsometer steam.*

Resistance observed.	Reduced to 1 at 0° .	Temperature by steam.	Resistance calculated (a) .	Date.	No. of observation.	
6.8432 8.4013	1.3459 1.3470	99.97 $100-30$	1:3459 1:3470	Feb. 13 Feb. 23	3 11. Ш. 2	
8.4004 8'4004	1.3468 1.3468	$100-18$ 100-20	1:3467 1.3467	Feb. 24 Feb. 25	Ш. Ш. 16	9 _{A.M.}
8:4004 8.3996	1.3468 1.3467	100-20 $100 - 19$	1:3467 1:3467	Feb. 25 Feb. 25	III. 10 III. 11	2 г.м. 4.2.34.

This Table illustrates well the absence of zero error and the constancy of the coefficient of increase of resistance. Between observations III. 6 and III. 10 the instrument was kept for some time at a red heat. It will also be seen that the two different spirals II. and III. agree perfectly in their temperature coefficient.

*Observations at Steady Temperatures.**

TABLE V.

* For correction of these observations, see Appendix, p. 222.

Note : Observation II. 1 is marked doubtful in mv book of notes, as there was a small glycerine bubble in the air tube connecting the mercury manometer with the sulphuric acid gauge ; moreover, it disagrees with observations taken a few minutes after with the same instrument, when the bubble had been dislodged (see II. 4, 5, &c., next Table). [Nevertheless, as the temperature was steady, it is not liable to the constant error (see p. 187, end).]

Observations with Temperature varying.

No. of ob- servation.	Temperature	Resistance observed.	Resistance calculated by empirical formulae		Resistance calcu- lated by	Difference.
	Centigrade.		(α)	(b)	exponential formula (e).	
23 22 21 20 19 18 17 16 15 14 13 12 11 10 -1000 654	207.2 $210 - 1$ 215.7 233.8 236-6 $239 - 4$ 257.7 263.4 $278 - 2$ 281.5 293-6 $299 - 6$ 317.8 $323 - 8$ $331 - 1$ $336 - 1$ $339 - 1$ 342.4 346.0 3486	1.7172 1.7270 1.7467 1.8057 1.8156 1.8254 1.8842 1:9038 1.9530 1-9629 2.0020 2.0217 2.0806 2.1003 2.1239 2:1394 $2 - 1493$ $2 - 1591$ $2 - 1709$ 2.1788	1:717 $1 - 727$ $1 - 746$ 1.809 1.819 1.828 1.891 1:911 1.963	1.712 1.722 1.740 1.801 1:810 1.819 1.881 1:900 1.948 1.959 1.999 $2 - 018$ 2.078 2.097 $2 - 121$ 2.137 $2 - 147$ $2 - 157$ $2 - 169$ 2.177	1.7145 $1 - 7242$ 1-7430 1.8042 1.8135 1.8224 1.8834 1.9028 19515 1-9625 2.0020 2.0213 2.0807 2.0998 $2 - 1235$ 2.1395 $2 - 14v2$ 2.1595 $2 - 1711$ 2.1793	-0027 -0028 -0037 -0015 -0021 -0030 -0008 -0010 -0005 -0004 $+0000$ -0004 $+0001$ -0005 -0004 $+0001$ -0001 $+000+$ $+0002$ $+0005$

Table VI.—Thermometer No. 2.

The above are all single observations, yet they are remarkably consistent with each other, and give a very smooth curve. They are given to show the capabilities of the method, and the great sensitiveness of a fine platinum spiral.

Empirical Formulae.

It is usual to apply the method of least squares to calculate the empirical formula which best suits the observations. This has the advantage of giving a great appearance of accuracy and completeness. In the present case, however, the gain, if any, would not compensate the trouble, and the simpler method of calculating from selected numbers gives equally good results.

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If we assume as an empirical formula

$$
R/R_0 = 1 + \alpha t + \beta t^2 + \gamma t^3,
$$

and, taking data from the curve, calculate the values of the constants α , β , γ , we shall obtain a more or less unsatisfactory formula of interpolation. To show how much the values of α , β , γ , vary for slightly different data, the following Table may be interesting :—

The formula (b') represents the observations fairly well within the experimental range, but is quite inadmissible for extrapolation, for it has a maximum $R/R_0 = 3.52$ at about 1090° C., whereas I have observed values of R/R_0 exceeding 5.0. The second formula,

$$
R/R_0 = 1 + \alpha t - \beta t^3, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (b)
$$

has only two constants, and represents the curve nearly as well, but is subject to the same objection. The third formula (e) is approximately the nearest parabola, but does not represent the observations so satisfactorily at low temperatures.*

SCHLEIERMACHER,[†] who has incidentally investigated the question, unfortunately gives no numbers, but represented his results graphically by drawing a series of straight lines for each interval of 100°, using the curve thus obtained to give the temperature in terms of the resistance. His observations extended to 1000°, but he does not publish the curve.

In 1871 SIEMENS suggested that the true law of change of resistance with temperature was $R = \alpha \theta + \beta \theta + \gamma$; where α , β , γ , are constants and θ the absolute temperature.

The nearest empirical formula of the SIEMENS type calculated from the above data is

R = -037710*+ -0025200--2450 *(s)*

This differs radically from the other empirical formulae. It represents the observations about as well as the parabola (c), but at high temperatures $dR/d\theta$ approaches

* For correction of this formula, see Appendix, p. 220.

t WIEDEMANN, ' Annalen,' vol. 26, p. 287, 1885.

the limit '00252, and does not vanish or give a maximum value for R. SIEMENS' formula makes R negative when $\theta = 0$.

SIEMENS found for platinum

$$
R = 039369\theta^4 + 00216407\theta - 2413,
$$

which happens to agree nearly with (s) , except that (s) is straighter and steeper.

It has been usual to use a formula of the type

$$
R/R_0 = 1 + \alpha t + \beta t^2
$$

for extrapolation, which corresponds to Formula *(d),* pp. 163, 165.

For instance, BENOIT gives $R/R_0 = 1 + 0.02454t - 0.000000594t^2$, and recently HUMPIDGE* $R/R_0 = 1 + 0.027t - 0.0000019t^2$; with these we may compare my formula.

From these we deduce, as on p. 165 :

BENOIT took the boiling point of cadmium to be 860° C., instead of about 770° C. But the discrepancies in the values of S seem too large to be entirely attributable to errors of observation.

Formulae of extrapolation, unless very accurately verified through a wide range, are unsatisfactory, since they disagree so widely at high temperatures, and a very small change in the data from which they are calculated makes a great difference in the value of the coefficients ; whereas, if instead a formula of the type $R/R_0= 1+\alpha t$ were used, it seems probable that different platinum wires would give almost identical results.

In support of this, the reader is referred to the " *Comparison of platinum wires*" (p. 200). For the value of α in this formula we substitute the mean coefficient between 0° and 100° C. For instance, in the present paper we use the formula (a) ,

$$
pt = \frac{R - R_0}{R_1 - R_0} 100, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(a)}
$$

and call the temperature so calculated " *temperature by platinum wire,"* just as we speak of " *temperature by mercurial thermometer,"* although mercurial thermometers differ much more widely and irregularly from each other.[†] Temperatures so calculated will be strictly comparable, and the actual relation between platinum and absolute temperature may be subsequently determined by a more enlightened and skilful

* ' Roy. Soe. Proc.,' vol. 39, No. 239, Feb. 1885.

t See REGNAULT, 'Mémoires cle l'Institut,' tome 21.

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generation : meanwhile, the wire may be used, as a standard, and preserve the record for comparison with future determinations. And, since the range of the platinum thermometer is very great, and different wires may be accurately compared throughout their range, we may expect that by adopting such a standard we shall at any rate secure consistency in place of the discrepancies at present prevailing.

[An exponential formula of the type $\log R/R_0 = \alpha t/(1+\beta t)^2$ was found to represent the comparison of platinum and iron very approximately (see p. 202). If we assume from Series A.-III. the data $t = 100^{\circ}$, R/R₀ = 1.3460: $t = 500^{\circ}$, R/R₀ = 2.6400, and calculate the values of the constants for platinum, we obtain $\alpha = 0.034259$, $\beta = 0.015290$. By an odd coincidence it happens that this formula satisfies almost exactly the observations at varying temperature in Series A.-II . Values of R calculated by this formula (e) are therefore given in Tables A.-II. and A.-III. for comparison.]

Comparison of Different Wires.

Different specimens of wire have very different coefficients ; when, however, the resistance-variation of one specimen of wire has been determined by direct comparison with an air thermometer as above described the resistance-variations of other wires may be compared with the standard by a method as accurate as the comparison of resistances, and practically independent of all knowledge of temperature. It is only necessary that the temperature should be approximately uniform and steady enough to allow observations to be taken. The method consists in winding the wires to be compared side by side on a cylinder of non-conducting material, such as clay, porcelain, or asbestos. By this arrangement we may be sure that their mean temperatures are the same, and we have only to measure their resistances several times in rapid succession when the temperature is steady, or oscillating slightly about a maximum., and take the mean of the observations. The resistance of the standard wire gives the mean temperature, which is the same for both coils. If, however, the resistance-variation of the standard wire be not considered known with sufficient accuracy, this does not affect the accuracy of the comparison as such ; the resistancevariation of the others is simply referred to temperature on the scale of the standard wire.

The simultaneous resistances are measured by precisely the same apparatus and the same method as before. They are therefore liable to the same errors and corrections ; that is to say, they are corrected for the resistance of the connecting wires and the temperature of the resistance-box : the latter is less material, since it affects both wires proportionately. The resistances are reduced to a unit at 0° C.; thermo-electric effects are especially to be avoided, and are, of course, eliminated as before.

That changes of structure may not occur, producing permanent changes in the resistance, the wire must be first annealed. To prevent chemical changes such as

* 'Mémoires de l'Institut,' torn. 21, p. 619.

oxidation, which would produce the same effect, the wires are sealed up in a hard glass or porcelain tube nearly exhausted, from which the air has been removed by substituting $CO₂$ or $N₂$.

The insulation resistance from one wire to the other can also be measured with the same bridge if less than a megohm. It may be neglected if it is greater than 100,000 ohms. This method affords also a fairly accurate means of measuring the temperature variation of the resistance of non-conductors, which begin to conduct electrolytically when heated. The chief difficulty is polarisation, but this may be avoided in the usual way.

It would, of course, be possible by this method of comparison to draw up very accurate Tables of the resistance variation of metals and other conductors referred to platinum as the standard. Such Tables would, however, be of little practical use, apart from the particular specimens of wire for which the comparisons were made, except in so far as they tended to elucidate the phenomenon itself. A Table of empirical formulae of the type $R/R_0 = 1 + \alpha t + \beta t^2$ has been published by BENOIT for most common metals.

The method of comparison was not adopted, as far as I can discover, in spite of its obvious advantages, and as he used different specimens of wire his results do not agree very closely with mine. It is, however, from a thermometric point of view that this method of comparison is of the greatest possible importance. For this reason we proceed to give full details of a comparison between two platinum wires. Since the same apparatus was used for all the comparisons it will be described once for all.

The Diagram of Connections (Plate 11, fig. 3) shows the double Wheatstone bridge arrangement adopted.

 $BC = 10$ The arm of the balance, AD , is divided in the ratio \overline{AC} = $\overline{1000}$, the adjustable resistances, AD, AE, are taken from post-office boxes, and may have any value up to 10,000. The sensitive galvanometer may be put in circuit between D and C, or C and E, or D and E, so that the resistances of either DB or BE, or their ratio, may be observed without the necessity of constantly altering the resistances in the arms AE, AD, except in so far as is necessary to follow the slow change of temperature. A complete observation of both resistances can be thus made in a few seconds. The actual arrangement of the apparatus is shown in Plan (fig. 4), which is lettered to correspond with the diagram. The ends of the wires to be compared are fused on to copper tails, and the junctions arranged close side by side at J to avoid the production of thermo-electric currents. F represents the rocking commutator in the battery circuit to eliminate any residual effects. The copper tails are in turn soldered to thick copper rods, passing, air-tight, through an indiarubber cork which fits the porcelain tube in which the wires are heated. The copper rods are amalgamated, and dip into mercury cups, numbered 1, 2, 3, 4, 5, on the plan. Cup No. 2 is connected by a* thick copper rod to the binding-screw, B, of the resistance-box. Cups 2 and 3

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are connected by a thick copper piece. Thick copper wires pass from D and E to Cups 1 and 5 ; C, D, and E, are connected to mercury cups *d, e, c,* into which the galvanometer terminals may be dipped. The porcelain tube and the apparatus for exhausting and heating it are not shown. The method of interwinding the wires is roughly indicated by the plain and dotted lines. To observe the resistance of the connexions, Cups 4 and 5 are short-circuited, and the resistance B3J4D is measured. The copper tails corresponding to Cups 3 and 4 are fused together at their extremities, J, where they join the platinum wire ; by symmetry, therefore, this resistance represents that of the connexions, which may be taken to be the same for both coils, and is observed on each occasion, since it varies slightly with the temperature.

To test the insulation, the copper piece connecting 2, 3, is removed, and the resistance between the coils observed as a matter of precaution. The insulation was, however, found, in all cases, to be amply sufficient. The more nearly the wires are alike, the more accurate the comparison, since all sources of error affect both more equally. This is illustrated by the following comparison between two platinum wires, one of which was the standard wire, described previously, and the other was sent from Messrs. JOHNSON, MATTHEY, and Co., in reply to the request for the purest possible platinum wire. As was expected, their temperature coefficients nearly agreed. The ratio of their resistances was, in consequence, very nearly constant. Let R, R', denote the simultaneous resistances of the wires, and r their ratio, then we have, evidently,

$$
\frac{\mathcal{R}}{\mathcal{R}_0}-\frac{\mathcal{R}'}{\mathcal{R}'_0}=\frac{\mathcal{R}}{\mathcal{R}_0}\Big(1-\frac{r}{r_0}\Big).
$$

if r be observed accurately, an approximate value of R will suffice to give the differences of the temperature coefficients with all the accuracy of which the resistance-boxes are capable. It is evidently unnecessary to correct the value of r for changes of temperature in the resistance-boxes. Errors will, however, be introduced by any want of uniformity in their temperatures, or in the material of which the various resistance coils are composed. Precautions were therefore taken to maintain the temperature of the boxes as uniform as possible. Since r is very nearly constant, the term $\left(1-\frac{r}{r_0}\right)$ is always very small; consequently,

The correction to be applied to the observed value of the ratio r to allow for the *z*resistance of the connexions is taken as $(r-1)^{\frac{r}{k}}$, where z is the observed resistance of the connexions ; this is sufficiently approximate, since *z* is small.

The great advantage of the method of ratio is that the observation affects both ocils simultaneously ; moreover, when the ratio is nearly constant, the reduction of observations is much more simple, and may be effected with sufficient accuracy by the aid of a small slide-rule, since it depends on small differences.

The following Table is given to show the method of recording observations, and practically explains itself. The letters M, E, refer to the resistance-boxes used. The galvanometer throws are given in scale-divisions, and could be read with great accuracy

for the purpose of interpolation. The close agreement of the values of the ratio r , obtained from different resistances and at considerable intervals, shows the accuracy of the resistance-boxes and the reliability of the method. Observations taken at lower temperatures were even more concordant. The porcelain tube was enclosed in an iron tube to render the temperature more uniform and steady.

The following Table X. shows the reduction of some of the observations. The first pair of observed resistances are reduced from the observations recorded in the previous Table. The difference of reduced resistances is found by the simplest possible reduction from the corrected ratio by means of the formula

$$
\begin{pmatrix}\textstyle\frac{\mathbf{R}}{\mathbf{R}_0}-\textstyle\frac{\mathbf{R}'}{\mathbf{R}_0'}\end{pmatrix}=\frac{\mathbf{R}}{\mathbf{R}_0}\hspace{-0.5mm}\Big(1-\frac{r}{r_0}\hspace{-0.5mm}\Big).
$$

The value of R/R_0 is only approximate, and the difference of the mean coefficients $\left(\begin{array}{cc} \mathbf{R} & \mathbf{R} \end{array} \right)$ $(a - a)$ is found by dividing $\left(\frac{R}{R} - \frac{L}{b} \right)$ by the approximate value of the temperature. The mean coefficient of the standard wire is assumed to be constant, and the relative variations of the other tabulated ; the column of temperatures is calculated by assuming for each wire a constant coefficient equal to the mean value between 0° and 100°; the difference column shows how very closely the two platinum wires agree: although their temperature coefficients differ about 3 per cent., yet the temperatures deduced by using either wire agree to nearly 1 in 1000. Several other observations were taken at different times with the same comparison coils ; they all agree within the limits of error of the resistance-boxes. No zero variation of either wire could be with certainty detected ; and observations taken with the temperature varying at the rate of 10° per minute agree to 1 in 5000 with the best.

TABLE P.-I.—Showing Reduction of Observations by Ratio Method.'

* For improved method of reduction, see Appendix, p. 225.

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Comparison of Platinum and Iron.

The comparison of platinum and iron is interesting because iron behaves so peculiarly. A considerable number of comparisons were made by different methods ; the most accurate is the last series, VI., for which the same apparatus was used as in the comparison of two platinum wires. All the series, however, agree with each other as nearly as can be expected, considering the different modes of treatment, and that ordinary commercial soft iron wire was used.

The first experiments were made at the beginning of November, 1885, with unannealed iron wire wound side by side with platinum on a strip of asbestos board, and heated in an air bath up to 200° C., a mercury thermometer being used to show when the temperature was steady.

The following simultaneous values of the resistances were observed :-

Afterwards the wire was partially annealed, and the same coil was heated in paraffin in the same air bath, with the following results :—

In order to command higher temperatures, a new comparison coil was made and enclosed in an exhausted tube, to prevent oxidation of the iron, which was first carbonised by annealing in coal gas ; the whole was heated in an iron tube by a regulated gas furnace. The following observations were taken :-

To investigate more particularly the effect of annealing, another comparison coil was wound with the iron wire unannealed, and observations were taken with it up to 100° C., with the following results :—

Before annealing, the resistances at 0° C. were :---Resistance of iron, 5°001 ohms; resistance of platinum, 9°887. After annealing, resistance of iron, 5°557 ohms; MDCCCLXXXVII.—A . 2 D

platinum, 9°886. So that the resistance of the iron was considerably increased, while that of the platinum remained practically unaltered. The following observations were then taken :—

They show how slightly the temperature coefficient was affected by annealing.

Curve I in the diagram, Plate 13, fig. 11, is constructed from the followingobservations, which were taken by heating platinum iron comparison coil in a vacuum in a porcelain tube which was continuously exhausted to remove the steam which is given off by the clay when first heated, and which vitiated the previous series.

Many other observations were taken with the same apparatus at different times. The resistance of the iron, when once annealed, was not found to be much permanently altered if due precautions were taken.

The curve representing these and other observations belonging to the same series at once suggests an exponential formula. If we assume that the resistance variations of platinum and iron may both be represented by formulae of the type

$$
\mathbf{R}=e^{\frac{\pi i}{1+\beta t}},\qquad \qquad \ldots \qquad \qquad \ldots \qquad \ldots \qquad \qquad \ldots \qquad \qquad (e)
$$

and if R_1 , R_2 , be any two observed values of the resistance of the platinum coil, and R_1 , R_2 , those of the iron coil observed simultaneously, we shall obtain at once, by equating values of the temperature for each observation, the conditions

$$
\frac{\alpha}{\log R_1} - \frac{\alpha'}{\log R_1'} = \frac{\beta - \beta'}{\log e} = \frac{\alpha}{\log R_2} - \frac{\alpha'}{\log R_2'}
$$

$$
\frac{1}{\log R_1} - \frac{1}{\log R_1}\Big) / \Big(\frac{1}{\log R_1'} - \frac{1}{\log R_2'}\Big) = \frac{\alpha'}{\alpha} = \text{constant}
$$

Whence the ratio

$$
\left(\frac{1}{\log R_1} - \frac{1}{\log R_2}\right) / \left(\frac{1}{\log R_1} - \frac{1}{\log R_2}\right) = \frac{\alpha}{\alpha} = \text{constant}.
$$

By taking for R_1 , R_2 , the extreme values at either end of the series

we obtain the mean value of the ratio $\frac{a}{\alpha'}$ for the whole series to be

$$
\frac{\alpha}{\alpha'} = \dot{.}75037.^{\circ}
$$

* By some oversight I used the value * 75034 in the calculations.

Testing the observations in pairs by this condition, the value of the ratio is found nearly constant ; a small deviation from the curve produces a large variation in the ratio, which is a ratio of small differences, and is of course immediately deducible from the differential equation corresponding to Formula (e) .

The comparison gives the values of the ratios $\alpha : \alpha' : (\beta - \beta')$, but not the absolute values of the coefficients. Its accuracy is not therefore affected by that of the particular values assumed for the standard wire constants a and */3.*

If we take the observations on the comparison of two platinum wires and treat them in the same way, we shall find, from observations (l) and (5), the mean value of the ratio

$$
\frac{\alpha'}{\alpha} = \cdot 97295.
$$

So that, if we assume $\alpha = 0.034259$,

$$
\alpha' = \cdot 0033332.
$$

From this we obtain

$$
\beta - \beta = 00000343,
$$

so that, if we take the value of β previously found, namely, β = 0015290, we shall find

$$
\beta = 0.015256.
$$

So that β' is nearly equal to β .

If $\beta = \beta'$, we have evidently $\frac{\log R}{\log R'} = \frac{\alpha}{\alpha'}$. R and R' being the values of the resistances at the same temperature.

For iron, assuming the same values of α and β , we shall find

$$
\alpha' = 0.045657, \qquad \beta' = 0.007767.
$$

The chief difficulty of the comparison is that of protecting the iron wire from alteration when it is maintained at a red heat for some time. In Table XI. the observations given in Series VI. are compared with the above exponential formula (e) . The observations were mostly taken on different days, and the resistances observed at the air temperature in the intervals show the direction in which the correction for zero variation should be applied, but not its amount. It is noteworthy that in all cases the correction for this would tend to reduce the small differences between the formula (e) and the observations. As it is, the mean difference is only 0° C.

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TABLE XI.-Comparison of Platinum and Iron.

It does not appear that any equally simple and convenient empirical formula could be found to represent the observations so closely. [For the explanation of the small deviations, see Appendix, p. 228.]

Comparison of Platinum and Tin.

Pure tin wire, diameter '025 centim.

Coil wound on cylinder of asbestos in paraffin in a glass tube.

Resistance of copper connexions -0150 B.A.

Resistance in melting ice of platinum 7'8113, of tin 3'2425.

In hypsometer steam at 100-34, platinum 10*520, tin 4-7268.

Insulation resistance at 200° C., 170,000 B.A.

Insulation resistance at 0° C., 300,000 B.A.

TABLE of Results; Means reduced.

The temperature coefficient of this platinum coil, taken from the observations in ice and steam, comes out "003462 : almost, within the limits of error, the same as for other specimens from the same reel. The chief difficulty encountered arose from the softness of the tin near its melting point. The last observation is rather uncertain, as the metal gave way before the temperature was sufficiently steady. The coil was

mended, but the wire gave way again below 100° C. It was, therefore, decided to try by a slightly different method, and in particular to protect the wire from strain. Some difficulty was found at first in fusing the fine tin wire on to the copper connecting wires. Solder was evidently inadmissible if the experiments were to be pushed up to the melting point of the tin.

The tin resistances, calculated from the formula

$$
R/R_0 = 1 + 0.04323t + 0.0000260t^3
$$
, whence $R_1/R_0 = 1.4583$,

for purposes of comparison, show that, as might be expected, the observations between 0° and 100° are very consistent and continuous. It is probable, however, that, as the last observation seems to indicate, the simple formula will only represent the observations well between narrow limits.

Other formulæ for tin are :-

BENOIT :—R/R₀ = 1+ '004028t+ '000005826t², whence R₁/R₀ = 1.4611. MATTHIESSEN : $-R_0/R = 1 - 0.036029t + 0.00006136t^3$, whence $R_1/R_0 = 1.4262$.

Effect of heating Wire in a Bunsen Flame.

A small spiral of the standard platinum wire was made, having a resistance of about 1 ohm, and its ends fused on to short lengths of stouter platinum, and these on to thick copper leads.

Resistance of the whole, cold, at 16°'0 O., 1-0496 B.A.

Resistance of copper connexions, about '0140 B.A.

The fine coil was raised to a bright orange (in full daylight) by being immersed in a solid FLETCHER gas flame; its resistance varied slightly on either side of 4°81 with varying draughts of air ; half the thick platinum was heated red-hot. This was continued for about an hour. When the whole had cooled again to the temperature of the air, which had risen to 16°'2 C., the resistance was measured, and found to be 1 0502 B.A. The increase is almost exactly accounted for by the higher temperature. Readings were then taken for some time with the coil in various parts of the flame, and with different states of flame, with the following approximate results :-

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In this experiment the wire is radiating freely, so that it attains, *not* the temperature of the flame, but a point at which the loss of heat by radiation balances the heat received from the impact of the burning gas. The more rapid the current, the higher the temperature reached ; this accounts partly for the higher temperature to which the spiral was raised in the edge of the flame, where the current is much stronger as well as the supply of air better. By suitably screening the wire it would probably be possible to raise it to a higher temperature. The temperature can only be roughly estimated by the radiation, because the latter is selective. If the wire be blackened (platinised) it appears much brighter, because it radiates better, but it is for that very reason not so hot, as the measurement of its resistance shows.

APPENDIX.

Received June 9, 1887.

Since the foregoing paper was communicated to the Royal Society, so many more extended and accurate experiments have been made that it was thought desirable to delay the publication of the paper for a few months, in order that some account of them might be included. It was felt that this would render the paper more useful without adding excessively to its length. The observations with the air thermometer in particular have been rendered more accurate, so that the temperature may be determined by aid of the platinum wire with a probable error of less than a degree at 600° C. A much improved method of representing the results graphically has also been, adopted (see Plate 13), which shows at a glance the kind of accuracy attained. More accurate and extended comparisons tend to confirm the general conclusions from the earlier experiments : that the curves of resistance-variations of different wires of the same metal are similar, but not coincident ; that the usual parabolic formulée give an accuracy, of the order of 1 per cent, only, through a range $0^{\circ}-600^{\circ}$ C.; that the deviations therefrom are not readily expressible by any simple formulae.

Considerable improvements have been made in the primitive apparatus. An improved form of gauge was devised and ordered about the middle of June 1886, which was subsequently found to work well and to possess many advantages over the primitive kind ; the principle was exactly the same as that described on page 172, but the mechanical provisions were more complete and perfect. They will be readily understood on reference to the diagram, fig. 6, Plate 12. The sulphuric acid U-gauge proper is represented by the tube $FGHJK$; it has a three-way tap T_1 , which may be turned in the middle of the acid, so that it cannot move either way, whatever the variations of pressure : this is a most important practical improvement.

The requisite amount of acid is introduced through the side-tube P_1 , and the scale

FG should be adjusted so that the acid stands at zero when the pressure is the same on either limb of the gauge at F and K.

In addition to the U-gauge there is another connection between the air thermometer C and the manometer W by way of the bulbs A, M, N, which is filled with pure dry mercury, and is used for observations at constant pressure, for calibrating the bulb with air on the method of the volumenometer, and as an open way through which the bulb may be exhausted and refilled with dry air. It communicates by a three-way tap T_2 with the manometer and P_2 ; and by T_3 with P_3 , and through a long rubber tube with a mercury reservoir Q, which may be adjusted at any height, and which communicates with the outer air through a drying tube R containing $CaCl₃$ and glass wool to keep out damp and dust. Mercury may be introduced or withdrawn *to any extent* by aid of the reservoir Q, whose height is adjusted to suit the pressure, or in *weighed quantities* by the tubes P_3 , P_5 , which dip into weighed beakers of mercury.

The bulbs M, N, H, J, in the figure are convenient for taking up leakage, and other practical details.

To determine the pressure correction in terms of mercury corresponding to each reading of the scale FG, the way AMN is cleared by drawing off the mercury into the reservoir Q, the tap T_3 is turned off, and T_3 turned thus (T) , and P_3 is connected with the open air through the drying tubes, so that the atmospheric pressure is communicated by way of P_2 to the F-limb of the U-gauge. Readings of the manometer and the gauge FG are taken at various adjustments, from which the probable error of a single pressure observation and the pressure correction are easily deduced ; capillarity is thus eliminated.

To dry and fill the air thermometer, the bulb is maintained at a temperature between 400° and 500° C., W is connected to the exhaust, and P_2 with the dry-air supply. By means of the three-way tap $T₃$ the bulb is connected alternately with either. Mercury is re-admitted to fill the bulb A, when the operation is considered complete.

To take observations at constant pressure, mercury is allowed to run out from the bulb Λ into the weighed beaker at P_3 , till the sulphuric acid gauge indicates that the pressure is approximately that of the air. The scale FG gives the small variations of pressure, and the weight of the mercury the auxiliary volume. The temperature of the bulb A is carefully observed, and is kept steady by being surrounded with a water reservoir. Total volume of Bulb A from S to $S' = 48.162$ c.c. at 15° C.

The gauge above described arrived about the beginning of August, 1886 . A new thermometer, No. 5, was at once made of hard glass, similar to No. 3, the expansion of which was known.

There are some difficulties in mounting an instrument of this description. The mounting of No. 5 is diagrammatically illustrated in fig. 7, Plate 12. The bulb is fitted with asbestos board in a brass tube AD, into which is screwed a smaller tube DC which carries and protects the electrodes of the spiral and the delicate capillary

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tube of the thermometer. The tube DC is soldered through a biscuit tin, which is filled with water, renewed periodically, to keep the tube cool and the conditions uniform. Another brass tube with a cap at A slides over AD, so that the glass bulb is completely protected. The electrodes of the spiral go to mercury cups 1, 2, 3, 4, into any of which the conducting wires from the resistance-boxes may be dipped. R_{13} or R_{13} gives the resistance of the spiral and connecting wires. R_{24} gives the resistance of the double electrodes, which is by symmetry twice that of the connecting wires. The resistance of the thick copper wires between the mercury cups and the boxes was measured. In Series IV. it was '0077 ohm, in Series V. '0164 ohm. The apparatus was heated in a very thick iron tube in a Fletcher tube furnace. The gas could be adjusted by a screw tap with a graduated head, and might be used with an air blast for obtaining higher temperatures.

For heating in steam a special pattern hypsometer was employed with a double jacket, through which a copious supply of steam was made to circulate from a boiler. The brass case AD of the thermometer should be made steam-tight, so that the steam cannot penetrate into the tube CD.

Air thermometer No. 5 was an improvement on No. 3 in several respects. The volume of the bulb was four times as large $(V = 63.3 \text{ c.c.})$. A double electrode of fine wire was sealed through the glass, so that no part of the spiral itself was outside the bulb.

The spiral was made of a different wire, diameter '013 cm., length 2 metres, resistance 20 ohms. It was therefore long and delicate. This proved a misfortune ; for some one, in inspecting the instrument in my absence, after it was made, held it in a vertical position and deformed the platinum spiral completely, so that it was not uniformly distributed throughout the length of the bulb. This could not be cured without making the whole instrument afresh, and was probably a serious source of error whenever the temperature was at all unsteady (see Observations (11), (13), Series Y.). The observations were taken precisely as before, perhaps with greater care and skill, acquired by experience. The electrode which passed out through the capillary tube consisted of 6 in. of Pt wire, diam. '036 cm., fused on to 12 in. of Cu wire, No. 26 B.W.G., dipping into mercury cup 1 (fig. 7). It was of necessity single. A double electrode was made of the same wires, exactly to imitate it, and coated with the same hard glass for insulation, and placed in close proximity to the capillary tube, inside the small brass tube CD (fig. 7) which carried the thermometer. Its position must be carefully adjusted, for any want of symmetry or misplacement of the imitation electrode may introduce apparent errors in the resistance measurements. The other double electrode consisted of a short length (10 cm.) of fine Pt wire, to the middle point of which the end of the spiral was fused : the fine wire was bent double and fused through the glass at A (fig, 7), and its two ends projecting were fused on to thicker ('096 cm.) Pt wires, coated with hard glass for insulation, and extending as far as the Cu-Pt junction of the other electrode inside the brass tube CD (fig. 7), where they were fused on to No. 20 Cu wire leading to the mercury cups 2, 3. By

this arrangement of the junctions thermo-electric effects were rendered almost inappreciable in spite of the great sensitiveness of the apparatus and the low resistance of the galvanometer. The correction for resistance of connections, owing to the use of so much fine wire, amounted to nearly 3 per cent., but it was measured on each occasion, and could be very accurately applied.

With the instrument above described upwards of 130 independent observations in several sets, at various steady temperatures, were taken during the days August *7* to 12, 1886. They were worked out on much the same plan as that explained below on page 218.

To save space, only the observations at steady temperatures are given in Table A.-IV . The experiments were interrupted on August 12 by the cracking of one of the glass joints of the gauge ; an attempt to mend it only made matters worse. It was sent to the maker (MÛLLER, of 89, Whitfielcl-street) for repairs ; and meanwhile other experiments were undertaken. The breaking of the gauge was particularly unfortunate, as I had so far taken no observations at constant pressure, for which the gauge had been specially designed. A great many observations were taken with the temperature varying to test the working of the apparatus ; these on reduction were never found to differ by more than a degree from the curve, and often happen to fall exactly on it. To insert them would only confuse the diagram. The earlier observations of Series IV., which were taken just after filling, before the apparatus had reached a steady state, give results which are too high by two or three degrees. This is an error of the air thermometer, and not due to change of the resistance of the platinum ; for the observations in ice and steam show that the platinum spiral suffered no change during this series of observations ; but the value of the constant *mk* fell slightly, probably owing to surface absorption. The air thermometer was filled with dry air on the 9th August, at a temperature of 350° C., after repeated exhaustion ; and it seemed probable that there would be a tendency for the air pressure to fall rather fast at first, owing to surface condensation ; between observations (3) and (4) the gas was left unaltered for $3\frac{1}{9}$ hours. The change in the difference column from 7.9 to 7.1 is in the direction of absorption, but condensation probably took place most rapidly as the instrument cooled at lower temperatures. The historical element seems to enter here : the dates and times of the observations are therefore given ; heating gradually dissipates the air-film, which may take some time to condense again, so that an observation *(e.g.,* No. 12) taken at a lower after a higher temperature may give results which are too high ; but this requires further investigation.

The later experiments seem to throw doubt on the suggestion offered a year ago (p. 181) as to the value of $\sigma_1 - \sigma_0$ explaining discrepancies in the values of the coefficient of dilatation according to different observers : the apparatus is not particularly suited for determining the absolute value of the constant θ_{0} , which depends on the *difference* of pressures in ice and steam, on which the probable error with my apparatus may amount to a quantity of the order of one in a thousand.

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[To exclude errors of this nature, and to render the observations of different series strictly comparable, the value of θ_0 assumed must be the same throughout, since the value of t deduced varies directly as that of θ_0 assumed. All the observations entered on Plate 3, fig. 1, are therefore reduced, assuming the same value of $\theta_{\rm o}$, namely, 272'90° C., which corresponds to a coefficient of dilatation for dry air of •0036642 per 1° C. This agrees very closely with REGNAULT, and is deduced from the pair of observations (16), (17), Table A.-v. An inspection of the values of *mk,* calculated with this coefficient from the observations in ice and steam, and at the air temperature, from day to day, will show that it satisfies all the observations practically within the limits of error of the pressure measurements, The largest discrepancy between observations *on the same day* (Table A.-v., March 8, observations (25), (26)) amounts to nearly 1 in 2000.]

The variations of *mk from day to day* are sometimes larger, and more unaccountable ; they are generally in the direction of absorption, but I have so far been unable to reduce them to rule. The difficulty is to a great extent avoided by observing *mk* frequently and using the appropriate value in the reduction of the day's observations : this method must, in part at least, eliminate the error, to *whatever* cause it is due.

Time.	Auxiliary thermo- meters.	ltesistances observed.		H_2SO_4 gauge.	Mercury manometer.		Barometer and		Results.
		Spiral.	Connec- tion.	α	\mathbf{M}_L	\mathcal{M}_n	attached thermo- meter.	Number of observation.	
Aug. 7	R. 19-7	$20 - 437$	1.062		Before filling aily		therm ometer	(1)	$R_n = 19.945$
Аug. 9 11-12 л.м.	A. 20.5 R. 188 M. 21.5	43.435 \mathcal{L} Mean of	2.021 A Text several	3.51 4.4.	$ M_n - M_n =$ observations.	$+7.721$	30-085" 70-2° F.	(2)	$pt = 333.5^{\circ}$ $t = 350.5^{\circ}$ $d = 17.0^{\circ}$
12.8 12.13 12.17 12.22	R. 193 A. 20-7 M. 21 4 $\frac{1}{2}$	36.64 36:51 36.42 $36 - 30$	$+11$ 1.730 $\ddot{}$ $\dddot{\bullet}$	3:70 2.60 1.87 3.32	48.09 48-11 48.10 $45 - 23$	41.55 41.52 41.51 38.07	30.075" 70.7° F.	(3)	$t = 240.4^{\circ}$ $pt = 232.5^{\circ}$ $d = 7.9^{\circ}$
3.30 3.41 3.48 3.52	A. 20.6 M. 20-9 R. 19-3 557	36.79 $36 - 75$ 36.73 36.76	35 1.756 55 $\mathcal{F}(\mathcal{A})$	3.40 $3 - 20$ 1.05 1.25	34.87 34.86 36-26 $36 - 26$	28.56 28:54 $30 - 42$ $30 - 41$	30.052" 71.7° F.	(4)	$t = 243.7^{\circ}$ $pt = 236.6^\circ$ $d = 71^\circ$

TABLE A.-IV.—Comparison of Platinum and Air Thermometers.

TABLE A.-IV.—Comparison of Platinum and Air Thermometers—(continued).

About the middle of February, 1887, the whole apparatus was thoroughly revised, improved in several minor details, and set up afresh. The gauge had meanwhile been mended and improved. A slight error in the position of one of the comparison electrodes was rectified, and the spiral made more uniform by cutting off a short portion and refixing: it was partially re-arranged by means of a wire introduced through the open end.

In mending the gauge, the tube DG had been made of larger bore ('0127 c.c. per cm.), so that it was necessary to affix a scale S and record the reading x' . The bore of the new gauge tube was 0.232 c.c. per cm. instead of 0.407 , as in Series IV., and the scale read 2:30 when the pressure was the same on both limbs of the gauge. In Series IV. it had been adjusted to read zero, but it was not considered worth while to adjust it afresh. A new legal ohm-box was used to measure the resistance in place of the B.A. box used in Series IV. The observations in the following Table $(A,-v.)$ were then taken in the order in which they are given \rightarrow

TABLE A.-V.--Comparison of Platinum and Air Thermometers.

TABLE A.-V.-Comparison of Platinum and Air Thermometers-(continued).

TABLE A.-V.-Comparison of Platinum and Air Thermometers-(continued).

TABLE A.-v.-Comparison of Platinum and Air Thermometers-(continued).

Explanation of the Tables.

The dates and times are given to show the sequence of the observations, the rate of variation of the temperature, to indicate how far the results may be relied on, and to trace the historical element.

The auxiliary thermometer readings are corrected for zero error. A. gives the temperature of the air near the gauge ; R., of the air inside the resistance-box; M., of the mercury of the manometer. The box used in this series of experiments was a

legal ohm-box by ELLIOTT, nominally correct at 18° C. , to which temperature the resistances are reduced. The temperature coefficient of the box was determined to be '00023 per 1° C., the coils being of platinum-silver wire. The relative values of the resistances were correct to more than 1 in 10,000.

The resistances observed are given in legal ohms, but have to be corrected for the temperature of the box R. The correction for the resistance of the connecting wires is $\frac{1}{2}R_{24} + 0.08$.

By observing also the resistance R_{34} of the capillary tube electrode, the mean temperature of the corresponding 15 cm. of the capillary tube could be determined, and an allowance for its varying temperature approximately made by reckoning part with the bulb and part at air temperature. In most cases the temperature was varying; and an exact balance was observed with the rocking commutator as previously described, and the simultaneous reading *x* of the U-gauge was recorded. When the temperature was too steady to admit of this a fifth figure was obtained by observing galvanometer throws and interpolating. The column headed *x* gives the reading of the level of the mercury by the scale S. In taking observations at constant pressure, mercury was allowed to run out from the bulb A (see fig. 6, Plate 12) and weighed in a beaker. The observed weight in grammes W. of the mercury and beaker is given in the manometer column ; the manometer was of course unnecessary in taking observations at the atmospheric pressure. The temperature indicated by a delicate thermometer immersed in the water surrounding the bulb A is then given in the *x* column. The readings given of the thermometers and barometer are mean or typical readings : all are not given, to save space. The observations are numbered to correspond with Plate 13.

No permanent change of resistance of the platinum wire was with certainty detected in this series of experiments, in spite of the prolonged heating to which the spiral was subjected, and although it was in contact with the glass of the bulb for a considerable portion of its length. The apparent change of temperature coefficient from $R_1/R_0 = 1.3391$, Series IV., to 1.3395, Series V., was probably due to the fact that the position of the loose comparison-electrode was shifted so as accurately to correspond with the single electrode inside the capillary tube ; it had been accidentally misplaced through an error in measurement in Series IV. The apparent change in the value of R_0 in Series A.-v. from 19'674 to 19'668 (the latter value exactly was observed again one month latter, on April 18) was probably partly due to a change in the comparisonelectrode, the copper portion of which was accidentally fused in re-coating with hard glass on March 4, so that it had to be re-made, and its resistance was slightly increased ; and partly, perhaps, to a change in the plug contacts in the 10-ohmarm of the bridge, which were thoughtlessly altered on that day to measure another resistance. The value $R_0 = 19.668$ should, of course, be used in reducing the observations from March 4 onwards.

On March 4, while the bulb of the air thermometer was immersed in steam, it was MDCCCLXXXVII.-A. 2 **F**

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filled afresh with dry air at 103 cm. pressure, corresponding to a zero pressure of almost exactly one megadyne per sq. cm. By allowing the mercury to run out till the bulb A. was emptied, and again measuring the pressure, and assuming the formula $pv = mk \theta$, the volume of the bulb up to the Cu-Pt junctions was calculated to be $V_1 = 63.41$. A repetition of the same operation on March 8 with the same air gave the same value.

The observations were all reduced, assuming $V_0 = 63.29$ as the volume of the bulb at 0° C., and its expansion to be that given by the formula on page 168 (linear expansion of glass). The correction for glass expansion amounts to nearly 12° at 600° C., and must be considered subject to greater uncertainty than the other elements of the calculations ; the apparent discrepancies between observations at constant volume and pressure may be in part due to errors of this nature.

The methpd of approximation used in previous portions of the paper in working out the results fails in the case of observations at constant pressure. Latterly I have used a Fuller's spiral slide-rule, which gives results correct to 1 in 10,000 at least. This is so exceedingly expeditious and convenient that the formula may be worked out directly with great rapidity. If *p* be the pressure of the air enclosed, Y the volume of the bulb, θ its temperature, and v any other portion of the volume which is at temperature θ' , the formula of the air thermometer may be stated thus—

$$
p \{ \nabla/\theta + \Sigma(v/\theta') \} = mk, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots
$$

where Σ implies that the summation is extended to all portions of the apparatus occupied by the mass of air under observation, and *mh* depends on the mass of air enclosed, and is theoretically constant for each filling. To make the statement more definite, we will define θ to be such a function that the above equation is true, p being constant and equal to one atmosphere: θ is, then, the temperature by normal air thermometer at constant pressure, and is nearly equal to the absolute temperature on the thermo-dynamic scale.

From Formula I. we obtain, as the value of θ ,

$$
\theta = \nabla / \{ mk/p - \Sigma(v/\theta) \}.
$$

To illustrate the corrections involved, we will proceed to calculate Observation (5) :-

Mean value of resistance observed, 54'909 legal ohms. Correction for connecting wires, $2.516/2 + 0.08 = 1.266$. R corrected, 53.643. Temperature of box, 16.9. Temperature correction $= - (54) (11) (00023) = -014$. R corrected, 53.629. $R/R_0 = 2.7258$. Assuming $R_0 = 19.674$ from Observation (16),

$$
pt = (R/R_0 - 1)/0033947 = 508.4^{\circ}
$$
 C.

Resistance of capillary tube electrode, $R_{34} = 750$. Resistance of the platinum portion, '690. Mean temperature, 340°. 5.2 cm. of this portion of the capillary tube is therefore reckoned at air temperature, the remaining 10 cm. at the temperature of the

bulb. Thus :—5.2 cm. $= 15 (508 - 340)/(508 - 18)$. The volume of this portion (5'2 cm.) (by curve constructed from calibration data) is '030 cub. cm. This has to be deducted from V_{0} , the volume of the bulb, and added to v, the volume at air temperature.

The volume of the bulb up to the platinum-copper junction of the electrode is calculated, assuming that air satisfies Boyle's Law, from the observations (20) and (26), both of which give the same result, $V_1 = 63'41$ c.c., $V_0 = 63'29$ c.c.

In our case $V_0 = 63.29 - 0.03 = 63.26$ c.c.

The glass expansion factor corresponding to $pt = 508.4$ is taken from the curve whose equation is given in the section on the expansion of hard glass, p. 168, $V = V_0 (1 + \gamma \theta) = (63.26) (1.0124)$. Small errors are less likely to be introduced if this correction is applied last of all to the value of θ .

To calculate the volume at air temperature $\Sigma(v/\theta) :=$

The volume from division $x' = 9$ of the scale S, and $x = 0$ of the scale FG, to the platinum-copper junction of the capillary tube electrode was determined by previous calibration to be 0*708 c.c., and is assumed to be, at the temperature of the air, $A = 18.2$; $\theta' = 291.1$.

The mean value of x, the reading of the gauge in Observation (5) , is 7.21 .

The corresponding volume is (7.21) (0.0232) = 167 c.c.

Thus $v' = 708 + 167 + 030 = 0.905$, and $v'/\theta = 0.003110$.

Mercury was allowed to run out by way of P_3 into a beaker till the difference between the pressures of the internal and external air came within the range of the $H_aSO₄$ gauge. The weight of the mercury and beaker was $W = 244.902$, that of the beaker 31°220. The same beaker was used in all the weighings here given.

Since the value of the temperature of the bulb A observed with the mercury thermometer G cannot be correct to more than 1 in 5000 (1/20 degree), it is needless to reduce the weight to *vacuo* or apply any of the other small corrections. The density of the mercury at 17°*55 O. being 13*553 grms. per c.c., the volume of 213.682 grms. is 15.668 c.c. Since the mercury stood at $x' = 9.2$ just before it was allowed to run out, we must add (2) ((0127) c.c. to reduce it to $x' = 9$.

Thus the auxiliary volume was 15.770 c.c. at a temperature

 $17^{\circ}55 + 272.90 = 290^{\circ}45$ C. by air thermometer.

Thus $v/\theta' = 0.54290$; $v'/\theta' = 0.03110$; $\sum (v/\theta') = 0.57400$.

The acid stood at 2*30 in the gauge when the pressure was the same in either limb, and by experiment it was found that the reducing factor 0*136 was required to give the pressure correction in terms of mercury. Thus the required correction in Observation (5) is $(7.21 - 2.30)$ $\cdot 136 = \cdot 670$.

The barometer reading reduced to centimetres is 77°659 cm., and the temperature] 6°'2 C. ; correction for temperature,— '228 cm. ; correction for level and capillarity, $+ 045$ cm.

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Correction for pressure of acid in gauge, $+$ '670.

Corrected value of pressure of air in thermometer, 78*146 cm.

The value of the constant *mk* was calculated each day by Formula I. from the observations at air temperature and at the fixed points, assuming the values $\theta_0 = 272^{\circ}$ 90 C., $V_0 = 63.29$ c.c. By observing the resistance of the platinum spiral the temperature of the air in the bulb could be very accurately deduced. On the morning of February 28 the value of *mk* observed was 10'578, Obs. (2), and next morning 10'577, Obs. (8). The agreement is very satisfactory, and perhaps closer than we have any right to expect, owing to the uncertainty of the pressure measurements. Using this value in Formula II., we obtain

$$
mk/p = 13535; \quad \theta = \nabla / \{mk/p - \Sigma (v/\theta)\} = 821^{\circ}6 \text{ C};
$$

$$
t = 821^{\circ}6 - 272^{\circ}9 = 548^{\circ}7 \text{ C}; \quad d = t - pt = 40^{\circ}3 \text{ C}.
$$

This value is' represented by the cross marked (5) on the curve of difference of temperature, Plate 13. All the observations in this series were calculated in this kind of way ; but, of course, the work was done on a regular systematic form, which ensured accuracy and rapidity, so that it should be free from serious errors.

Graphic Representation of Results.

The best method of representing the results graphically is that which REGNAULT adopted in his comparison of mercury thermometers, namely, that of drawing the curve of difference of temperature. This has the advantage of indicating all errors and deviations on a very large scale. In the curve diagram, Plate 13, fig. 9, the abscissa represents temperature Centigrade by air thermometer on a scale of 10° to $\frac{1}{4}$ -inch, and the ordinate the difference of temperature between the platinum and air thermometers at the rate of 1° to $\frac{1}{4}$ -inch.* On this scale errors of 1 in 10,000 are distinctly appreciable in the upper part of the scale, as they correspond to a distance of $\frac{1}{50}$ -inch or $\frac{1}{2}$ -millimetre. Observations taken near the standard pressure of 76°0 cm. in Series V. are represented by large crosses $(+)$; observations at other pressures by small crosses (x) . The Arabic numbers belong to Series V.; the Roman numbers to other series.

If the variation of R follows the parabolic formula

$$
R/R_0 = 1 + \alpha t + \beta t^2,
$$

we shall have $d = t - pt = \delta[(t/100)^2 - (t/100)]$, where $\delta = -10,000\beta/(\alpha + 100\beta)$. The parabola in Plate 4 corresponds to the value $\delta = +1.57$.

Since $\alpha + 100\beta = 0033947$, this gives $a = +0.034480$, $\beta = -0.000000533$, but the change of resistance does not seem to follow this law with absolute accuracy.

Observation (1) was taken within an hour pf drying the air thermometer by repeated exhaustion and re-admission of clean dry air at 550° C.

* The curves are reduced to half-size in the plate.

The value $mk = 10.578$ is assumed in its reduction. This is a little uncertain, because in Observation (2) the sun had been allowed to shine on half of the barometer in the room upstairs, causing the high reading 74° \overline{r} . of the attached thermometer, and rendering the temperature correction uncertain ; the same uncertainty, of course, applies to the reduction of Observations (3) , (4) , (5) , into which the same value of mk enters. A change of less than 1 in 1000 in the value of mk or V would suffice to account for the deviation of this group from the curve. Observations (4) and (5) indicate a difference of 1° C. between the values of the temperature by air thermometer at constant pressure and at constant density respectively at 540° C. This may be similarly due in part to errors in the assumed volume or expansion of the glass, or merely to changes in the temperature distribution between Observations (4) and (5).

Between 200° and 300° C. the observations seem to deviate in a regular way, as indicated by the dotted curve, from the parabola. That this deviation is not merely due to errors of observation is, T think, indicated by the curves of comparison of different platinum wires, which seem to show that the increase of resistance does not strictly follow the parabolic law, but is affected by some minor and comparatively unimportant variations which, from their very smallness (being of the order of 1° C.), are difficult to take account of otherwise than in a graphic record. Moreover, the observations in question were taken on different days and under different circumstances, so that it would be difficult to account for their agreement on any other hypothesis than that of some constant error affecting either the platinum or the air thermometer.

Observations (11) and (13) differ excessively from those in their immediate neighbourhood. On reference to the Table $A.-v.$, it will be noticed that they were both taken with the temperature varying much too fast for purposes of accuracy ; on the day in question the gas pressure was very variable, and it was difficult to get good observations at steady temperatures. Observation (11) was further vitiated by the fact that some of the water had leaked from the glass case surrounding the bulb A, and its level had been allowed to get too low. Observations (37) and (34) were taken at constant density, and differ from (35), (36), in the same direction and for the same reasons that (5) differs from (4). This apparent difference is greater than that indicated by theory, and may be due to some error in the value of Y, the volume of the bulb ; further and more careful experiments are required to clear up this point.

Observations at steady temperatures from the previous series of experiments (Tables A.-II, III., IV.) are entered in the diagram by means of small circles; they are seen to agree with the curve as well as can be expected, considering the various errors pointed out in each case to which the earlier experiments were liable. Had the observations been more complete, the agreement would probably have been more perfect. In order to render them comparable with the results of Series A.-v., the same value of the coefficient of dilatation, namely, $\theta_0 = 272.90$, has to be employed in their reduction in place of the coefficient $\theta_0 = 270.1$, which is used in the Tables A.-II. and III. in the earlier portions of the paper. This anomalous value of θ_0

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was probably due to an imperfection in the drying apparatus which I subsequently discovered. The exit tube from the last drying bottle was plugged with cotton and glass wool, to stop dust, so tightly that the air could not pass freely, and was connected to the apparatus by an old and rather rotten, piece of black seamed rubber tubing through which damp air probably leaked when it was suddenly connected with the vacuum of the air thermometer bulb. The whole drying apparatus was, therefore, set up afresh before Series A.-Iv. with new sulphuric acid U-tubes (prepared by STAS' method) and seamless solid rubber tubing, and the joints made perfect with hot paraffin wax. The whole was tested, and found to be perfectly air-tight.

Assuming that the anomalous value of $\theta_0 = 270$ ^o 1 was due to the presence of water vapour, the error may be eliminated beyond 100° C. by applying from this point onwards the usual value of the coefficient of dilatation for dry air, namely $\theta_0 = 272.90$. A correction $(t-100)^{\frac{3}{2}}$ has, therefore, to be added to the values of t given in the Tables A.-II., A.-III.

The values of *pt* require no correction, and are calculated, assuming the coefficient •003460.

Thus reduced, the latter observations in Table V., p. 192, become the following :-

TABLE A.-VI.

Mean error, 2.1° C.

The broken line on Plate 13, fig. 9, is used for deducing the temperature *t* by air thermometer from the formula

$$
t - pt = 1.57\{(t/100)^2 - (t/100)\},\
$$

the temperature *pt* being known by observation.

It gives at once the difference $(t - pt)$ in terms of pt as abscissa.

It is readily constructed by measuring off from each point of the first curve, backwards along the abscissa, a distance equal to one-tenth of the ordinate.

By using a curve like this an accuracy of $\frac{1}{10}$ th degree Cent, at 600° may be obtained in the *relative* values of *t* deduced from observations with a known platinum wire, or with platinum wires which have been compared with a known wire. The *absolute*

value of *t* may be in error to the extent of about 1°, as it depends on the air thermometer observations. These, however, may be rendered still more accurate, and the uncertainty further reduced ; they do not affect the claim of the platinum thermometer to rank as a *practical* thermometric standard.

The platinum air thermometer gives us the means of comparing theory with experiment, and of testing the accuracy of the formula

$pv = mk \theta$

at high temperatures by taking observations at various pressures in rapid succession, while the temperature is maintained nearly constant. The platinum spiral may at least be relied on to give any small changes of temperature which may occur. Nevertheless, for experiments of such delicacy it was felt to be necessary to maintain the conditions as uniform as possible, because any slight variation might introduce errors comparable with the differences that might be expected to exist between the indications of the air thermometer at constant pressure and at constant density.

Consequently, when on my return from India in February, 1887, I set to work again with the same glass air thermometer, a small gasometer was ordered in order to keep the gas pressure perfectly constant during any observation. This want had not been so much felt in August, when there were few students at work and little gas was being used ; but the unsteadiness of the gas pressure was a great source of annoyance during the series of observations given in Table A.-v., which were taken during February and March in full term time, pending the arrival of the gasometer. On one occasion the temperature rose 100° in five or ten minutes, owing to change of gas pressure. Such changes of temperature would have been less material, had the platinum spiral been uniform ; so that its mean temperature would have been more nearly that of the air enclosed. The gasometer arrived about the end of April ; it leaked badly, and had to be mended. After that it performed satisfactorily, and a few observations were taken at steady temperatures one morning with its aid. Unfortunately, the observations at constant density were pushed too far this time, and the capillary tube gave way at about 550° C. under two atmospheres' pressure.

Porcelain Air Thermometer.

For higher temperatures it is necessary to use an air thermometer of porcelain. The difficulties to be encountered are that the wire must not touch the glaze and cannot safely be fused through the porcelain air-tight at any point exposed to the high temperature ; and that the expansion of the material must be determined with some accuracy. To meet these difficulties, a somewhat peculiar type of instrument has been made.

A cylindrical bulb of porcelain, AB, Plate 12, fig. 8, 3 cm. diam., 200 c.c. capacity, opens at either end into thick side-tubes AC, BD, of small rectangular bore, 3 mm.

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by 1 mm. (one of which is shown in section, fall size, at E), which extend 6 inches on either side beyond the tube gas-furnace in which the bulb is heated. The sidetubes AC, BD, are fitted to contain double electrodes of thickish platinum wire, to the ends of which, at A and B, a single length of fine wire is fused, which extends through the bulb from A to B. By means of these double electrodes we can determine the resistance of the fine wire independently of its connections, and we can also determine the mean temperature of the side-tubes AC, BD. One end D is fixed and connected with wax to the tube of the pressure-gauge. The free end C is closed with wax, and observed by means of a reading microscope. The expansion of the bulb itself is thus simultaneously observed, and the electrodes pass air-tight at the points C and D, which are never heated. Moreover, the form of the bulb renders it suitable for heating in a tube gas-furnace, which is very convenient. \cdot

Comparison of Platinum Wires.

Owing to the importance, from a thermometric point of view, of the comparison of different platinum wires, another comparison coil was wound with greater precautions, to ensure perfect symmetry. The wires compared were pieces from the reels 1 and 3 used in making the platinum spirals for the air thermometers of Series III. and V. respectively. They were fused on to platinum electrodes and wound on terra-cotta slips, as previously described (pp. 199, 200).

The following observations were taken :—

An attempt was made to take an observation at a temperature of about 800°, but the insulation was not quite good enough ; the temperature was allowed to fall again, and the following observations were taken :—

•

Time.			Resistance observations.	Approximate temperature.		Difference	Number of	
Date.	Hour.	$R + z$	$(B + z)/(B' + z)$	'n	$p\bar{t}$		$p_{4} - p_{1}$	observation.
1886. Aug. 24 29 Ħ IJ $+1$ Aug. 25 In steam Ang. 27 $(In$ $ice)$	12 NOON to 1 P.M. 1 to 1.30 P.M. 1.40 to 2.20 p.m. 2.20 to 3 P.M. 6.30 г.м. 11.15 A.M. 12 NOON to 1.30 P.M. 11.30 A.M. to 1.30 P.M.	$15 - 55$ 14.83 12:96 10.88 5:51 5.398 6.800 5.0537	-61801 -61775 .61702 -61600 .61074 .61067 -61306 -60986	-0875 -0839 -0740 0635 -0384 -0379 $+0458$ -0357	603 562 455 335 $26 - 1$ $20 - 0$ 100·17 θ	. in 661 611 484 34.9 26 20 100-170 α	$+0.39$ $+0.45$ $+0.51$ $+0.50$ $+0.07$ $\ddot{\mathbf{0}}$ Ω	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$ (4) (5) (5) (8)

TABLE P.-III.

The value of *t* is taken from the curve $t - pt = 1.57 \{(t/100)^2 - (t/100)\}$. The observations are reduced as follows :—

Let R be the resistance of the wire pt_1 , R' that of pt_3 , r the ratio R/R', and z the measured resistance of the connecting wires.

Then
$$
r = (R + z)/(R' + z)\{1 + (r - 1)z/R\}
$$
 (z being small).

Let τ stand for 100/($R_1/R_0 - 1$), so that τ is a constant exactly analogous to θ_0 in the case of the air thermometer.

Then
$$
pt_1 = \tau_1(R/R_0 - 1);
$$
 $pt_3 = \tau_3(R/R'_0 - 1).$

And the difference $pt_5 - pt_1$ may be put into a form more convenient for calculation, namely,

$$
pt_3 - pt_1 = (\tau_3 - \tau_1) (R/R_0 - 1) - \tau_3 (R/R_0 - R/R'_0).
$$
 (T)

The small difference $(\tau_3 - \tau_1)$ may be accurately determined from the observations in ice and steam, for we have

whence

$$
1/\tau_1 - 1/\tau_3 = (R_1/R_0 - R'_1/R'_0) / 100 ;
$$

$$
\tau_3 - \tau_1 = \tau_1 \tau_2 (R_1/R_0 - R'_1/R'_0) / 100,
$$

and the small difference $(R/R_0 - R/R_0')$ is accurately given by the formula $(R/R_0 - R/R_0') = R/R_0 (r - r_0)/r$, where r is the ratio R/R'. The only quantity, therefore, requiring the fullest accuracy of observation is $(r - r_0)$, the change of r. Since this is small, approximate values of the others will suffice.

From the observations (1) and (2) of Table P.-II. the deduced value of $\tau_3 - \tau_1$ is 6°-36; from Observations (7), (8), Table P.-III., $\tau_3 - \tau_1 = 6$ °-23. These values are used in the reduction of Tables P.-II. and P.-III. respectively. A rise of zero MDCCCLXXXVII.—A. 2 G

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amounting to nearly 1° C. was caused in each wire by the half-hour's exposure to the temperature of 800° in contact with clay and in the presence of copper, and probably tin and zinc. The comparison at higher temperatures has to be effected by a different method to secure good insulation and guard the wire from contamination, but the experiments have not yet been completed. The results of the comparison are shown graphically in Plate 13, fig. 10. The dotted portions of the curves are somewhat hypothetical, but there is naturally a family resemblance between them. They all show a comparatively sudden change (due to pt_1) somewhere between 200° and 300°, which, though small in amount, is distinctly marked ; it is in each case followed by a flattening due to similar changes in the other wires, differing chiefly in phase. A similar deviation is also indicated by the most accurate of the air thermometer observations (see page 221). The differences between different thermometers of pure platinum wire are seen to be very small, and to be capable of accurate measurement. I do not think they can possibly be due to any constant error affecting the method of comparison, as I have been unable to think of any that would at all account for the observed phenomena ; but I have procured a stock of various specimens of platinum for more extended investigations.

Comparison of Platinum and Iron.

The comparisons of platinum and iron wires given in the earlier part of the paper were felt to require confirmation. The agreement with the exponential empirical formula was so close that I was inclined at the time to think that the deviations from it were errors of observation without meaning. Commercial tinned iron wire had been used (the tin having been removed with glass paper as far as possible), and sufficient precautions had not been taken to avoid oxidation. The wire had ultimately reached a very steady state, but not until it had become covered with a film of black oxide. A new comparison coil was therefore wound with *pure* iron wire and platinum wire No. 2. By an improved method of winding very good insulation was secured, and the wire was carefully heated in dry nitrogen and very little oxidised. (The steam which always escapes from the clay when heated probably produced the slight oxidation observed.) The results of this comparison are given in Table F.-II.; they are simultaneous mean values of the resistances deduced, as before, from several observations at steady temperatures.

To facilitate the comparison of the two series of observations, the' results of the first series are reproduced in Table F.-l., and reduced on the same plan as those in Table F.-n.

TABLE F.-L.-Comparison of Platinum (No. 1) and Commercial Iron Wire. (The observations in this Table are the same as those in Table XI., p. 206.)

The value of *t* is given by the formula

$$
t - pt = 1.57\{(t/100)^2 - (t/100)\}, \dots, \dots, \dots, \dots, (d)
$$

The value of the difference is calculated from the formula

$$
fe - pt = 15.0 \{(t/100)^2 - (t/100)\}.
$$

The temperature by iron wire is given by the formula

$$
f_e = 100 \frac{\text{R}}{\text{R}_0} - 1 \frac{\text{R}_1}{\text{R}_1} - 1
$$

where $R_1/R_0 = 1.5274$.

The formulae are as before, but the values of R_1/R_0 are different. (See Obs. (2).) The deviations are taken from the last column and set down on Plate 13, fig. 11 ; the abscissa is the approximate temperature by air thermometer ; the similarity of the curves shows that the resistance-variations of the wires are similar in character.

Herein we see the treachery of the common empirical formula. Had we only the

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observations in Table II., we might naturally suppose that the parabolic formula accurately represented the phenomenon, and that the numbers in the " deviation " column were errors of observation ; and regret that after all our trouble the results were so inaccurate. On the other hand, had we only the observations in Table F.-1., we might be carried away (as I was) with the idea that the exponential formula was the true solution of the problem, and that the small deviations were accidental, as in this case they very well might have been. But, having both series, F.-I. and F.-II., in every way independent, and yet exhibiting such a marked similarity, we are led to inquire what it means. Each curve is marked by a small subsidiary wave at about 400° before the final upward rush. This is not altogether fanciful, but is just such in position and magnitude as would be produced by an irregularity in the resistancevariation of the platinum of the order of 1° taking place between 200° and 300° ; for in calculating the value of t and $(fe - pt)$ we have assumed smooth parabolic formulas, which take no account of the small irregularities which are shown to exist by the curves of comparison of platinum wires, and one of which is indicated also by the air thermometer observations. In the curve F_{\cdot} -II, the phase of this subsidiary wave is retarded. Now the curve P.-1, containing the comparison between platinum wires (1) and (2) , which were used in the comparisons $F.-I$., $F.-II$., respectively, shows that the curve of pt_2 is affected by a deviation similar in magnitude and sign to that of *pt1}* but taking place about 100° later. If this curious correspondence of the curves had been foreseen, the comparisons between the platinum wires would have been made more extensive and complete, and, in particular, the form of the curves between 100° and 300° would have been carefully explored.

Professor TAIT has observed that at about a dull-red heat the resistance of iron increases very rapidly ; the thermo-electric and mechanical qualities of the metal also change suddenly about this point. It is well known that very slight impurities exert a very marked effect on the softening point of iron ; we need not be surprised, therefore, that the upward rush in the case of F.-II . does not come within the limit of observation, like that of F.-i. I propose to make a direct comparison between the wires F.-I. and F.-II. to confirm this. Unfortunately, my first impression on reducing the observations was that they disagreed completely ; the nature of the agreement was not noticed till the apparatus had been dismounted and the wires used for other purposes, so that no more observations could be taken with the same coils.

The curves F.-I. , F.-II., sufficiently illustrate the futility of applying empirical formulae calculated from observations between narrow limits for purposes of extrapolation. I have known cases where an empirical formula, calculated by the method of least squares from observations at *varying* temperatures with a *mercurial* thermometer between 20° and 100° C., has been applied to estimate temperatures above 1000°. This is an extreme instance of a method to be avoided.

Between the limits 0° and 500°, however, the parabolas—

$$
R/R_0 = 1 + 0.0045346t + 0.000007034t^8, \ldots \ldots \ldots \ldots \text{ II}.
$$

$$
R/R_0 = 1 + 0.0045658t + 0.000007082t^8, \ldots \ldots \ldots \ldots \ldots
$$

both of which correspond exactly to the formula—

$$
fe - t = 13.43 \left\{ \frac{(t/100)^2 - (t/100)}{t}, \right\}
$$

represent the resistance-variations of the wires I. and II. with an accuracy of about 1 per cent.

BENOIT gives for Iron—

 $R/R_0 = 1 + 0.004516t + 0.000005828t^3$; $R_1/R_0 = 1.5099$; for Steel— $R/R_0 = 1 + 0.004978t + 0.000007351t^2$; $R_1/R_0 = 1.5713$,

These correspond to

$$
fe - t = 11.43 \{ (t/100)^2 - (t/100) \} \quad . \quad \text{(Iron)}
$$

and

 $\hat{f}e - t = 12.87 \left\{ \frac{(t/100)^3 - (t/100)}{1000} \right\}$. (Steel)

respectively.

MATTHIESSEN, by observations between 0° and 100° with a mercury thermometer, found for very pure iron the formula

$$
R_0/R = 1 - 0.051182t + 0.00012915t^2,
$$

whence $R_1/R_0 = 1.6197$. But this kind of formula is quite inadmissible for extrapolation, as it makes R a maximum when $t = 198^\circ$. Between the limits 0° and 100° C. the formula of the parabolic type which agrees most nearly with it is

$$
fe - t = 12.74 \left\{ \frac{(t/100)^2 - (t/100)}{\ldots} \right\}.
$$

He similarly found for two specimens of commercial platinum, between 0° and 100°,

$$
R_0/R = 1 - 0.027225t + 0.00005776t^2 \t . \t (1); \text{ whence } R_1/R_0 = 1.2730.
$$

$$
R_0/R = 1 - 0.025777t + 0.00005054t^2 \t . \t (2); \text{ whence } R_1/R_0 = 1.2613.
$$

Wire (1) at 50° gives $pt = 50.70$. No. (2) gives $pt = 50.20$. These differ by half a degree, whereas the pure wires of Tables P give *pt —* 50'40 approximately, and differ by only one or two hundredths of a degree. MATTHIESSEN'S formula (L) makes R a maximum when $t = 236^{\circ}$, and is of course inadmissible for extrapolation.

Comparison of Platinum and Platinum-Silver Alloy.

This is of little interest, except that the platinum-silver wire is used for standard resistance-coils. It is quite unsuited for thermometry, because of its small coefficient and variable composition.

$$
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$$

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The resistance of the platinum-silver wire was found to be increased about 5 per cent, by annealing for three hours at a red heat till it reached a steady state ; while its mean coefficient between 0° and 100° fell from '000279 before annealing to '000236 after. For this reason it seems desirable that the wire used in the construction of standard coils should be well annealed.

The resistance-variation of this specimen of platinum-silver between 0° and 650° C. was well enough represented by the formula

$R/R_0 = 1 + 0002327t + 0.000000033t^3$.

Comparisons at High Temperatures.

The coil used in the experiments recorded in Table P.-L., p. 202, was tried in the porcelain tube alone, without the iron tube, at the highest temperature the gas-furnace would produce with the air blast. The insulation was too bad and the thermo-electric effects too large to allow of accurate measurements : and so, when the apparatus cooled, a copper tube was inserted inside the porcelain. On again heating the tube the thermo-electric effects had disappeared, but the resistance was found to change enormously. When cold, the resistance, of the wire was doubled, and it had become quite brittle. The copper tube came out as bright as if it had been heated in hydrogen ; metallic copper was deposited all over the cooler parts of the electrodes and terra-cotta ; the porcelain tube was bent with the heat. It is, therefore, necessary to try some other method at high temperatures. The apparatus is not yet complete, but promises well. I hope soon to be able to extend the comparisons accurately to 1000° at least.

NOTE.

[The experiments on surface condensation, mentioned on page 181, were not sufficiently precise to be applied to the case of the air thermometer ; they only served to confirm the results of recent experiments, to show that the phenomenon is dependent in great measure on the past history, and to emphasise the importance of eliminating aqueous vapour and $CO₃$. It has not been thought worth while to use Equation (E), p. 179, in the reduction of the observations, partly because they are not yet sufficiently accurate, and partly because it is doubtful whether Equation (E) itself is strictly applicable beyond the limits of the experiments on which it is founded. The corrections it involves are of the same order as the errors of observation, and anyone who thinks it worth while can easily apply them.—July 11, 1887.]

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Phil.Trans.IS87.A. Plate 11.

Callendar.

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Fig $. \, 7$.

