XIII. Notes on platinum thermometry

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These real resultants of imaginary waves are not plane waves. They are forced linear waves sweeping the interface, on which they travel with velocity a^{-1}; and they produce disturbances penetrating to but small distances into the medium to which they belong. Their interpretation in connexion with total internal reflexion, both for vibrations in the plane of the rays, and for the simpler case of vibrations perpendicular to this plane (for which there is essentially no condensational wave) constitutes the dynamical theory of Fresnel's rhomb for solitary waves.

XIII. *Notes on Platinum Thermometry. By* H. L. CAL-LENDAR, *M.A., F.R.S., Quain Professor of Physics, University College, London*.*

SINCE the date of the last communication, which I made to this Journal in February 1892, I have been continually engaged in the employment of platinum thermometers in various researches. But although I have exhibited some of my instruments at the Royal Society and elsewhere and have described the results of some of these investigations, I have not hitherto found time to publish in a connected form an account of the construction and application of the instruments themselves, or the results of my experience with regard to the general question of platinum thermometry. As the method has now come into very general use for scientific purposes, it may be of advantage at the present time to collect in an accessible form some account of the progress of the work, to describe the more recent improvements in methods and apparatus, and to discuss the application and limitations of the various formulæ which have from time to time been proposed.

The present paper begins with a brief historical summary, with the object of removing certain common misapprehensions and of rendering the subsequent discussion intelligible. It then proceeds to discuss various formulæ and methods of reduction, employing in this connexion a proposed standard notation and nomenclature, which I have found convenient in my own work. I hope in a subsequent paper to describe some of the more recent developments and applications of the platinum thermometer, more particularly those which have occurred to me in the course of my own work, and which have not as yet been published or described elsewhere.

Historical Summary.

The earlier experiments on the variation of the electrical resistance of metals with temperature were either too rough, or too limited in range, to afford any satisfactory basis for a formula. The conclusion of Lenz (1838), that the resistance reached a maximum at a comparatively low temperature, generally between 200° and 300° C., was derived from the empirical formula,

$$R°/R = 1 + at + bt^2, \quad . \quad . \quad . \quad . \quad (L)$$

in which $R°$ and R stand for the resistances at 0° and $t°$ C., respectively. This conclusion resulted simply from the accident that he expressed his results in terms of *conductivity* instead of resistance, and could be disproved by the roughest qualitative experiments at temperatures beyond the range 0° to 100° C., to which his observations were restricted. Matthiessen (1862), in his laborious and extensive investigations, also unfortunately fell into the same method of expression. His results have been very widely quoted and adopted, but, owing to the extreme inadequacy of the formula, the accuracy of his work is very seriously impaired even within the limits of the experimental range to which it was confined. The so-called Law of Clausius, that the resistance of pure metals varied as the absolute temperature, was a generalization founded on similarly incomplete data. The experiments of Arndtsen (1858), by which it was suggested, gave, for instance, the temperature-coefficients ·00394 for copper, ·00341 for silver and ·00413 for iron, all of which differ considerably from the required coefficient ·003665. The observations, moreover, were not sufficiently exact to show the deviation of the resistance-variation from lineality. The experiments of Sir William Siemens (1870) did not afford any evidence for the particular formula which he proposed, at least in the case of iron. These formulæ have been already discussed in previous communications[*], but considering the extent to which they are still quoted, it may be instructive to append the curves representing them, as a graphic illustration of the danger of applying for purposes of extrapolation formulæ of an unsuitable type. The curves labelled Morris[†] and Benoit, which are of the same general character but differ in steepness, may be taken as representing approximately the resistance-variation of specimens of pure and impure iron respectively.

The first experiments which can be said to have afforded any satisfactory basis for a general formula were those of

[*] Callendar, Phil. Mag. July 1891; G. M. Clark, Electrician, Jan. 1897.
[†] Phil. Mag. Sept. 1897, p. 213.

Benoit (*Comptes Rendus*, 1873, p. 342). Though apparently little known and seldom quoted, his results represent a great advance on previous work in point of range and accuracy.

Fig. 1.
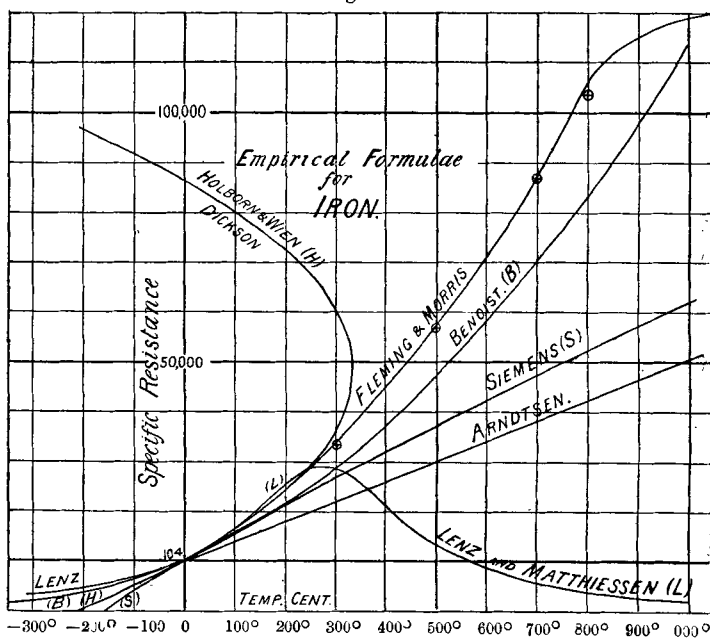
The wires on which he experimented were wound on clay cylinders and heated in vapour-baths of steam (100°), mercury (360°), sulphur (440°), and cadmium (860°), and in a liquid bath of mercury for temperatures below 360°. The resistances were measured by means of a Becquerel differential galvano-meter and a rheostat consisting of two platinum wires with a sliding mercury-contact. It is evident that the values which he assumed for the higher boiling-points are somewhat rough. The boiling-point attributed to cadmium, following Deville and Troost, is about 50° too high according to later experi-ments by the same authorities, or about 90° too high according to Carnelley and Williams. It would appear also that no special precautions were taken to eliminate errors due to thermoelectric effects, to changes in the resistance of the leading wires, and to defective insulation, &c. In spite of these obvious defects it is surprising to find how closely the results as a whole agree with the observations of subsequent investigators. The resistance-variation of all the more common

metals, according to Benoit, is approximately represented by an empirical formula of the type

$$R/R^\circ = 1 + at + bt^2, \quad \ldots \ldots \quad (B)$$

where R is the resistance at any temperature t, and R° the resistance at 0° C. The values of the constants a and b which he gives for iron and steel represent correctly (in opposition to the formula of Siemens) the very rapid increase in the rate of change of resistance with temperature, as shown by the relatively large positive value of the coefficient b. He gives also in the case of platinum a small negative value for b (a result since abundantly confirmed), although the specimen which he used was evidently far from pure[*]. This formula, which is the most natural to adopt for representing the deviations from lineality in a case of this kind, had been previously employed to a limited extent by others for the variation of resistance with temperature; but it had not previously been proved to be suitable to represent this particular phenomenon over so extended a range.

The work of the Committee of the British Association in 1874 was mainly confined to investigating the changes of zero of a Siemens pyrometer when heated in an ordinary fire to moderately elevated temperatures. Finding that the pyrometer did not satisfy the fundamental criterion of giving always the same indication at the same temperature, it did not seem worth while to pursue the method further, and the question remained in abeyance for several years. In the meantime great advances were made in the theory and practice of electrical measurement, so that when I commenced to investigate the subject at the Cavendish Laboratory, the home of the electrical standards, in 1885, I was able to carry out the electrical measurements in a more satisfactory manner, and to avoid many of the sources of error existing in previous work. The results of my investigations were communicated to the Royal Society in June 1886, and were published, with additions, in the 'Philosophical Transactions' of the following year. Owing to a personal accident, no complete abstract of this paper as a whole was ever published; and as the paper in its original form is somewhat long and inaccessible, many of the points it contained have since been overlooked. The greater part of the paper was occupied with the discussion of methods and observations with air-thermometers; but it may not be amiss at the present time to give a summary of the main conclusions

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[*] It may be remarked that the sign of this coefficient for platinum and palladium is wrongly quoted in Wiedemann, *Electricität*, vol. i. p. 525.

which it contained, so far as they relate to the subject of platinum thermometry.

(1) It was shown that a platinum resistance-thermometer, if sufficiently protected from strain and contamination, was practically free from changes of zero over a range of $0°$ to $1200°$ C., and satisfied the fundamental criterion of giving always the same indication at the same temperature.

(2) It was proposed to use the platinum thermometer as a secondary standard, the temperature pt on the platinum scale being defined by the formula

$$pt = 100(R - R°)/(R' - R°), \quad . \quad . \quad . \quad (1)$$

in which the letters R, R°, R' stand for the observed resistances at the temperatures pt, $0°$, and $100°$ C. respectively.

(3) By comparing the values of pt deduced from different pairs of specimens of platinum wires, wound side by side and heated together in such a manner as to be always at the same temperature, it was shown that different wires agreed very closely in giving the same value of any temperature pt on the platinum scale, although differing considerably in the values of their temperature-coefficients. (See below, p. 209.)

(4) A direct comparison was made between the platinum scale and the scale of the air-thermometer by means of several different instruments, in which the coil of platinum wire was enclosed inside the bulb of the air-thermometer itself, and so arranged as to be always at the same mean temperature as the mass of air under observation. As the result of this comparison, it was shown that the small deviations of the platinum scale from the temperature t by air-thermometer could be represented by the simple difference-formula

$$D = t - pt = d(t/100 - 1)t/100, \quad . \quad . \quad . \quad (2)$$

with a probable error of less than $1°$ C. over the range $0°$ to $650°$ C.

(5) It was inferred from the comparisons of different specimens of wire referred to in (3) (which comparisons were independent of all the various sources of error affecting the air-thermometer, and could not have been in error by so much as a tenth of a degree) that the simple parabolic formula did not in all cases represent the small residual differences between the wires.

(6) It was shown by the direct comparison of other typical metals and alloys with platinum, that the temperature-variation of the resistance of metals and alloys in general could probably be represented by the same type of formula over a considerable range with nearly the same order of accuracy as in the

case of platinum. But, that the formula did not represent singularities due to change of state or structure, such as those occurring in the case of iron at the critical temperature, or in the case of tin at the point of fusion.

This paper attracted very little attention until the results were confirmed by the independent observations of Griffiths*, who in 1890 applied the platinum thermometer to the determination of certain boiling- and freezing-points, and to the testing of mercury thermometers of limited scale. The results of this work appeared at first to disagree materially with the difference-formula already quoted, the discrepancy amounting to between 6° and 7° at 440° C. After his work had been communicated to the Royal Society a direct comparison was made with one of my thermometers in his apparatus; and the discrepancy was traced to the assumption by Griffiths of Regnault's value 448°·38 C. for the boiling-point of sulphur. We therefore undertook a joint redetermination of this point with great care, employing for the purpose one of my original air-thermometers which had been used in the experiments of 1886. The results of this determination were communicated to the Royal Society in December 1890, and brought the observations of Griffiths into complete harmony with my own and with the most accurate work of previous observers on the other boiling- and freezing-points in question. The agreement between his thermometers when reduced by the difference-formula (2), employing for each instrument the appropriate value for the difference-coefficient d, was in fact closer than I had previously obtained with platinum wires from different sources. But the agreement served only to confirm the convenience of the method of reduction by means of the Sulphur Boiling-Point (S.B.P.) which we proposed in that paper †.

Proposed Standard Notation and Nomenclature.

It will be convenient at this stage, before proceeding to discuss the results of later work, to explain in detail the notation and phraseology which I have found to be useful in connexion with platinum thermometry. This notation has already in part been adopted by the majority of workers in the platinum scale, and it would be a great saving in time and space if some standard system of the kind could be generally recognized. In devising the notation special attention has been paid to the limitations of the commercial typewriter, as the majority of communications to scientific societies at

* Phil. Trans. clxxxii. (1891), A, pp. 43–72.
† *Ibid. t.c.* pp. 119–157.

the present time are required to be typewritten. It is for this reason desirable to avoid, wherever possible, the use of Greek letters and subscript diacritics and indices.

The Fundamental Interval.—The denominator, $R' - R^\circ$, in formula (1) for the platinum temperature *pt*, represents the change of resistance of the thermometer between 0° and 100° C., and is called the fundamental interval of the thermometer, in accordance with ordinary usage. It is convenient, as suggested in a previous communication, to adjust the resistance of each thermometer, and to measure it in terms of a unit such that the fundamental interval is approximately 100. The reading of the instrument will then give directly the value of *pt* at any temperature, subject only to a small percentage correction for the error of adjustment of the fundamental interval.

The Fundamental Coefficient.—The mean value of the temperature-coefficient of the change of resistance between 0° and 100° C. is called the fundamental coefficient of the wire, and is denoted by the letter *c*. The value of *c* is given by the expression $(R' - R^\circ)/100 R^\circ$. The value of this coefficient is not necessary for calculating or reducing platinum temperatures, but it is useful for identifying the wire and as giving an indication of its probable purity.

The Fundamental Zero.—The reciprocal of the fundamental coefficient *c* is called the fundamental zero of the scale of the thermometer, and is denoted by the symbol pt°, so that $pt^\circ = 1/c$. The fundamental zero, taken with the negative sign, represents the temperature on the scale of the instrument itself at which its resistance would vanish. It does not necessarily possess any physical meaning, but it is often more convenient to use than the fundamental coefficient (*e. g.*, Phil. Trans. A, 1887, p. 225). It may be remarked that, if the resistance has been accurately adjusted so that the fundamental interval is 100 units, R°, the resistance at 0° C., will be numerically equal to pt°.

The Difference Formula.—It is convenient to write the formula for the difference between *t* and *pt* in the form already given (2), as the product of three factors, $d \times (t/100 - 1) \times t/100$, rather than in the form involving the square of $t/100$, which I originally gave, and which has always been quoted. Owing to the form in which it was originally cast, I find that most observers have acquired the habit of working the formula in the following manner. First find the square of $t/100$, then subtract $t/100$, writing the figures down on paper, and finally multiply the difference by the difference-coefficient *d* with the aid of a slide-rule. It is very much easier to work

the formula as the product of three factors, because the sub-traction $(t/100-1)$ can be safely performed by mental arithmetic. The whole process can then be performed by one application of the slide-rule, instead of two, and it is unnecessary to write down any intermediate steps on paper.

The Parabolic Function.—It is convenient to have an abbreviation for the parabolic function of t vanishing at $0°$ and $100°$, which occurs so frequently in questions of thermometry. I have found the abbreviation $p(t)$ both sug-gestive and useful for this purpose. The formula may then be written in the abbreviated shape, $t = pt + d \times p(t)$.

The "S.B.P." Method of Reduction.—Assuming the differ-ence-formula, the value of the difference-coefficient d may be determined by observing the resistance R'', and calculating the corresponding value of the platinum temperature pt'', at some secondary fixed point t'', the temperature of which is known on the scale of the gas-thermometer. The boiling-point of sulphur (S.B.P.) is generally the most convenient to use, and has been widely adopted for this purpose. As-suming that this point is chosen for the purpose, and that the height of the barometer at the time is $760 + h$ millims., the corresponding temperature is given by the formula

$$t'' = 444\cdot53 + \cdot082\, h,$$

provided that h is small, and the corresponding value of the parabolic function by the formula

$$p(t'') = 15\cdot32 + \cdot0065\, h,$$

whence $d = (t'' - pt'')/p(t'')$.

With the best apparatus it is possible to attain an order of accuracy of about $0\cdot1$ per cent. in the value of d obtained by this method, at least in the case of thermometers which are not used at temperatures above $500°$. At higher temperatures the exact application of the formula would be more open to question, and it may be doubted whether the value of the difference-coefficient would remain constant to so small a fraction of itself.

Other Secondary Fixed Points.—For very accurate work between $0°$ and $100°$ C. it might be preferable to use a value of d determined at $50°$ C., either by direct comparison with an air-thermometer or by comparison with a standard platinum thermometer. The latter comparison would be much the easier and more accurate. Although the most careful com-parisons have hitherto failed to show that the value of d obtained by assuming the S.B.P. does not give correct results

between 0° and 100° C., it is quite possible that this might not always be the case.

For work at low temperatures it would be preferable, from every point of view, to make use of the boiling-point of oxygen as the secondary fixed point. There appears to be a very general consensus of opinion that the temperature of *liquid* oxygen boiling under a pressure of 760 mm. is $-182°\cdot5$ C., on the scale of the constant-volume hydrogen or helium thermometer [*]. It is quite possible that, as in the case of water and most other liquids, the temperature of the boiling liquid would be different from that of the condensing vapour at the same pressure; but the boiling liquid is the most convenient to employ, and it appears that its temperature is steady to two or three tenths of a degree, and reproducible by different observers to a similar order of accuracy. I have found it convenient for purposes of distinction to employ the symbol $d°$ to denote the value of d deduced from the boiling-point of oxygen, and the symbol d'' to denote that deduced from the boiling-point of sulphur. The formulæ for the pressure correction in the case of oxygen are approximately

$$t = -182\cdot5 + \cdot020\,h; \quad p(t) = 5\cdot16 - \cdot00093h.$$

The Resistance Formula.—I have shown in the paper already referred to that the adoption of the parabolic difference-formula for the relation between pt and t is equivalent to assuming for the resistance-variation the formula

$$R/R° = 1 + at + bt^2. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The values of the coefficients a and b are found in terms of c and d, or *vice versâ*, by means of the relations

$$a = c(1 + d/100), \quad b = -cd/10,000.$$

Graphic Method of Reduction.—The quickest and most generally convenient method of reducing platinum temperatures to the air-scale is to plot the difference $t - pt$ in terms of t as abscissa, and to deduce graphically the curve of difference in terms of pt as abscissa, as described and illustrated in my original paper. This method is particularly suitable at temperatures up to 500° C., as the difference over this range is relatively small and accurately known. It is also very convenient if a large number of determinations are to be made with a single instrument. It is not so convenient in the case of a number of different instruments with different coefficients,

* The experimental evidence for this number is not quite satisfactory, owing to differences in the atmospheric pressure and impurities in the oxygen. It must be understood that the adoption of this value is provisional and subject to correction.

each of which is used for a comparatively limited number of determinations. In such a case the trouble of drawing the separate curves, with sufficient care to be of use, would more than counterbalance the advantage to be gained by the method.

Heycock and Neville's Method.—In order to avoid this difficulty Messrs. Heycock and Neville, in their classical researches at high temperatures * devised an ingenious modification of procedure, which has given very good results in their hands, but is not quite identical with the simple difference-formula. They described a difference-curve in the usual manner, giving the value of the difference in terms of pt as abscissa for a standard value $d = 1\cdot50$ of the difference-coefficient. The appropriate values of d were determined in the case of each pyrometer by the S.B.P. method. In reducing the observations for any given values of pt and d, the value of the difference corresponding to pt was taken from the curve for $d = 1\cdot50$, and was then multiplied by the factor $d/1\cdot50$ and added to pt. This method is very expeditious and convenient, and gives results which are in practical agreement with the pure difference-formula, provided that, as was almost invariably the case in their observations, the values of d do not differ materially from the average $1\cdot50$. If, however, the pure difference-formula is correct, the method could not be applied in the case of values of d differing considerably from the average. The difference between the methods cannot be simply expressed in terms of either pt or t for considerable variations in the value of d. But for a small variation δd in the value of d in the vicinity of the normal value, it is easy to show that the difference δt between the true value of t as given by the difference-formula $t - pt = dp(t)$, and the value found by the method of Heycock and Neville, is approximately

$$\delta t = \delta d (\mathrm{d}t/\mathrm{d}pt - 1)p(t)\,\dagger.$$

Neglecting the variation of d entirely, the error would be

$$\delta't = \delta d (\mathrm{d}t/\mathrm{d}pt)p(t).$$

For example, at $t = 1000°$, $p(t) = 90$, $(\mathrm{d}t/\mathrm{d}pt) = 1\cdot40$, we should find for a variation of d from $1\cdot50$ to $1\cdot60$, the values $\delta t = 3°\cdot8$ (H. & N.), and $\delta't = 12°\cdot8$ (variation neglected).

This is an extreme case. In the observations of Heycock and Neville, the values found for the coefficient d seldom

* Trans. Chem. Soc. Feb. 1895, p. 162.

† The value of $\mathrm{d}t/\mathrm{d}pt$ at any point is readily found by differentiating the difference-formula (2), $\mathrm{d}pt/\mathrm{d}t = 1 - (t/50 - 1)d/100$.

varied so much as ·04 on either side of the mean, in the case
of their standard wire. It is, moreover, quite possible that
these variations may have been partly due to fortuitous differ-
ences at the S.B.P. and at the fixed points, in which case it
is probable that the Heycock and Neville method of reduction
would lead to more consistent results than the pure difference-
formula, because it does not allow full weight to the apparent
variations of d as determined by the S.B.P. observations.
It is clearly necessary, as Heycock and Neville have shown,
and as the above calculation would indicate, to take some
account of the small variations of d, at least in the case of
pyrometers in constant use at high temperatures. The method
of Heycock and Neville appears to be a very convenient and
practical way of doing this, provided that the variations of d
are small. It must also be observed that, although the indi-
vidual reductions by their method may differ by as much as
$1°$ or $2°$ at $1000°$ from the application of the pure difference-
formula, the average results for the normal value of d will be
in exact agreement with it.

Difference-Formula in Terms of pt.—In discussing the
variation of resistance as a function of the temperature, it is
most natural and convenient to express the results in terms of
the temperature t on the scale of the air-thermometer by
means of the parabolic formula already given. This formula
has the advantage of leading to simple relations between the
temperature-coefficients; and it also appears to represent the
general phenomenon of the resistance-variation of metals
over a wide range of temperature with greater accuracy than
any other equally convenient formula. When, however, it
is simply a question of finding the temperature from the
observed value of the resistance, or from the observed reading
of a platinum thermometer, over a comparatively limited
range, it is equally natural, and in some respects more con-
venient, to have a formula which gives t directly in terms of
pt or R. This method of expression was originally adopted
by Griffiths, who expressed the results of the calibration of
his thermometers by means of a formula of the type

$$t - pt = a\,pt + b\,pt^2 + c\,pt^3 + d\,pt^4. \quad . \quad . \quad . \quad \text{(G)}$$

The introduction of the third and fourth powers of pt in
this equation was due to the assumption of Regnault's value
for the boiling-point of sulphur. If we make a correction
for this, the observations can be very fairly represented by a
parabolic formula of the type already given, namely,

$$t - pt = d'(pt/100 - 1)pt/100 = d'p(pt). \quad . \quad . \quad \text{(4)}$$

This formula is so simple and convenient, and agrees so closely over moderate ranges of temperature with the ordinary difference-formula, as to be well worth discussion. I have been in the habit of using it myself for a number of years in approximate reductions at moderate temperatures, more particularly in steam-engine and conductivity experiments, in which for other reasons a high degree of accuracy is not required. It has also been recently suggested by Dickson (Phil. Mag., Dec. 1897), though his suggestion is coupled with a protest against platinum temperatures.

The value of the difference-coefficient d' in this formula may be determined as usual by reference to the boiling-point of sulphur, or it may be deduced approximately from the value of the ordinary difference-coefficient d by means of the relation

$$d' = d/(1 - \cdot 077d), \quad \text{or} \quad d = d'/(1 + \cdot 077d').$$

If this value is chosen for the coefficient, the two difference-formulæ will of course agree at $0°$, $100°$, and $445°$ C., but will differ slightly at other temperatures. The order of agreement between the formulæ is shown at various points of the scale by the annexed table, in which t represents the temperature given by the ordinary formula $t - pt = 1\cdot50p(t)$, and t' the temperature calculated by formula (4) for the same value of pt, choosing the value $d' = 1\cdot695$, to make the two formulæ agree at the S.B.P.

TABLE I.

Comparison of Difference-Formulæ, (2) & (4).

t	$-300°$	$-200°$	$-100°$	$+\cdot50°$	$200°$	$300°$
$t-t'$ ...	$-4°\cdot5$	$-1°\cdot95$	$-0°\cdot54$	$+\cdot050°$	$-\cdot23°$	$-\cdot42°$

t	$400°$	$600°$	$800°$	$1000°$	$1200°$	$1500°$
$t-t'$ ..	$-\cdot25°$	$+2°\cdot2$	$+9°\cdot3$	$+22°\cdot9$	$+46°\cdot6$	$+97°\cdot2$

It will be observed that the difference is reasonably small between the limits $-200°$ and $+600°$, but that it becomes considerable at high temperatures. A much closer agreement may be readily obtained over small ranges of temperature by choosing a suitable value of d'. The two formulæ become practically indistinguishable between $0°$ and $100°$, for instance, if we make $d' = d$. For steam-engine work I generally selected the value of d' to make the formulæ agree at $200°$ C.

For work at low temperatures, it would be most convenient to select the boiling-point of oxygen for the determination of either difference-coefficient. The two formulæ are so similar that they cannot be distinguished with certainty over a moderate range of temperature. But if the values of the difference-coefficients are calculated from the S.B.P., the balance of evidence appears to be in favour of the original formula (2). Formula (4) appears to give differences which are too large between 0° and 100° C.; and it does not agree nearly so well as (2) with my own air-thermometer observations over the range 0° to 650° C. It appears also from the work of Heycock and Neville to give results which are too low at high temperatures as compared with those of other observers.

It is obvious, from the similarity of form, that the difference-formula (4) in terms of pt corresponds, as in the case of formula (2), to a parabolic relation between the temperature and resistance, of the type

$$t = -t° + a'R/R° + b'(R/R°)^2 = a''(R/R° - 1) + b''(R/R° - 1)^2. \quad (5)$$

When $R = 0$, $t = -t° = -(a'' - b'')$. Also $b' = b''$, and $a' = a'' - 2b''$.

The values of the fundamental coefficient c, and of the fundamental zero $pt°$, are of course the same on either formula, provided that they are calculated from observations at 0° and 100° C., but not, if they are calculated from observations outside that range. The values of the coefficients a'' and b'' are given in terms of d', and either $pt°$, or c, by the relations

$$a'' = pt°(1 - d'/100) = (1 - d'/100)/c, \quad \text{and} \quad d' = 10,000 b'' c^2.$$

Formulæ of this general type, but expressed in a slightly different shape, have been used by Holborn and Wien for their observations at low temperatures, and recently by Dickson for reducing the results of Fleming and other observers. But they do not employ the platinum scale or the difference-formula.

Maximum and Minimum Values of the Resistance and Temperature.—It may be of interest to remark that the difference-formulæ (2) and (4) lead to maximum or minimum values of pt and t respectively, which are always the same for the same value of d, but lie in general outside the range of possible extrapolation. In the case of formula (2), the resistance reaches a maximum at a temperature $t = -a/2b = (5000/d)(1 + d/100)$. The maximum values of pt and R are given in terms of d and c by the equations

$$pt \text{ (max.)} = (1 + d/100)\, t/2 = (2500/d)(1 + d/100)^2,$$

$$R/R° \text{ (max.)} = 1 + pt \text{ (max.)}/pt° = 1 + (2500c/d)(1 + d/100)^2.$$

Similarly in the case of the difference-formula (4) in terms of *pt*, the maximum or minimum value of *t* is given in terms of d' by the equation

$$t(\text{max.}) = (1 - d'/100)\,pt/2 = -(2500/d')\,(1 - d'/100)^2.$$

Dickson's Formula.— In a recent number of this Journal (Phil. Mag., Dec. 1897) Mr. Dickson has proposed the formula

$$(R + a)^2 = p(t + b). \quad \ldots \ldots \quad (6)$$

He objects to the usual formula (3) on the grounds, (1) that it leads to a maximum value of the resistance in the case of platinum at a temperature of about $t = 3250°$ C., and (2) that any given value of the resistance corresponds to *two* temperatures. He asserts that " both of these statements indicate physical conditions which we have no reason to suppose exist." In support of contention (1), he adduces a rough observation of Holborn and Wien * to the effect that the

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* Wied. *Ann.* Oct. 1895, p. 386. Mr. Dickson and some other writers appear to attach too much weight to these observations of Messrs. Holborn and Wien. So far as they go, they afford a very fair confirmation of the fundamental principles of platinum-thermometry at high temperatures; but the experiments themselves were of an incidental character, and were made with somewhat unsuitable apparatus. Only two samples of wire were tested, and the resistances employed were too small for accurate measurement. The wires were heated in a badly-conducting muffle and were insulated by capillary tubes of porcelain or similar material. The temperature of the wire under test was assumed to be the mean of the temperatures indicated by two thermo-junctions at its extremities ; but the authors state that " the distribution of temperature in the furnace was very irregular." The resistance was measured by a modification of the potentiometer method, and no attempt was made to eliminate residual thermoelectric effects. Under these conditions the observations showed that the resistance was not permanently changed by exposure to a temperature of 1600° C., at least within the limits of accuracy of the resistance measurements. It is quite easy, however, by electric heating as in the " meldometer," to verify the difference-formula at high temperatures, with less risk of strain or contamination or bad insulation. (See Petavel, Phil. Trans. A (1898), p. 501.)

The two series of observations (excluding the series in which the tube of the muffle cracked, and the thermocouples and wire were so contaminated with silicon and furnace-gases as to render the observations valueless) overlapped from 1050° to 1250° C., and showed differences between the two wires varying from 10° to 45° at these temperatures, the errors of individual observations in either series being about 10° to 15°. It must be remembered, however, that the two wires were of different sizes and resistances; they were heated in different furnaces ; they were insulated with different materials; and their temperatures were deduced from different thermocouples. Taking these facts into consideration, it is remarkable that the observed agreement should be so close. The observations at the highest temperatures in both cases, with the furnaces full blast and under the most favourable conditions for securing uniformity of temperature throughout the length of the wire, are in very close agreement with the difference-formula (2), assuming $d = 1{\cdot}75$.

The second specimen was also tested at lower temperatures, but the

resistance of one of their wires had already nearly reached $6R^\circ$ at a temperature of about 1610° C., whereas the maximum calculated resistance in the case of one of my wires (with a coefficient $c = \cdot00340$) was only $6\cdot576\,R^\circ$. He omits to notice that the result depends on the coefficients of the wire.

The wire used by Holborn and Wien had a fundamental coefficient $c = \cdot00380$, and the highest value of the resistance actually observed was not $6R^\circ$ as suggested, but $R/R^\circ = 5\cdot53$, at a temperature $t = 1610^\circ$ C., deduced from thermo-junctions at each end. If we assume $d = 1\cdot70$ as a probable value of the difference-coefficient for their wire, the difference-formula (2) would give,

at $t = 1610^\circ$, $D = 414^\circ$, $pt = 1196^\circ$, whence $R/R^\circ = 5\cdot54$.

It would be absurd to attach much weight to so rough an observation, but it will be seen that, so far as it goes, the result is consistent with the usual formula, and does not bear out Mr. Dickson's contention. A more important defect in arguments (1) and (2) lies in the fact that maximum and minimum values of the resistance are known to occur in the case of manganin and bismuth within the experimental range, and that such cases can be at least approximately represented by a formula of the type (3), but cannot be represented by a formula of the type (6).

As shown by Table I. above, the formula proposed by Dickson agrees fairly well with formula (3), in the special case of platinum, through a considerable range. But the case of platinum is exceptional. If we attempt to apply a formula of Dickson's type to the case of other metals, we are met by practical difficulties of a serious character, and are driven to conclude that the claim that it is " more representative of the connexion between temperature and resistance than any formula hitherto proposed," cannot be maintained.

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observations are somewhat inconsistent, and lead to values of d which are rather large and variable, ranging from $3\cdot7$ to $2\cdot6$. These variations are probably due to errors of observation or reduction. This is shown by the work of Mr. Tory (B.A. Report, 1897), who made a direct comparison between the Pt—PtRh thermocouple and the platinum-thermometer by a much more accurate method than that of Holborn and Wien. He found the parabolic difference-formula for the platinum thermometer to be in very fair agreement between 100° and 800° C. with the previous series of observations of Holborn and Wien on this thermocouple (Wied. *Ann.* 1892), and there can be little doubt that the discrepancies shown by their later tests were due chiefly to the many obvious defects of the method. For a more detailed criticism of these observations, the reader should refer to a letter by Griffiths in ' Nature,' Feb. 27th, 1896. It is sufficient to state here that the conclusions which these observers drew from their experiments are not justified by the observations themselves.

If, for instance, we take the observations of Fleming on very pure iron between 0° and 200° C., and calculate a formula of the Holborn and Wien, or Dickson, type to represent them, we arrive at a curve similar to that shown in fig. 1 (p. 193). (The values of the specific resistance of Fleming's wire are reduced, for the sake of comparison, to the value $R = 10,000$ at 0° C.)   This curve agrees very closely with that of Morris and other observers between 0° and 200° C.   The peculiarities of the curve beyond this range are not due to errors in the data, but to the unsuitable nature of the formula.   A similar result would be obtained in the case of iron by employing any other sufficiently accurate data.   It will be observed that the formula leads to a maximum value of the temperature $t = 334°$, and makes the resistance vanish at $-197°$.   Below 334° there are *two* values of the resistance for each value of the temperature, and the value of dR/dt at 334° is infinite, both of which conditions are at present unknown in the case of any metal, and are certainly not true in the case of iron.   If, instead of taking the value observed at $+196°\cdot 1$ C., we take the value obtained at the O.B.P. to calculate the formula, we should find a better agreement with observation at low temperatures, but the disagreement at higher temperatures would be greater.

If, on the other hand, we take *the same observations*, namely, $c = \cdot 00625$, and $R/R° = 2\cdot 372$ when $t = 196°\cdot 1$, and calculate a difference-formula of the type (2) corresponding to (3), we find $d = -12\cdot 5$, $a = \cdot 005467$, $b = \cdot 000,007825$.   The points marked $\oplus$ in fig. 1 are calculated from this formula, and are seen to be in practical agreement with the observations of Morris up to 800°.   As this formula stands the test of extrapolation so much better than that of Holborn and Wien or Dickson, we are justified in regarding it as being probably more representative of the connexion between resistance and temperature.

Advantages of the Difference-Formula.—Mr. Dickson's objections to the platinum scale and to the difference-formula appear to result from want of familiarity with the practical use of the instrument.   But as his remarks on this subject are calculated to mislead others, it may be well to explain briefly the advantages of the method, which was originally devised with the object of saving the labour of reduction involved in the use of ordinary empirical formulæ, and of rendering the results of observations with different instruments directly and simply comparable.

(1) In the first place, a properly constructed and adjusted platinum thermometer reads directly in degrees of temperature

on the platinum scale, just like a mercury thermometer, or any other instrument intended for practical use. The quantity directly observed is not the resistance in ohms, but the temperature on the platinum scale, either pt, or $pt + pt^\circ$. The advantage of this method is that the indications of different instruments become directly comparable, and that the values of pt for different wires agree very closely. If this method is not adopted, the resistances in ohms of different instruments at different temperatures form a series of meaningless figures, which cannot be interpreted without troublesome reductions.

(2) The second advantage of the difference-formula lies in the fact that the difference is *small*, more especially at moderate temperatures, and can be at once obtained from a curve or a table, or calculated on a small slide-rule, without the necessity of minute accuracy of interpolation or calculation. In many cases, owing to the smallness of the difference between the scales, the results of a series of observations can be worked out entirely in terms of the platinum scale, and no reduction need be made until the end of the series. For instance, in an elaborate series of experiments on the variation of the specific heat of water between 0° and 100° C., on which I have been recently engaged, by a method described in the Brit. Assoc. Report, 1897, all the observations are worked out in terms of the platinum scale, and the reduction to the air-scale can be performed by the aid of the difference-formula in half an hour at the end of the whole series. As all the readings of temperature have to be taken and corrected to the ten-thousandth part of a degree, and as the whole series comprises about 100,000 observations, it is clear that the labour involved in Mr. Dickson's method of reduction would have been quite prohibitive. It is only by the general introduction of the method of small corrections that such work becomes practicable.

On the Method of Least Squares.—There appears to be a widespread tendency among non-mathematical observers to regard with almost superstitious reverence the value of results obtained by the method of least squares. This reverence in many cases is entirely misplaced, and the method itself, as commonly applied, very often leads to erroneous results. For instance, in a series of observations extending over a considerable range of temperature, it would be incorrect to attach equal weight to all the results, because all the sources of error increase considerably as we depart further from the fixed points of the scale. In a series of air-thermometer observations, the fixed points themselves stand in quite a different category to the remainder of the observations. The

temperature is accurately known by definition, and is not
dependent on uncertain errors of the instrument.   It is a
mistake, therefore, in reducing a series of observations of this
kind, to put all the observations, including the fixed points,
on the same footing, and then apply the method of least
squares, as Mr. Dickson has applied it in his reduction of the
results of various observers with platinum thermometers.   For
instance, in order to make his formula fit my observations at
higher temperatures, he is compelled to admit an error of no
less than $0°·80$ on the fundamental interval itself, which is
quite out of the question, the probable error of observation on
this interval being of the order of $0°·01$ only.   The correct
way of treating the observations would be to calculate the
values at the fixed points separately, and to use the remainder
of the observations for calculating the difference-coefficient.
Even here the graphic method is preferable to that of least
squares, because it is not easy to decide on the appropriate
weights to be attached to the different observations.   Cor-
recting the method of calculation in this manner, we should
find a series of differences between my observations and
Dickson's formula, of the order shown in Table I.   It would
be at once obvious that the deviations from (6) were of a
systematic type, and that it did not represent the results of
this series of observations so well as that which I proposed.
The deviations shown in Dickson's own table are of a syste-
matic character; but they would have been larger if he had
treated the fixed points correctly.

Limitations of the Difference-Formula.—The observations
of Messrs. Heycock and Neville at high temperatures may be
taken as showing that the simple parabolic difference-formula,
in which the value of d is determined by means of the S.B.P.
method, gives very satisfactory results, in spite of the severe
extrapolation to which it is thus subjected, provided that the
wire employed is of pure and uniform quality.   If, however,
the S.B.P. method of reduction is applied in the case of impure
wires at high temperatures, it may lead to differences which
are larger than the original differences in the values of pt
before reduction.   For instance, I made a number of pyro-
meters some years ago with a sample of wire having the
coefficients $c = ·00320$, $d'' = 1·75$.   My observations on the
freezing-points of silver and gold (Phil. Mag., Feb. 1892)
were made with some of these pyrometers.   All these instru-
ments gave very consistent results, but they could not be
brought into exact agreement with those constructed of purer
wire by the simple S.B.P. method of reduction, employ-
ing either difference-formula (2) or (4).   This is not at all

surprising when we consider the very large difference in the fundamental coefficient *c*, which is approximately ·00390 in the case of the purest obtainable wire. The remarkable fact is that, as stated in my original paper (see above, p. 195), the values of *pt* for such different specimens of wire should show so close an agreement through so wide a range. The difference in the fundamental coefficients in this extreme case is about 20 per cent.; but the values of *pt* for the two wires differ by only 4° at the S.B.P., and this difference, instead of increasing in proportion to the square of the temperature, remains of the same order, or nearly so, at the freezing-points of silver and gold. Thus the wire *c* = ·00320 gave *pt* = 830° at the Ag. F.P., but I shortly afterwards obtained with a specimen of very pure wire (*c* = ·003897), the value *pt* = 835° for the same point. Messrs. Heycock and Neville, using the same pure wire, have confirmed this value. They also find for the F.P. of gold, with different instruments, constructed of the same wire, the average value *pt* = 905°·8. I did not test this point with the pure wire, but the value found by Messrs. Heycock and Neville may be compared with the value *pt* = 902°·3 (Phil. Mag., Feb. 1892), which I found at the Mint with one of the old instruments.

From these and other comparisons of the platinum scales of different wires, it appears likely that the deviation of the impure wire from the parabolic curve is generally of this nature. As shown by the comparison curves in my original paper, the deviation follows approximately the parabolic law up to 400°, beyond that point the curves tend to become parallel, and at higher temperatures they often show a tendency to approach each other again. The application of the S.B.P. method of reduction to impure wires at high temperatures will therefore give results which are too high, because the value of *d* is calculated from the S.B.P., where the difference between the wires is nearly a maximum. Thus, taking the values of *d* from the S.B.P. for the two specimens of wire above quoted, we find, calculating the values of *t* for the Ag.F.P., and Au.F.P. from the data,

Impure wire, *c* = ·00320, *d* = 1·751 ;
    Ag. F.P., *t* = 981·6 ; Au. F.P., *t* = 1092·0.
Pure wire, *c* = ·00390, *d* = 1·520 ;
    Ag. F.P., *t* = 960·7 ; Au. F.P., *t* = 1060·7.

The results for the impure wire obtained by the S.B.P. method of reduction are not so high as those found by Barus with a Pt-PtIr thermo-element, which he compared with an air-thermometer up to 1050°. There can be little doubt,

however, that they are too high, and that the results given by the pure wire are the more probable. The latter are approximately a mean between the values of Violle 954°, and Holborn and Wien 971°, and may be taken, in the present state of the science of high-temperature measurement, to be at least as probable as any other values, in spite of the extrapolation from 445°, by which they are obtained.

The extrapolation is not really so unreasonable as many observers seem to think. The parabolic formula for resistance variation has been verified for a great variety of cases, through a very wide range, and with much greater accuracy than in the case of many so-called laws of nature. For instance, a similar formula, proposed by Tait and Avernarius, is often regarded as the law of the thermocouple, but the deviations of thermocouples from this law are far wider than those of the most impure platinum thermometer. If we take a Pt-PtRh thermocouple, and apply the S.B.P. method of reduction in the same manner as in the case of a platinum thermometer, taking the data, $t=100°$, $e=650$ microvolts ; $t=445°$, $e=3630$ mv. ; we should find $d=-7\cdot4$. At $t=1000°C.$, $e=9550$ mv., the temperature on the scale of the thermocouple is $et=1470°$. The temperature calculated by the parabolic formula is $t=804°$. Whence it will be seen that the deviation from the formula is about ten times as great as in the case of a very impure platinum wire. A cubic formula was employed by Holborn and Wien to represent their observations at high temperatures with this thermocouple, but even this formula differs by more than 20° from their observations at 150° C. It is, moreover, so unsatisfactory for extrapolation that they preferred to adopt a rectilinear formula for deducing temperatures above 1200° C.

There are, however, more serious objections to the adoption of the thermocouple, except to a limited extent, as a secondary standard :— (1) The scale of the thermocouple is seriously affected, as shown by the observations of Holborn and Wien and Barus at high temperatures, and of Fleming at low temperatures, by variations in the quality of the platinum wire and in the composition of the alloy. (2) The sensitiveness of the Pt—PtRh thermocouple at moderate temperatures is too small to permit of the attainment of the order of accuracy generally required in standard work. (3) No satisfactory method has yet been devised in the case of the thermocouple for eliminating residual thermal effects in other parts of the circuit, which materially limit * the

* My present assistants, Prof. A. W. Porter, B.Sc., and Mr. N. Eumorfopoulos, B.Sc., whose work on Emissivity and Thermal Conductivity has already in part been published in this Journal, employed this thermo-

attainable accuracy. In the case of the platinum thermo-
meter these effects are relatively much smaller, owing to the
large change of resistance with temperature, and can be
completely eliminated in a very simple manner.

Ag. F.P. Method of Reduction for Impure Wires.—The
simplest method of reduction for such wires at high tempera-
tures, would be to take the Ag. F.P. as a secondary fixed
point instead of the S.B.P. for the determination of the
difference-coefficient d. This would in general lead to a very
close agreement at temperatures between 800° and 1200°C.,
but would leave residual errors of 3° or 4° at temperatures in
the neighbourhood of the S.B.P. To obtain a continuous
formula giving results consistent to within less than 1°
throughout the range, it would be necessary to adopt the
method which I suggested in my last communication (Phil.
Mag., Feb. 1892), assuming d to be a linear function of the
temperature of the form $a + bt$, and calculating the values of
a and b to make the instrument agree with the pure wire at
both the S.B.P. and the Ag. F.P., taking the latter as 960°·7.
We should find for the wire $(c = ·00320)$ above quoted, $d =$
1·580 at the Ag. F.P. If we apply this value at the Au. F.P.,
we should find $t = 1063°·0$. But if we employ the second
method, and calculate a linear formula for d to make the
results agree throughout the scale, taking $d = 1·751$ at the
S.B.P., we obtain $d = a + bt = 1·898 - ·000331t$. Hence
the appropriate value of d to use at the Au. F.P. would be
$d = 1·547$, giving for the Au. F.P. $t = 1060°·0$, which is in
closer agreement with the value 1060°·7 given by the pure
wire. This method has also the advantage that it gives
practically perfect agreement at the S.B.P., and at all points
between 0° and 1000°. In the case of the mercury thermo-
meter, or the thermocouple, a similar cubic formula is required
to give an equally good agreement between 0° and 200° C.

In the original paper in which the suggestion was made, I

couple very extensively in their investigations. They inform me that
they were compelled to abandon the method shortly before my appoint-
ment, because in spite of every precaution which their experience could
suggest they found it impossible, owing to these residual thermal effects,
to effect a sufficiently accurate calibration of the Pt–PtRh thermo-
couple at temperatures between 0° and 100° C. The substitution of
baser metals such as iron and german-silver at low temperatures would
no doubt partly meet this difficulty, but would involve the abandonment
of the wide range and constancy and uniformity of scale characteristic of
the platinum metals, which are qualifications so essential for a standard.
We conclude on these grounds that the application of this thermo-
couple is limited to high temperatures, and that the contention that it is
preferable to the platinum thermometer as a secondary standard cannot
be maintained.

assumed tentatively a much lower value $t = 945°$ for the Ag. F.P., giving a result $t = 1037°$ for the Au. F.P., which naturally does not agree with the results of subsequent work. These results have since been misquoted in a manner which has the effect of suggesting that the platinum thermometer gives very capricious results at high temperatures.   Holborn and Wien, for instance, quote my value $981°{\cdot}6$ for the Ag. F.P., obtained with the impure wire by the S.B.P. method of reduction, and at the same time quote the value $1037°$ for the Au. F.P., which was obtained by assuming the value $945°$ for the Ag. F.P.   Comparing these with the values obtained by Heycock and Neville with the pure wire, one might naturally conclude, in the absence of information as to the manner in which the two results were calculated, that different wires gave very inconsistent results.   The truth is, on the contrary, that very different wires agree with remarkable uniformity in giving approximately the same platinum-scale, and that they also give consistent values of t provided that the reduction is effected in a consistent manner.   But, although it is evident that this method may be made to give consistent results in the case of impure wires, it is in all cases preferable to use pure wire of uniform quality.   If, for instance, a pyrometer gives a value of c less than $\cdot0035$, or a value of d greater than $1{\cdot}70$, it would be safer to reject it, although it may possibly give very consistent results.   Values of d greater than $2{\cdot}00$ at the S.B.P. sometimes occur, but may generally be taken as implying that the wire is contaminated.   Such instruments as a rule deteriorate rapidly, and do not give consistent results at high temperatures.

The Difference-Formula at Low Temperatures.—The suitability of the Platinum thermometer as an instrument for low-temperature research is shown by the work of Dewar and Fleming, and Olszewski.   It has also been adopted by Holborn and Wien, in spite of their original prejudice against the instrument.   The first verification of the platinum scale at very low temperatures was given by Dewar and Fleming, whose researches by this method are the most extensive and important.   They found that two different specimens of wire with fundamental coefficients $c = \cdot00353$, and $c = \cdot00367$ respectively, agreed very closely in giving the same values of the platinum temperature down to $-220°$.   The values of the difference-coefficients for these wires, calculated by assuming $t = -182°{\cdot}5$ for the boiling-point of liquid oxygen, are $d = 2{\cdot}75 *$ and $d = 2{\cdot}72$, respectively.   The first of these refers to the particular wire which Dewar and Fleming selected as their standard.

<p style="text-align:center">* See below, p. 219, middle, and footnote.</p>

As an illustration of the method of reduction by the difference-formula, it may be of interest to reproduce a table exhibiting in detail the complete calculation of such a table of reduction for the standard wire employed by Dewar and Fleming. We select for this purpose the following corrected data, taken from their paper in the Phil. Mag., July 1895, p. 100.

Thermometer in Melting Ice, $R^\circ = 3 \cdot 1059, t = 0^\circ$ C.

„ Steam at 760 mm., $R' = 4 \cdot 2034, t = 100^\circ$ C.

„ Liquid Oxygen, $R'' = 0 \cdot 9473, t = -182^\circ \cdot 5$ C.

From these data we deduce :—

Fundamental Interval, $R' - R^\circ = 1 \cdot 0975$.

Fundamental Coefficient, $(R' - R^\circ)/100 R^\circ = \cdot 003533$.

Fundamental Zero, $pt^\circ = 1/c = 283^\circ \cdot 00$.

In Liquid Oxygen,

$pt = -196^\circ \cdot 7, t = -182^\circ \cdot 5, D = t - pt = 14^\circ \cdot 2$.

Difference-Coefficient, $d = D/p(t) = 14 \cdot 2/5 \cdot 16 = 2 \cdot 75$.

Difference-Formula, $D = t - pt = 2 \cdot 75 (t/100 - 1) t/100$.

To find the difference-formula in terms of pt, we have similarly,

Difference-Coefficient, $d' = D/p(pt) = 14 \cdot 2/5 \cdot 84 = 2 \cdot 43$.

Pt Difference-Formula, $D' = t' - pt = 2 \cdot 43 (pt/100 - 1) pt/100$.

As a verification we may take the observation in solid CO_2 and ether, assuming Regnault's value $t = -78^\circ \cdot 2$ for the true temperature.

Difference-Formula (D) gives, $t - pt = 2 \cdot 75 \times 1 \cdot 39 = 3^\circ \cdot 82$.

„ „ (D') „ $t' - pt = 2 \cdot 43 \times 1 \cdot 49 = 3^\circ \cdot 62$.

The observed value of pt is given as $-81^\circ \cdot 9$. Thus the two formulæ give, (D) $t = -78^\circ \cdot 1$, and (D') $t' = -78^\circ \cdot 3$, respectively.

The following Table shows the comparison of the formulæ for every ten degrees throughout the range. The first three columns contain the whole work of the calculation for formula (D'). The second column contains the values of D' calculated by the aid of a small slide-rule. These when added to the values of pt in the first column, give the values of t shown in the third column. The fourth column contains the corresponding values of the difference in t for $1^\circ pt$, obtained by differentiating the difference-formula. These are written down by the method of differences. The fifth column contains the difference $t - t'$ between the values of t deduced by the two formulæ. The sixth contains the values of t by formula (D) ; and the seventh is added for comparison with the table given by Dickson (Phil. Mag., June 1898, p. 527).

TABLE II.—Table of Reduction for Dewar and Fleming's
Standard Platinum Thermometer.

pt (°C.).	D'.	t'(°C.).	dt/dpt.	$t-t'$.	t(°C.)	Dickson.
+100	0	+100	1·024	0·0	+100	+99·85
+ 50	−0·61	+49·39	1·000	−0·08	+49·31	+49·47
+ 0	0	0	·976	0	0	+ 0·20
− 10	+0·27	− 9·73	·971	+0·03	− 9·70	− 9·51
− 20	+0·58	−19·42	·966	+0·05	−19·37	−19·18
− 30	+0·95	−29·05	·961	+0·08	−28·97	−28·81
− 40	+1·36	−38·64	·956	+0·11	−38·53	−38·39
− 50	+1·82	−48·18	·951	+0·14	−48·04	−47·92
− 60	+2·33	−57·67	·947	+0·17	−57·50	−57·42
− 70	+2·89	−67·11	·942	+0·19	−66·92	−66·83
− 80	+3·50	−76·50	·937	+0·22	−76·28	−76·25
− 90	+4·15	−85·85	·932	+0·23	−85·62	−85·61
−100	+4·86	−95·14	·927	+0·25	−94·89	−94·92
−110	+ 5·60	−104·4	·922	+0·26	−104·1	−104·2
−120	+ 6·41	−113·6	·917	+0·26	−113·3	−113·4
−130	+ 7·28	−122·7	·912	+0·25	−122·5	−122·6
−140	+ 8·14	−131·9	·907	+0·24	−131·6	−131·7
−150	+ 9·12	−140·9	·903	+0·22	−140·7	−140·8
−160	+10·1	−149·9	·898	+0·19	−149·7	−149·8
−170	+11·2	−158·8	·893	+0·16	−158·6	−158·8
−180	+12·3	−167·7	·888	+0·11	−167·6	−167·8
−190	+13·4	−176·6	·883	+0·05	−176·5	−176·7
−200	+14·6	−185·4	·878	−0·02	−185·4	−185·5
−210	+15·8	−194·2	·874	−0·09	−194·3	−194·3
−220	+17·1	−202·9	·869	−0·20	−203·1	−203·1
−230	+18·4	−211·6	·864	−0·31	−211·9	−211·8
−240	+19·8	−220·2	·859	−0·43	−220·6	−220·5
−250	+21·3	−228·7	·855	−0·58	−229·3	−229·1
−260	+22·8	−237·2	·850	−0·73	−237·9	−237·7
−270	+24·3	−245·7	·845	−0·90	−246·6	−246·3
−280	+25·8	−254·2	·840	−1·08	−255·3	−254·8
−283	+26·4	−256·6		−1·16	−257·8	−257·3

The above table affords a good illustration of the point
already mentioned, that the results obtained from the two
difference-formulæ (D) and (D') agree so closely over a limited
range, as in the present case, that it is often quite immaterial
which of the two is used for purposes of reduction. The
largest difference over the experimental range in the present
instance is only 0°·3, which is less than many of the errors of
observation, except at the fixed points and under the most
favourable conditions. In comparing the two formulæ the
following expression for the difference between them is
occasionally useful :—

$$D - D' = t - t' = dD(2pt + D - 100)/10,000 + (d/d' - 1)D'.$$

It is generally sufficient to put $D = D'$ on the right-hand side of this formula, so that if either is known the difference between them may be determined with considerable accuracy.

It will be observed that the table of reduction given by Dickson agrees very closely with either of the difference-formulæ. But, on the whole, most closely with (D). If Dickson had calculated his formula from the same data it would have given results *identical* with (D'). By giving equal weight, however, to all the observations, without regard to steadiness of temperature or probable accuracy, he is compelled, as in the previous instance, to admit an error of $0°\cdot35$ in the fundamental interval itself, which is quite impossible. Except at these points the probable error of his reduction is not of vital importance ; on the contrary, the general agreement with (D) is so close that it is difficult to see on what grounds he can regard the latter as being either incorrect or inadequate.

For practical purposes a table of this kind is not convenient owing to the continual necessity for interpolation. A graphic chart in which t is plotted directly against pt is objectionable, because it does not admit of sufficient accuracy unless it is plotted on an unwieldy scale. The difference-curve avoids this difficulty, and is much to be preferred for laboratory work. But for occasional reduction it is so easy to calculate the difference directly from the formula that it is not worth while to take the trouble to plot a curve.

Reduction of Olszewski's Observations.—The observations of Olszewski on the critical pressure and temperature and boiling-point of hydrogen, described in the Phil. Mag. for July 1895, were made with a platinum thermometer of $\cdot001$ inch wire wound on a mica frame in the usual manner. He graduated this thermometer by direct comparison with a constant-volume hydrogen thermometer at the lowest temperatures which he could obtain by means of liquid oxygen boiling under diminished pressure. The lower temperatures, observed with the thermometer immersed in temporarily liquefied hydrogen, were deduced from the observed resistances by *rectilinear* extrapolation, assuming that the resistance of the platinum thermometer continued to decrease, as the temperature fell, at the same rate as over the lowest temperature interval, $-182\cdot5$ to $-208\cdot5$, included in the range of the comparison with the hydrogen thermometer. It is possible that, at these low temperatures, the resistance of platinum does not continue to follow the usual formula, but it may be interesting to give a reduction of his observations by the difference method for the sake of uniformity of expression.

We select for this purpose the following data:—

Thermometer in Melting Ice,
$R/R° = 1·000$, $t = 0°$ C.

Thermometer in solid CO_2 at 760 mm.,
$R/R° = ·800$, $t = -78·2°$ C.

Thermometer in Liquid O_2 at 760 mm.,
$R/R° = ·523$, $t = -182°·5$ C.

From these we deduce the following values of the coefficients:—

$a = ·002515$, $b = -·000,000,53$, $c = ·002462$, $d = 2·13$,
$pt° = 406°·2$.

As a verification we have the observation $R/R° = ·453$, at $t = -208°·5$ C. This gives $pt = -222·2$, $D = 13°·7$, which agrees with the value given by the difference-formula calculated from the three higher points.

The following Table gives the reduction of the observations taken with this thermometer in partially liquid hydrogen.

TABLE III.—Reduction of Olszewski's Observations in Boiling Hydrogen.

Pressure.	R/R° Obs.	pt.	D.	t (° C.).	t Olszewski.	t'.
atmos. 20	·383	$-250°·6$	$16°·6$	$-234°·0$	$-234°·5$	$-233°·4$
10	·369	$-256·3$	$17·3$	$-239·0$	$-239·7$	$-238·4$
1	·359	$-260·4$	$17·7$	$-242·7$	$-243·5$	$-242·0$

The effect of this change in the method of reduction is to make the temperature of the boiling-point of hydrogen nearly one degree higher than the value given by Olszewski. If we employ instead the difference-formula in terms of pt, we should find $c' = ·002472$, $pt° = 404°·5$, $d' = 1·85$. This formula leads to the values given in the column headed t', which are a little higher.

The value found by Dewar for *liquid* hydrogen (Proc. R. S. Dec. 16, 1898) is much higher, namely $t = -238°·8$ at one atmo, and $-239°·6$[*] at 1/30th atmo. The difference may possibly be due to the superheating of the liquid, or, more probably, to some singularity in the behaviour of his thermometer at this point (see below, p. 218).

Observations of Holborn and Wien (Wied. *Ann.* lix. 1896). —Holborn and Wien made a direct comparison between the

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[*] Values calculated from observed resistances by formula (2). Dewar gave $-238°·4$, and $-239°·1$.

hydrogen and platinum thermometers, adopting my method of enclosing the spiral inside the bulb of the air-thermometer. The majority of their observations were taken while the temperature of the instrument was slowly rising. This method of procedure is very simple, but it is open to the objection that the mean temperature of the spiral is not necessarily the same as that of the gas enclosed, especially when, as in their apparatus, the spiral is asymmetrically situated in an asymmetrical bulb. If we take their observations in melting ice, in solid CO_2, and in liquid air, which are probably in this respect the most reliable, and calculate a difference-formula in terms of pt, we shall find $c' = \cdot 003621$, $d' = 1 \cdot 69$. Calculating the values of t' by this formula, we find that all the rest of their observations make the temperature of the platinum spiral on the average 1° higher than that of the gas. This might be expected, as the temperature was not steady, and the warmer gas would settle at the top of the bulb, the spiral itself being also a source of heat.

If we take their own formula, and calculate the equivalent difference-formula, we find $c' = \cdot 003610$, $d' = 1 \cdot 79$. This agrees fairly well with the values found above, as they appear also to have attached greater weight to the observations in CO_2 and liquid air. But, if we take the formula calculated by Dickson (Phil. Mag. Dec. 1897), who attaches equal weight to all their observations, we find $c' = \cdot 003527$, $d' = 2 \cdot 43$. The excessive difference in the values of the coefficients deduced by this assumption is an index of the inconsistency of the observations themselves[*].

Behaviour of Pure Wire at Low Temperatures.—In the case of ordinary platinum wire, with a coefficient $c = \cdot 0035$ or less, the effect of the curvature at low temperatures of the t, R, curve, as represented by the positive value of the difference-coefficient d, is to make the resistance diminish more rapidly as the temperature falls, and tend to vanish at a point nearer to the absolute zero than the fundamental zero of the wire itself. When, however, the value of $pt°$ is numerically less than 273°, the effect of this curvature would be to make the resistance vanish at some temperature higher than the absolute zero. If, therefore, we may assume that the resistance ought not to vanish before the absolute zero, we should expect to find a singular point, or a change in sign of the difference-coefficient, at low temperatures. If this were the case, it would seriously invalidate the difference-formula method of reduction, at least at low temperatures, and as

[*] Contrast the close agreement of Dickson's reduction in the case of Fleming's observations.

applied to wires for which pt° was numerically less than
273°.   When, therefore, I succeeded in obtaining in 1892 a
very pure specimen of wire, with the coefficient $c = \cdot 00389$,
$pt^\circ = 257^\circ$, I quite expected to find it behave like iron and
tin, with the opposite curvature to the impure platinum, and
a *negative* value for the coefficient d.   On testing it at the
S.B.P. and also at the Ag.F.P. I found, on the contrary, that
it gave a value $d = +1 \cdot 50$, and that its scale agreed very
closely with that of all the other platinum wires I had tested,
at least at temperatures above 0° C.   I sent a specimen to
Prof. Fleming shortly afterwards and he used it as the
" working thermometer P_2 " in his researches on the thermo-
electric properties of metals at low temperatures.   The test
of this wire is given by Fleming in the Phil. Mag. July
1895, p. 101, from which the following details are extracted:—

$$c = \cdot 003885, \, pt^\circ = 257^\circ \cdot 4. \quad CO_2 \text{ B.P.}, \, pt = -81^\circ \cdot 3.$$
$$\text{O.B.P.}, \, pt = -193^\circ 3.$$

Assuming $t = -182^\circ \cdot 5$ at the O.B.P., we have $d = +2 \cdot 10$,
which gives $t = -78^\circ \cdot 4$ for the temperature of solid CO_2.
The value of the difference-coefficient, so far from vanishing
or changing sign, appears to be actually greater at very low
temperatures.   According to this formula, the resistance of
the wire tends to vanish at a temperature $t^\circ = -240^\circ \cdot 2$, cor-
responding to $pt^\circ = -257^\circ \cdot 4$.   It seems not unlikely, however,
according to the observations of Dewar, that the resistance,
instead of completely vanishing at this temperature, which is
close to the boiling-point of hydrogen, ceases to diminish
rapidly just before reaching this point, and remains at a small
but nearly constant value, about 2 per cent. of its value at 0° C.

*Application of the Difference-Formula to the case of other
Metals.*—The application of the difference-formula is not
limited to the case of platinum.   It affords a very convenient
method of reduction of observations on the resistance-varia-
tion of other metals.   I employed it for this purpose in the
comparison of platinum and iron wires *, as a means of veri-
fying the suitability of the parabolic formula for the expres-
sion of variation of resistance with temperature.   Thus, if the
symbol ft stands for the temperature by an iron-wire thermo-
meter, defined by formula (1), in exactly the same manner
as the platinum temperature, and if d and d' stand for the
difference-coefficients of platinum and iron respectively, as-
suming that both wires are at the same temperature t, we
have clearly the relation

$$ft - pt = (d - d') \times p(t).$$

* Phil. Trans. A. 1887, p. 227.

As an illustration of the convenience of this method of re-
duction a table is appended giving the values of the constants
at low temperatures for the specimens tested by Dewar and
Fleming. The data assumed in each case are (1) the value
of the fundamental coefficient c given in the first column, and
(2) the value of the temperature of the O.B.P. on the scale
of each particular metal, calculated from the observed re-
sistance by formula (1), and given in the third column. The
value of the difference-coefficient $d°$ for each metal as deduced
from the O.B.P. is found at once by the relation

$$d° = (-pt - 182 \cdot 5)/5 \cdot 16.$$

The sign of this coefficient indicates the direction of the cur-
vature of the temperature-resistance curve, and its magnitude
is approximately proportional to the average relative curvature
over the experimental range.

The values of the coefficients a and b, given in the last two
columns, are readily calculated from those of c and d by
means of the relations already given (p. 199). These co-
efficients refer to the equivalent resistance - formula (3),
and are useful for calculating the specific resistance at any
temperature.

In comparing the values of $d°$, given in this table, with
those deduced from observations at higher temperatures, it
will be noticed that they are in most cases algebraically
greater, the difference amounting to nearly 30 per cent. in
many cases between the values deduced from the O.B.P. and
the S.B.P. respectively. It is possible that this indicates a
general departure from the exact parabola requiring further
experiments for its elucidation. It would be unsafe, however,
to infer from the results of the present investigation that this
is always the case, because, owing to the construction of the
coils with silk and ebonite insulation, it was impossible to
test the wires directly in sulphur, and they could not be
annealed after winding at a higher temperature than 200°.
It is well known that annealing produces a marked effect on
the form of the curve and on the value of $d*$. It is also stated
in the paper that trouble was experienced from thermoelectric
disturbances, owing to the use of thick copper leads 4 mm.
in diameter. Such effects cannot be satisfactorily eliminated
except by the employment of a special method of compensa-

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* With reference to this point it is interesting to remark that Messrs.
Heycock and Neville with one of their perfectly annealed pyrometers of
pure wire, for which $c = ·00387$, $d = 1·497$, found the value $pt = -80°·3$,
$t = -78°·2$ C., for the CO_2 B.P. This would perhaps indicate that the
larger values of d were due to imperfect annealing.

TABLE IV.—Application of the Difference-Formula to other Metals.

Metal.	Fundamental Coefficient. c.	Fundamental Zero. $-pt°$.	O.B.P. Observed. pt.	Difference-Coefficient. $d°$.	Vanishing Temperature. $t°$.	$(dR/dt)/R°$ at 0° C. $a×10^6$.	$\dfrac{(d^2R/dt^2)}{2R°}$ $b×10^6$.
Platinum (1)...............	·003533	-283·0	-196·7	+2·75	-257·7	3600	-0·97
„ (2)...............	·003669	-272·5	-196·5	+2·72	-248·8	3769	-0·99
„ (3)...............	·003885	-257·4	-193·3	+2·10	-240·2	3967	-0·82
Gold	·00377	-265·2	-183·0	+0·10	-264·2	3774	-0·04
Palladium	·00354	-282·4	-205·5	+4·46	-244·7	3698	-1·58
Silver.....................	·00400	-250·0	-183·5	+0·19	-248·4	4008	-0·08
Copper	·00428	-234·0	-190·2	+1·49	-223·2	4344	-0·64
Aluminium	·00435	-230·0	-186·4	+0·75	-224·5	4383	-0·33
„ 99 °/₀	·00423	-236·0	-185·0	+0·29	-233·7	4242	-0·13
Iron (A)...............	·00544	-184·0	-143·0	-7·68	-252·2	5014	+4·18
„ (H.W.)	·00625	-160·0	-138·5	-8·75	-223·7	5703	+5·47
Nickel (Mond)	·00622	-161·0	-135·8	-9·06	-228·5	5656	+5·63
Tin.........................	·00440	-227·5	-168·2	-3·60	-261·3	4242	+1·58
Magnesium	·00381	-262·5	-202·0	+3·80	-232·0	3955	-1·45
Zinc	·00406	-276·7	-182·5	+0·00	-246·7	4060	+0·00
Cadmium	·00419	-238·7	-168·3	-3·57	-275·7	4040	+1·50
Lead	·00411	-244·0	-171·7	-2·10	-244·2	4014	+0·86
Thallium	·00398	-251·6	-181·3	-0·23	-253·6	3971	+0·09

tion, which will be described in a subsequent communication. The general result of any residual thermal effects which may be present is to produce a change in the apparent value of d, since the thermo-E.M.F. follows approximately a parabolic formula. It is possible, for this reason, to obtain consistent and accurate measurements of temperature with a platinum thermometer in spite of large thermal effects, but the value of d would be very considerably affected.

On the " Vanishing Temperature."—There appears to be a very general consensus of opinion, based chiefly on the particular series of experiments which are under discussion, that the resistance of all pure metals ought to vanish, and does tend to vanish at a temperature which is no other than the absolute zero. If, however, there is any virtue in the parabolic method of reduction, it is quite obvious, on reference to the column headed " Vanishing Temperature " in the above table, that the resistance " tends to vanish " in the case of most of the common metals at a much higher temperature. The vanishing temperature t° is the value of t deduced from the fundamental zero pt° in each case by means of the difference-formula, employing the value of d° given in the table. The most remarkable metals in this respect are pure copper and iron, which tend to become perfect conductors at a temperature of -223° approximately, a point which is now well within the experimental range. These are followed at a very short interval by aluminium, nickel, and magnesium. In the case of copper and iron special experiments were made at a temperature as low as -206° C., at which point the rate of decrease of resistance showed little, if any, sign of diminution. The exact value of the vanishing temperature in each case is necessarily somewhat uncertain owing to the necessity of extrapolation, and also on account of possible uncertainties in the data; but there can be no doubt that the conclusion derived from the formula represents, at least approximately, a genuine physical fact. Whether or no the resistance does actually vanish at some such temperature may well be open to doubt. It would require very accurate observations to determine such a point satisfactorily, as the experimental difficulties are considerable in measuring so small a resistance under such conditions. It is more probable that there is a singular point on the curve, similar to that occurring in the case of iron at the critical temperature, at which it ceases to be magnetic. It is also likely that the change would not be sudden, but gradual, and that indications of the approaching singularity would be obtained a few degrees above the point in question. Below this point it is even pos-

sible that the resistance might not tend to vanish, but, as in the case apparently of bismuth, might increase with further fall of temperature. It has been suggested that at very low temperatures all metals might become magnetic. It is very probable that the change of electrical structure here indicated would be accompanied by remarkable changes in the magnetic properties. These are some of the points which experiment will probably decide in the near future. The only experimental verification at present available is the observation of Dewar in the case of platinum No. 3 when immersed in boiling hydrogen at $-240°$ C., that the resistance after attaining a very low value apparently refused to diminish further, in spite of a considerable lowering of the pressure. It would be extremely interesting to repeat this observation with specially constructed thermometers of copper or iron, which ought to show the effect in a more striking manner and at a higher temperature.

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XIV. *A Calorimetric Determination of Energy Dissipated in Condensers.* By EDWARD B. ROSA *and* ARTHUR W. SMITH*.

IN a former paper (*suprà,* p. 19) we gave the results of measurements by means of a wattmeter of the energy dissipated in condensers when they were subjected to an alternating electromotive force. The results were such that we desired to confirm them by a totally independent method : and, in addition, to measure the energy dissipated in some paraffinedpaper condensers which showed so small a loss that with the coils at our disposal the Resonance Method, employed successfully on beeswax and rosin condensers, would not give sufficiently accurate values. We therefore constructed a special calorimeter for the purpose of measuring the total quantity of heat produced in the condensers, which represents the total energy dissipated.

Fig. 1 gives an external view of the calorimeter, and fig. 2 a vertical section. The calorimeter proper, A, is the inner of three concentric boxes, and is 33 cm. long, 30 cm. deep, and 10 cm. in breadth. It has a copper lining, *a*, and a copper jacket, *b*, and is protected by the two exterior boxes from fluctuations of temperature without. The general principle of the calorimeter is (1) to prevent any loss or gain of heat

* Communicated by the Authors.