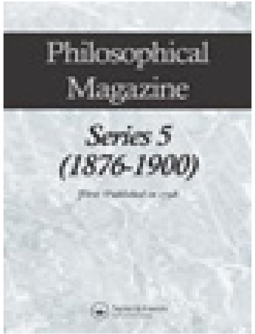

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XVII. On the construction of platinum thermometers

H. L. Callendar M.A.

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[I have been informed that a very high authority has brought forward as an argument against Mr. Pickering's methods the fact that a spring (or lath) may be pinned down so as to coincide to any desired degree of accuracy with any number of experimental points, and trust that I may be excused if I attempt to answer the objection. The use of an unlimited number of applied forces (one at each pin) is open to the same theoretical objections as would apply to an equation containing an unlimited number of constants. As Mr. Pickering used for drawing his curves a part of the lath throughout which no applied forces were acting, two distinct curves of the kind used by him would meet at each pin, and a discontinuity would exist, which can be shown by mathematical analysis to involve an abrupt change in the value of $\frac{d^3y}{dx^3}$, *i. e.* there would be a *break* at these points. Rapid changes too in the value of $\frac{d^2y}{dx^2}$ might take place if the applied forces were large, or the flexural rigidity of the lath small. In fact the pinning-down process simply masks any real breaks which may exist by substituting a (probably much larger) number of others. It would even seem to be theoretically possible that experiments as to the minimum number of applied forces required might indicate the points at which the breaks occur.—E. H. H.]

XVII. *On the Construction of Platinum Thermometers.* By H. L. Callendar, *M.A., Fellow of Trinity College, Cambridge**.

THE great superiority of the platinum-resistance thermometer over other instruments for measuring temperature lies in its comparative freedom from change of zero. Provided that the wire is pure to start with, and that it is protected from strain and from contamination, its resistance, when once annealed, is always very nearly the same at the same temperature.

This statement, which I made in 1886, has been received in some quarters with surprise and incredulity. The evidence on which it has been rejected appears to rest mainly on two well-known facts. Firstly, that the Siemens electrical pyrometers have always shown large and continuous changes of zero†; and, secondly, that platinum wires when used as

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* Communicated by the Author.

† British Association Report, 1874.

filaments for incandescent lamps undergo more or less rapid deterioration.

The Siemens pyrometer is a commercial and not a scientific instrument. I have myself examined some of the most recent pattern, and I should have been surprised if they had not been found to exhibit changes of zero when used at high temperatures. The wire is wound on common clay, which is apt to attack it, and is inclosed in an iron tube without sufficient protection from the metallic and other vapours which are sure to be present.

In the case of lamp-filaments which are heated by a current *in vacuo*, it might appear at first sight as though the wire were perfectly protected from strain or contamination; but this is far from being the case. The sudden heating and cooling of the wire when the current is turned on or off, and the intense radiation which keeps the surface at a lower temperature than the central portions, must be a severe strain on the wire. It is also evident that any crack or flaw in the surface will tend to be intensified by the local development of greater heat; and if the wire is heated to a temperature near its melting-point where it begins to be appreciably volatile, this action must inevitably produce serious results. If a wire which has been thus treated be examined under the microscope, its surface will generally be found to be cracked and scored in a manner which is of itself amply sufficient to account for the increased resistance and brittleness.

The wire of a platinum thermometer which is properly protected does not undergo any alterations of this kind, if treated with reasonable care. I have recently succeeded in making these thermometers of a very convenient and accurate form; and I have reason to believe, from inquiries which have reached me from various sources, that a description of the pattern which I have found to give the best results would be useful to other observers who require a sensitive and trustworthy thermometer.

The simplest form of platinum thermometer is made by fusing or welding a coil of fine wire to leads of relatively low resistance. The coil and leads must be suitably insulated and supported; for most purposes it is convenient to inclose the instrument in a tube of similar dimensions to an ordinary thermometer. For use at temperatures below 700° C. the leads may be of copper or silver, and the tube of hard glass.

For rough work at temperatures below 1000° C. very fair results may be obtained by the use of a wrought-iron tube. The leads should also be made of iron. Copper and silver are too volatile. Their vapours will attack the platinum, and very small traces of either are sufficient to ruin the wire for thermometric purposes.

For accurate work at high temperatures it is necessary to use platinum leads, and to inclose the coil in a tube of glazed porcelain or silica.

For insulating the coil and leads I have found nothing that answers so well as mica. Biscuit porcelain is fairly good, but most varieties of clay are apt to attack the wire at high temperatures. If the wire is wound on a clay cylinder, the relatively large mass of the clay has also the effect of materially reducing the sensitiveness.

The wire is preferably doubled on itself like an ordinary resistance-coil, and wound on a thin plate of mica. The leads are insulated by being made to pass through a series of mica wads cut to fit the tube containing the instrument. This method has the advantage of giving very perfect insulation, and of preventing convection-currents of air up and down the tube.

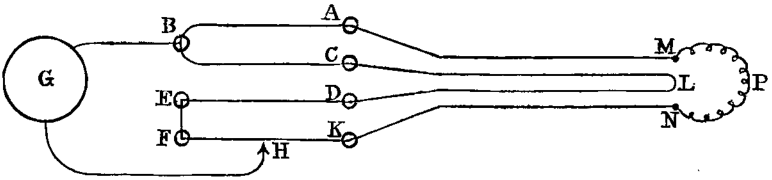
The resistance of such an instrument may conveniently be measured by means of an ordinary post-office box. If the resistance-coils are of German-silver wire, the temperature of the box must be taken at each observation and a correction applied. It is better therefore to use a box with coils of copper-nickel-manganese, or one of the many other alloys that do not change appreciably in resistance at ordinary temperatures.

With the above simple arrangement it is not difficult to obtain results consistent to a few hundredths of a degree at 500° C., provided that the resistance of the leads is relatively very small and fairly constant, and that the stem of the thermometer is always immersed to nearly the same extent. There are some objections, however, to the use of thick leads. They are necessarily wanting in lightness and flexibility, and they tend to cool the bulb of the thermometer by conduction along the stem.

For most purposes it is better to insert in the stem of the thermometer a second pair of leads similar to those of the coil itself, so that their resistance can be measured separately. It is then possible to use leads of any convenient length and flexibility, and to make the observations of temperature independent of the length of stem immersed.

In the ordinary method of measuring a resistance with a post-office box, it is necessary to observe galvanometer-throws in order to find the last two figures of the value of the resistance. If, however, a divided bridge-wire be used in conjunction with the resistance-box for determining the fractions of an ohm in the manner now to be described, the apparatus can at the same time be arranged so that the variable resistance of the leads is eliminated. The reading of the bridge-wire scale when the balance is found is then independent of the length of stem immersed, and gives the temperature of the thermometer-coil without the necessity of observing galvanometer-throws or of measuring the resistance of the leads.

The annexed figure represents, somewhat diagrammatically, the arrangement of the apparatus.



A B, B C are equal resistances forming the arms of the balance. The battery is connected at A and C, and one terminal of the galvanometer G at B. D E represents a set of resistance-coils, which together with A B and B C may be supplied by an ordinary post-office box. F K represents a straight bridge-wire with a divided scale attached. The other terminal of the galvanometer is connected to the contact-piece H, which slides along this wire. The leads A M, K N, from the pyrometer-coil P, are connected to A and K; and the compensating leads C L, L D, the resistance of which is equal to A M, K N, are connected to C and D. These four leads may be of any convenient length; they are symmetrically arranged so that corresponding parts are always at the same temperature. When the balance is found by unplugging suitable resistances in the arm D E and sliding the contact-piece H, it is plain that, since the resistances A B, B C are equal, the resistance of the pyrometer and its leads, plus that of the length H K of the bridge-wire, will be equal to the resistance of the remaining portion F H of the bridge-wire together with that of the coils D E and the compensator C L D. Thus the changes of resistance of the pyrometer-leads A M, K N are compensated by the equal changes in the leads C L, L D; and the resistance of the pyrometer-coil itself is directly given by the sum of the coils D E and the reading of the bridge-wire.

It is convenient to graduate the bridge-wire scale so that 100 or 1000 divisions are equivalent to the unit coil in the arm D E. It is also convenient to adjust the resistance of the pyrometer-coil, so that the change of its resistance between 0° and 100° C. may be equal to 1, 10, or 100 units. The divisions of the bridge-wire will then represent degrees of temperature on the platinum scale, and the temperature can be deduced from the observed resistance by simply subtracting its zero value.

The arrangement, however, will work equally well with an arbitrary scale. The really important point is that an observation of temperature is reduced to a single scale-reading, and that it is independent of the length of stem immersed.

The chief errors to be apprehended with this form of apparatus are changes in the screw and plug contacts, especially the latter. Instead of the ordinary plug for short-circuiting the terminals of a resistance-coil, I prefer to use a flat nut screwing down on to two flat plates. I find that better contact may thus be secured, and, what is more important, that the contact-surfaces may be more easily kept clean and good. It is almost impossible to keep a plug-hole free from grit and grease, even if the plug fits perfectly; whereas the screw-nut can be kept screwed down when not in use, and the flat surfaces are easily cleaned if necessary. Moreover the wedge-like action of the plugs almost invariably loosens the blocks between which they are inserted, so that taking out one plug alters the contacts of its neighbours. This cannot occur with the screw-nuts. Among minor advantages it may be mentioned that the screw-nuts, not being loose, are not so liable to get lost or soiled.

Perhaps the best way to make the sliding-contact at H is to connect the galvanometer to a fixed wire of the same material as F K and stretched parallel to it. Connexion is made between the two wires by pressing down a button carrying a short cross-wire fixed to a spring on the lower side of the sliding contact-piece. The advantages of this arrangement are that the wire from the galvanometer is not attached to the sliding-piece itself but to a *fixed* binding-screw, and that there is less danger of thermoelectric effects being produced by the warmth of the hand at H.

The current used in measuring the resistance must not be too large or the fine wire will be heated. It appears that a platinum wire of 0·015 centim. (·006 inch) diam., which is a convenient size to use for these thermometers, will take a current of one hundredth of an ampere when cooled by air contact, without heating much more than one hundredth of a degree C. If a higher order of accuracy is desired, the current-heating must be measured and allowed for.

The degree of sensitiveness and accuracy attainable with these instruments depends largely on the adjustment of the galvanometer and on the perfection of the optical means for reading its deflexions. A convenient method is to use a microscope * with a micrometer-eyepiece, and to observe the reflected image in the galvanometer-mirror of a scale attached to the objective. The power of the microscope in magnifying the deflexions is proportional to the length of its body and to the power of the eyepiece, and does not depend on the focal length of the objective. A telescope does equally well, but the arrangement is then less compact. Either method is superior to the lamp and scale in point of accuracy and for other reasons, particularly in not requiring a darkened room. This is a great advantage, because a good light is preferable for reading the scale of the bridge-wire and noting down the observations.

With regard to the formula to be used for reducing the observed platinum-temperature pt to the temperature t by air-thermometer, the very careful experiments made by Griffiths on the boiling- and freezing-points of various substances † seem to show that the simple parabolic formula

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

holds over a wide range even more accurately than I had previously imagined. The values of t for various boiling- and freezing-points, deduced by the aid of this formula from observations with thermometers of very different patterns and with different coefficients, were rarely found to differ from each other by more than a few hundredths of a degree over the range 0°–450° C. The value of the constant δ for any thermometer may be readily deduced from a single observation of the boiling-point of sulphur or mercury as described in the paper above referred to ‡.

The air-thermometer experiments § on which this formula was founded did not extend beyond 650° C., but I have recently succeeded in verifying it roughly at a higher temperature by an observation of the freezing-point of silver. This point appears to be very clearly marked and well adapted for a high-temperature standard. Several independent observations with a platinum thermometer gave the same result, 982°·1 C., within a small fraction of a degree. The specimen of silver, however, was not perfectly pure, so that the result

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* I owe this suggestion to Mr. Horace Darwin of the Instrument Co., Cambridge, to whom I am also much indebted for the care and skill bestowed on the construction of my apparatus.

† Phil. Trans. 1891, A. pp. 43 & 148.

‡ Phil. Trans. 1891, A. p. 146.

§ Phil. Trans. 1887, A. p. 161.

is probably a little too low. Moreover, on account of the wide discrepancies at present existing in the estimates of the temperature of the freezing-point of silver on the air-thermometer scale, according to different authorities, the result would in any case serve only as a *rough* verification of the formula (*d*). The difficulties in the way of making accurate determinations with an air-thermometer at this temperature are undoubtedly considerable; but I have recently succeeded in devising a special form of instrument with which I hope to be able to obtain more trustworthy results.

Sir Wm. Siemens was the first to attack the problem of determining the variation of electrical resistance at high temperatures. He showed that the formula given by Matthiessen,

$$R_0/R_t = 1 - \alpha t + \beta t^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (m)$$

was entirely inapplicable except between the limits 0° and 100° C. His own experiments led him to suggest the formula

$$R = \alpha T^{\frac{1}{2}} + \beta T + \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S)$$

This formula has been very widely quoted and adopted, but it does not, so far as my experience goes, represent the results of observation so well as the simpler formula $R/R_0 = 1 + \alpha t + \beta t^2$, which was used by Benoit, and which is equivalent to formula (*d*).

I have only recently succeeded in finding a published account of Sir Wm. Siemens's experiments *. It appears from this that they were undertaken rather with a view of graduating a commercial pyrometer than of investigating the law of change of electrical resistance. Temperatures up to 350° were determined *by mercury thermometers* in an air- or oil-bath, and it does not appear that any corrections were applied to their readings. The individual observations are somewhat irregular, and often show divergencies amounting to 2 per cent. and over. Only three observations at higher temperatures are given; they show a mean deviation of about 30° C. A copper ball-pyrometer was used to determine the temperatures, which are given as 810°, 835°, and 854° C.; the corresponding temperatures deduced by formula (S) from the observed resistances of the platinum pyrometer were 772°, 811°, and 882° C.

The formula Siemens gives for *iron* makes the rate of increase of its resistance *diminish* considerably with rise of temperature. The formula given by Benoit makes it *increase*

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* 'Transactions of the Society of Telegraph Engineers,' 1875.

very largely. All the specimens I have tried agree very closely with Benoit's formula. I am inclined to think that the Siemens formula must be wrong. It is at least noteworthy that two of his observations differ by 6 and 3½ per cent. respectively from his formula in the direction of agreeing with Benoit's, and that if allowance is made for the probable errors of the mercury thermometers at 350° the discrepancy may be still further reduced. The resistances apparently were only measured to about 1 per cent. in most cases, and the temperatures are given only to the nearest degree. The Siemens formula is undoubtedly superior to that given by Matthiessen, but the evidence in its favour is hardly sufficient to justify its continued use in preference to the much simpler and more convenient formula (*d*).

The superior capabilities of platinum thermometers as compared with instruments in general use do not appear as yet to be sufficiently appreciated. It will perhaps help to bring out more clearly several of the points mentioned in their construction, if I give a brief summary of some of the advantages which they present in point of range, constancy, and sensitiveness, as compared with the best mercury thermometers.

The range of a mercury thermometer is obviously limited to temperatures between −40° and +400° C. That of a platinum thermometer may extend from absolute zero to above 1500° C.

The superiority of the platinum thermometer is still greater in point of constancy. It is a fact familiar to those who have studied mercury thermometers, that if a new thermometer be kept at a temperature of 350° C. for a week or so, its zero will be found to rise by 10° or 20° owing to the contraction of the glass. After a time this rise reaches a limit; but if a thermometer which has been thus annealed and allowed to cool *slowly* be again heated to 350° for a few minutes and allowed to cool *rapidly* by free exposure to the air, its zero will be found to be *depressed* by a quantity which varies with different thermometers, but which generally amounts to about 2°. A similar depression, but less in amount, is observed if the thermometer is heated to some intermediate point of the scale. The extent of depression also depends on the time during which the thermometer is heated, and on the rate at which it is cooled. Thus even in the best mercury thermometers, which have been carefully annealed by a special process, the position of the zero is constantly shifting in a manner which depends on the past history of the instrument. It is consequently very difficult, and in many cases impossible, to attain an accuracy of the order of a tenth of a degree even at temperatures as low as 200° C.

On the other hand, when a platinum thermometer has once been annealed (a process which can be completed in a few minutes), its zero will not be found to vary even by a hundredth of a degree—if it is properly constructed—when used at any temperatures up to 500° C.; and in some thermometers which I have used at temperatures as high as 1300° C., I have not found any changes of zero amounting to more than a tenth of a degree.

Sensitiveness and rapidity of observation are often of considerable importance. A mercury thermometer with an open scale must necessarily contain a relatively large mass of mercury, since there are objections to unduly diminishing the bore of the tube. Thus it cannot be made so sensitive as a platinum thermometer in which the actual mass of metal may be very small. A still more important point is that, owing to the imperfect elasticity of the glass, it is desirable to allow the mercury thermometer some time to settle before taking a reading. This is of course unnecessary in the case of the platinum thermometer.

In ordinary work with mercury thermometers it is generally necessary to expose some portion of the stem to the air. If a volume of mercury corresponding to any considerable number of degrees be thus exposed, the error becomes serious. It may amount to as much as 10° at 350° C. This correction is so uncertain that it is now generally considered inexpedient to attempt to apply it. The only way to avoid it, and at the same time to secure a sufficiently open scale for accurate work without unduly increasing the length of the stem, is to use a *series* of thermometers of "limited scale." Each of these must have at least two points of its scale specially determined. It has hitherto been the custom to graduate such thermometers by means of substances of known boiling- and freezing-points; but, as Griffiths * has shown, the graduation may be much more easily and accurately effected by comparison with a single platinum thermometer, a method which has the further advantage of saving the trouble of calibrating the stem.

It is easy to construct a platinum thermometer with a scale of 1 centim., or even 10 centim., to the degree, whose reading shall be entirely independent of the length of stem immersed. The divided wire on which the readings are taken need not be more than 20 centim. in length, and can be made to correspond to any part of the scale by simply unplugging a few

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* B. A. Report, 1890.

resistances. Thus a single platinum thermometer will do the work of a whole series of mercury thermometers, and that with far greater accuracy and without the necessity of applying any troublesome and uncertain corrections.

It may be objected that the use of a platinum thermometer requires electrical apparatus and some knowledge of electrical measurement. I quite admit that it requires some special skill and experience to *make* a good thermometer, but the rest of the apparatus required is obtainable in almost any laboratory, and it is easy to take the readings quickly and accurately after a little practice. The great superiority of the platinum thermometer in range, accuracy, and durability, will be found in the end to save so much time and expense as will more than compensate for the small trouble of learning to use it.

XVIII. *On a probable Relationship between Specific Inductive Capacity and Latent Heat of Vaporization.* *By* EUGENE OBACH, *Ph.D., F.C.S.*[*]

THE discovery of a near relationship between physical constants hitherto considered independent of each other seems of sufficient interest to merit a place in the Philosophical Magazine, notwithstanding that the experimental data which can be brought forward in support of such relationship are somewhat meagre and not particularly accurate.

I have recently been led to investigate whether specific inductive capacity and latent heat of vaporization of a liquid are in any way related to each other, and I find this actually to be the case, at least as far as certain series of chemically related organic compounds are concerned, viz. the esters of formic, acetic, and benzoic acid, and the monatomic alcohols. For these bodies, as will be shown hereafter, inductive capacity and latent heat are directly proportional.

The numerical values of these two physical constants obtained by different observers are in many cases very discordant; and it was therefore considered desirable to adhere as far as possible to the figures given by one and the same authority, and to introduce those of others only where absolutely necessary.

The specific inductive capacities here adopted are those published by S. Tereschin[†] in 1889, and the latent heats of

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[*] Communicated by the Author.

[†] Wied. *Annal.* vol. xxxvi. pp. 792-804 (1889).