CHAPTER V.

ELECTRICAL RESISTANCE PYROMETER.

Introduction. — In this method use is ordinarily made of the variations of electric resistance of a platinum wire as a function of the temperature; these variations are of the order of magnitude of those of the expansion of gases. The ratio of the resistances is 1.39 at 100°, and 4.4 at 1000°. As electrical resistances are measurable with great accuracy, this process of estimation of temperatures offers a very great sensibility, and applying exactly the law that connects the variation of resistances to that of temperature most excellent results may be obtained.

The electric pyrometer was proposed by Siemens in 1871 (Bakerian Lecture); it rapidly came into use in metallurgical works on account of the reputation of its inventor, but it was soon abandoned for reasons which will be given later. This method of temperature measurement was revived twenty years afterwards by Callendar and Griffiths, and has been growing in favor ever since, both in the laboratory and in the industries, especially in England, and more recently in America. It is perhaps of interest to note that in Cambridge, England, the resistance thermometer was first brought into a satisfactory condition as a physical instrument and its theory successfully worked out by Callendar and Griffiths; there it was first used in most delicate measurements of chemical phenomena by Heycock and Neville; and finally, the Cambridge Scientific Instrument Company were pioneers in the manufacture of instruments suitable for industrial and scientific use.

Work of Early Investigators.— *Siemens.*— The Siemens pyrometer consists of a fine platinum wire 1 m. long and 0.1 mm. in diameter, wound on a cylinder of porcelain or fire clay; the whole is inclosed in an iron tube, destined to protect the instrument from the action of the flames.

Siemens tried also, but without success, ceramic materials impregnated with metals of the platinum group.

To measure the resistance he employed either a galvanometer, for laboratory experiments, or a voltameter, for the measurements in works. In this latter case the current from a cell divides between the heated resistance and a standard resistance at constant temperature; in each one of the circuits was placed a voltameter: the ratio of the volumes of gas set free gives the ratio of the current strengths and thus the inverse ratio of the resistances.

Finally Siemens gave a formula of three terms connecting the electrical resistance of platinum to temperatures on the air thermometer, but without publishing the experimental data on which this graduation was based.

Experiment soon showed that the apparatus did not rest comparable with itself. A committee of the British Association for the Advancement of Science found that the resistance of platinum increases after heating. It would be necessary then to calibrate the apparatus each time that it was used. This change of resistance is due mainly to a chemical alteration of platinum, which is enormous when heated directly in the flame, less, but still marked, if placed in an iron tube, and which almost disappears if use is made of a platinum or porcelain tube. This increase of resistance may reach 15 per cent by repeated heatings to 900°.

Platinum being very costly and porcelain very fragile, it was impossible to use these two bodies in the industries, which alone at that time occupied themselves with measurements of high temperatures, and this method was abandoned completely during twenty years.

Callendar and Griffiths. — These savants revived this method for laboratory purposes; it seems the best for many kinds of work of precision to moderately high temperatures, on the condition of being assured of the invariability of the resistance of platinum.

Callendar found that clay helps to cause the variation of resistance, that the platinum wire becomes brittle on its support and sticks there; this action is probably due to impurities in the clay. With mica, on the other hand, which the wire touches only at the edges (the reel is made of two perpendicular slices of mica), there is perfect insulation without cause of alteration; but mica becomes dehydrated at 800° and then becomes very fragile.

All metallic solderings should be proscribed, for they are volatile and attack platinum.

Pressure joints (screw or torsion) are equally bad, for they become loose. One should use only autogenous soldering by the fusion of platinum.

Copper conductors should also be rejected, at least in the heated portions, on account of the volatility of the metal. A pyrometer with such conductors, heated during an hour at 850°, showed an increase of resistance of $\frac{1}{3}$ per cent.

Holborn and Wien. — These investigators made a very complete study of this alterability of platinum wires, in a comparison between the methods of measurement of temperatures by electric resistance and thermoelectric forces; they worked with wires of 0.1 mm. to 0.3 mm. diameter. They soon found that above 1200° platinum commences to undergo a feeble volatilization which suffices to increase notably the resistance of the very fine wires. Hydrogen in presence of silicious materials causes at about 850° a rapid alteration of the platinum.

Below are the results relative to wires of 0.3 mm. of a length of 160 mm.:

Wire α.	R at 15°.
At start	0.239 ohm
After heating red-hot:	
Twice in air at 1200°	0.238 ohm
Once in vacuo at 1200°	0.240 ohm
Once in H at 1200°	0.262 ohm
Once in vacuo at 1200°	0.253 ohm

Wire β.	R at 15°.
At start	0.247 ohm
After several days in hydrogen at 15°	0.246 ohm
After heating in hydrogen to 1200°	0.255 ohm

Wire γ.	R at 15°.
At start	0.183 ohm
After heating in air to 1250° (three times)	0.182 ohm
After heating in H to 1250°	0.188 ohm
After heating in H to 1250°	0.195 ohm

Wire γ heated to 1350° in an earthenware tube and in hydrogen became brittle; this result may be explained by a siliciuration of the platinum, for there is nothing observed if the wire is heated by the electric current in the interior of a cold glass tube, even in hydrogen. Similar experiments were made by the same observers with palladium, rhodium, and iridium. We shall return to this question of the constancy of the resistance of platinum.

Law of the Variation of Platinum Resistance. — Callendar and Griffiths have compared the resistance of platinum with the air thermometer up to 550° C.; they found that up to 500° the relation could be represented at least to 0.1° by a parabolic formula of three parameters. In order to graduate such a pyrometer it would be sufficient then to have three fixed points: ice, steam, and boiling sulphur.

They gave a special form to the relation; let p_t be the platinum temperature defined by the relation

$$p_t = \frac{R_t - R_0}{R_{100} - R_0} \cdot 100,$$

that is to say, the value of the temperature in the case in which the resistance varies proportionally to the temperature.

They then placed

$$t - p_t = \delta \left[- \frac{t}{100} + \left(\frac{t}{100} \right)^2 \right].$$

It would appear as if this formula contained the single parameter δ; but in reality p_t includes two.

Substituting for p_t its value, we have

$$R_t = R_0 + \frac{(1 + \delta)(R_{100} - R_0)}{(100)^2} \cdot t - \delta \frac{R_{100} - R_0}{(100)^3} \cdot t^2,$$

an equation of the form

$$R_t = R_0 (1 + at - bt^2),$$

which it is sometimes convenient to use. Callendar and Griffiths used their pyrometer before having standardized it against the air thermometer. Not being able to compute t, they provisionally computed the approximate temperatures p_t, and later determined the correction between t and p_t, after having sought the formula expressing the difference between these two quantities by means of a careful determination of the sulphur boiling point on the air thermometer. By extrapolation up to 1000° the points of fusion of gold and of silver were found quite near to those determined by other observers.

Harker, working at the National Physical Laboratory, England, has compared the readings of platinum thermometers, when reduced to the gas scale by the use of Callendar's difference formula, with the readings of thermocouples calibrated at the Reichsanstalt, and with the indications of an inglazed porcelain-bulb nitrogen thermometer at contant volume of the Reichsanstalt form. Specially constructed, compensated electric furnaces were used for heating.

As shown by the accompanying table, taken from one series of Harker's measurements, the agreement between the scales of the platinum-resistance and thermoelectric pyrometers was within 0.5° C. throughout the temperature range up to 1000°, although the gas pyrometer gave somewhat discordant results.

COMPARISON OF PYROMETRIC SCALES BY HARKER.

Temperature.			G − Pt.	G − Th.	P − Th.
Gas thermometer.	Thermocouple.	Pt thermometer.			
523.1	524.3	524.39	−1.3	−1.2	−0.1
598.5	597.8	597.62	+0.9	+0.7	−0.2
641.1	641.1	641.75	+0.6	+0.0	−0.6
776.7	775.5	775.13	+1.6	+1.2	−0.4
820.0	818.4	818.31	+1.7	+1.6	−0.1
875.0	875.4	875.24	−0.2	−0.4	−0.2
959.8	956.0	955.47	+4.3	+3.8	−0.5
1005.0	1004.4	1004.37	+0.6	+0.6	−0.0

A very careful direct comparison of the reduced indications of several platinum thermometers with the gas scale as furnished by the constant-volume nitrogen thermometer has also been made by Chappuis and Harker at the International Bureau at Sèvres, and their results give further evidence that the indications of the platinum thermometer up to 600° C. can be sufficiently well expressed by Callendar's formula.

There is another method of comparison of temperature scales which is capable of great accuracy, namely, the determination on the several scales of the freezing and boiling points of a number of pure substances. This method has some decided advantages over the above method of comparison even in a most carefully compensated electric furnace. Heycock and Neville in England, and more recently Waidner and Burgess at the Bureau of Standards, have determined the freezing points of several pure metals in terms of the scale of the platinum thermometer standardized at 0°, 100°, and 444.70° C. (the boiling point of sulphur), and find that the freezing points so determined give temperatures on the gas scale as closely as the latter can be reproduced, as shown in the following table:

GAS AND RESISTANCE TEMPERATURE SCALES.

	Gas scale.		Resistance scale.	
	Holborn and Day.	Day and Sosman.	Heycock and Neville.	Waidner and Burgess.
Cd	321.7	320.0	320.7	321.0
Zn	419.0	418.2	419.4	419.4
Sb	630.6	629.2	630.1	630.7
Al	657.0	658.0	.....	658.0
Ag	961.5	960.0	961.9	960.9
Cu	1084.1	1082.6	1082.0	1083.0

These results confirm the view of the sufficiency of the Callendar difference formula for the most accurate work up to the upper limit of the safe use of the platinum-resistance thermometer.

Holborn and Wien have shown that at very high temperatures the interpolation formula is certainly inexact. The resistance seems to become asymptotic to a straight line, while the formula leads to a maximum evidently inacceptable; in their opinion it would be better represented by an expression of the form

$$R \cdot t = a + b\,(t + 273)^m.$$

Here are the results of two series of their experiments made on the same wire:

t Degrees.	R Ohms.	t Degrees.	R Ohms.
0	0.0355	0	0.0356
1045	.1510	1040	.1487
1193	.1595	1144	.1574
1303	.1699	1328	.1720
1395	.1787	1425	.1802
1513	.1877	1550	.1908
1578	.1933	1610	.1962

Using the Callendar formula and platinum wires, Petavel found the melting point of palladium to be 1489°, which Callendar and Eumorfopoulos found to be 1550°. This latter number is in exact agreement with the best determinations of this temperature.

Although the work of Holborn and Wien, as well as that of Tory and others, shows that the platinum-resistance thermometer made of fine wire cannot be depended upon to remain constant above 1000° C., yet, in the range from −200° C. to +1000° C., it serves as the most accurate, and, on the whole, most convenient method of measuring temperatures where great precision is required, and is particularly adapted for the delicate control of a given temperature.

Dickson has proposed the formula

$$(R + a)^2 = p\,(t + b),$$

in which a, b, and p are constants. It possesses the possible theoretical advantage over the Callendar formula of not requiring a maximum value for the resistance of platinum. This form, however, does not lend itself to the convenient graphical treatment applicable to the difference formula; and furthermore, for thermometers of pure platinum calibrated at three temperatures in the usual way, the Dickson formula does not reproduce the same temperature scale as the difference formula as shown by Waidner and Burgess, it giving, for instance, 1051° C. for copper instead of 1083° C. for calibration in ice, steam, and sulphur vapor.

Nomenclature. — To determine a temperature by means of a platinum thermometer, if the instrument has not been calibrated already in degrees, it is necessary to know the difference coefficient δ of the wire, which may be obtained by finding the platinum temperature pt at some known point, as the sulphur boiling point (S.B.P.), or by comparison with a calibrated instrument.

Callendar has suggested the following notation which seems convenient for platinum thermometry:

Fundamental Interval. — The denominator $R_{100} - R_0$ in the formula

$$pt = \frac{100\,(R - R_0)}{(R_{100} - R_0)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the platinum temperature pt, represents the change of resistance of the thermometer between 0° and 100°.

Fundamental coefficient $= c =$ mean value of temperature coefficient of change of resistance between 0° and 100°:

$$c = \frac{(R_{100} - R_0)}{100\,R_0}.$$

Fundamental zero $= pt_0 = \frac{1}{c} =$ reciprocal of fundamental coefficient. It represents the temperature on the scale of the instrument itself at which its resistance would vanish.

Difference Formula. — The following form is the most convenient for computation:

$$D = t - pt = \delta \cdot \left(\frac{t}{100} - 1\right) \cdot \frac{t}{100}. \quad . \quad . \quad . \quad . \quad (2)$$

Parabolic function expresses the vanishing at 0° and 100° of above formula, which becomes

$$t = pt + \delta \cdot p\,(t).$$

"S.B.P." Method of Reduction. — D is obtained very conveniently by determining R'', and thus pt'' at t'' = the boiling point of sulphur (= S.B.P.).

Resistance Formula. — The parabolic difference formula is equivalent to assuming

$$\frac{R}{R_0} = 1 + at + bt^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$a = c\left(1 + \frac{\delta}{100}\right), \quad b = -\frac{c\delta}{10,000};$$

or

$$\delta = -\frac{b \cdot 10^4}{a + b \cdot 10^2}.$$

Graphic Method of Reduction. — An easy way to reduce platinum temperatures to the gas scale is to plot the difference $t - pt$ in terms of t as abscissas, and to deduce graphically the curve of difference in terms of pt as abscissas. This is most convenient for a single instrument up to 500°.

Other methods have been used by Heycock and Neville and by Tory.

Difference Formula in Terms of pt. —

$$t - pt = d'\left(\frac{pt}{100} - 1\right)\frac{pt}{100} = d'p\,(pt). \quad . \quad . \quad . \quad (4)$$

This formula is to be used only where a high degree of accuracy is not required. The value of d' may be determined from S.B.P., or approximately

$$d' = \frac{\delta}{(1 - 0.077\,\delta)}.$$

Construction of the Platinum Thermometer. — Callendar first devised a satisfactory and perhaps the most commonly used form of platinum thermometer, in which the platinum wire is wound on two strips of mica set crosswise. In Fig. 61 is shown a laboratory form of Callendar's potential terminal thermometer used at the Bureau of Standards in precision work to 1100° C. The heavy copper head insures a minimum of thermoelectric effects at the platinum-copper junctions, and provision is made for air cooling of the head, which is an advantage for work at the highest temperatures. The junctions of the leads to the platinum coil

are easily made by arc soldering, using platinum as one terminal and a graphite pencil as the other. No material other than platinum should enter into joints to be heated. Forms of mica supporting frame are shown in Fig. 62.

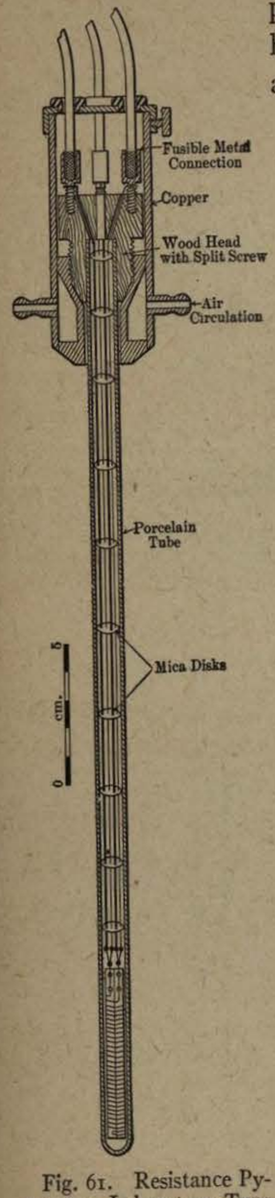
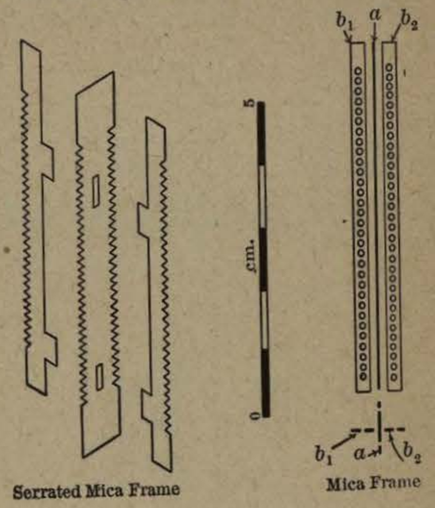


Fig. 61. Resistance Pyrometer, Laboratory Type.



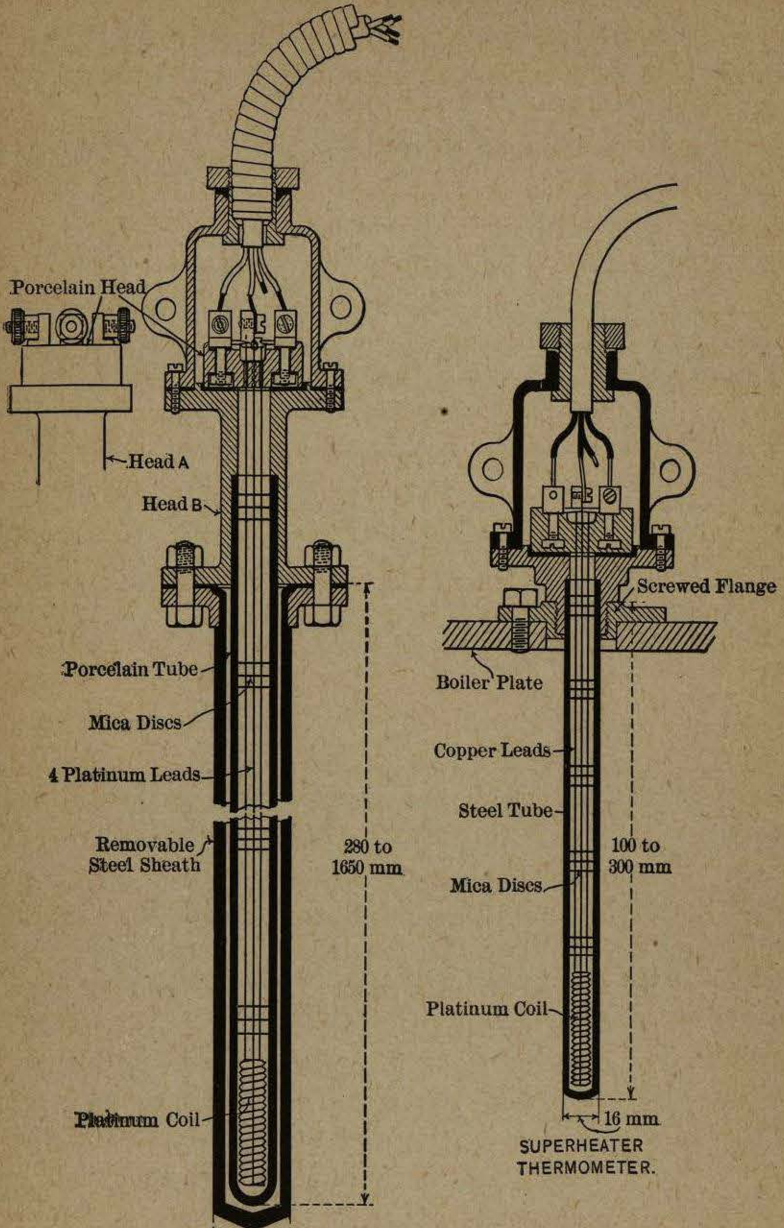
Serrated Mica Frame

Mica Frame

Fig. 62. Mica Frames.

Various modifications of the above design are used in the industrial forms, they being in general so arranged as to secure the maximum of protection and robustness to the platinum coil. Mica frames are sometimes replaced by steatite by Leeds and Northrup except for the highest temperatures. Industrial types of mounting used by the Cambridge Company are shown in Fig. 63.

The outer containing tubes for industrial instruments are preferably of metal, such as nickel or iron, over a quartz or porcelain tube, the actual material of the sheath depending, however, on the use to which it is to be put.



SUPERHEATER THERMOMETER.

THERMOMETER FOR FLUE TEMPERATURES.

Fig. 63. Types of Industrial Mounting.

For use at very high temperatures, Leeds and Northrup have designed the form of potential lead thermometer shown in Fig. 64. Heavy wire (0.6 mm.) is used in the coil, which is freely suspended and therefore not subject to strains on cooling. Due to its very low resistance, special precautions have to be taken in the temperature measurements to secure sensibility. Such heavy-wire thermometers will change their constants very much less than those of fine wire when heated to high temperatures. Thus Waidner and Burgess found that heating them for several hours to 1200° or 1300° C. changed the zero reading by only a few tenths degree, after they had been once annealed at 1300° C.

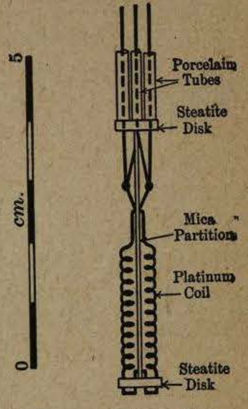


Fig. 64. Freely Suspended Coil.

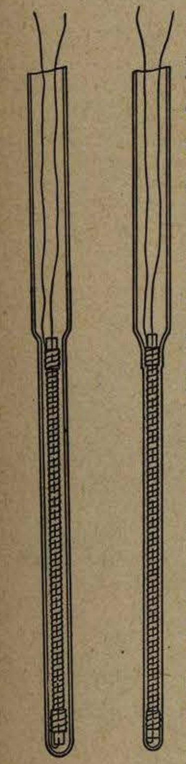


Fig. 65. Mountings in Quartz.

In order to secure an instrument of small volume and at the same time satisfactorily protect and rigidly mount the platinum coil, Heræus has devised the form shown in Fig. 65, in which the platinum coil is embedded in fused quartz glass.

The behavior of this type of thermometer, with wires of 0.05 to 0.15 mm., has been studied at the Reichsanstalt. The effect of embedding in quartz is to decrease the value of a (equation (3), page 202) and increase the value of δ. As compared with wires mounted in the usual way, and receiving the same heat treatment, the change in the constants is very great for these thermometers. For the former, a decreased by 0.45 per cent and δ by 0.65 per cent; for the latter, the changes were 1.7 per cent and 6.7 per cent respectively.

Where very great rapidity of action is desired the form of construction shown in Fig. 66, due to Dickinson, may be used in certain cases, the metallic parts being preferably all of platinum where great permanence is desired, and the insulation of mica strips.

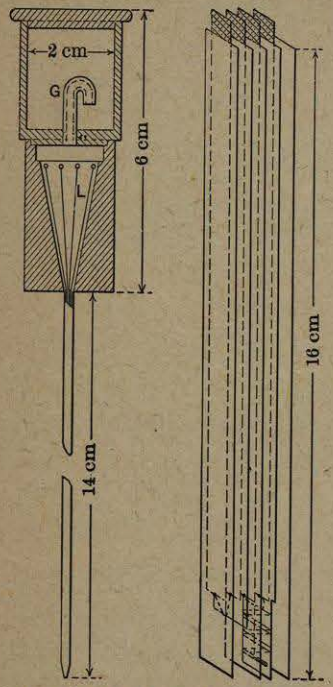


Fig. 66. Thermometer of Small Lag.

Where platinum thermometers are to be used with a definite form of measuring apparatus, or where several such thermometers are to be used with a single bridge, recorder, or other indicating or registering device, it is convenient to have them all adjusted to exactly the same resistance at zero and of the same fundamental interval, and so make them interchangeable. This is done by several firms by means of auxiliary manganin coils set into the thermometer head.

Choice of Size of Wire. — Regarding the choice of the diameter of wire to use in constructing a thermometer coil of given resistance, there are several points to consider besides the current-carrying capacity without undue heating of the coil, which is in favor of the heavy wire; such as the greater temperature lag, heat conduction along the leads, and excessive size of the thermometer coil, which, together with the cost, are the main inconveniences of heavy wire; and liability to strains, fragility, and greater evaporation, which limit the use and precision of too small wire. It is easy to get enough current sensibility, constancy of resistance, and robustness with wires of 0.15 to 0.20 mm. diameter except for very low-resistance pyrometers, 2 ohms or less, which are to be avoided, save for work at very high temperatures, as taxing too severely the sensitiveness of ordinary forms of measuring apparatus.

Precautions in Construction and Use. — The platinum thermometer, as usually constructed, is a fragile instrument in spite of its appearance of robustness when encased in a metal tube, therefore careful handling is required. To avoid breaking from sudden heating when porcelain or similar containing tubes are used, the pyrometer should be installed in advance in the furnace, or preheated in a muffle if it is necessary to introduce it into the hot furnace. It is necessary, also, to heat a sufficient length of the stem in the furnace in order to avoid the effect of heat conductivity, which would prevent the thermometer spiral from taking up the temperature of the space in which it is immersed. Platinum is readily attacked and its resistance changed by contact with most substances, including many vapors and gases, so that the thermometer coil must be carefully shielded by materials impervious to the atmosphere in which it is placed, such as porcelain glazed on the *outside*. As platinum changes its nature with heating, and as the frame on which the coil is wound may permanently change its dimensions, especially if mica is used, the thermometer before calibration should be annealed at a temperature higher than that at which it is to be used. A platinum thermometer will change its readings with time the more rapidly, the higher the temperatures at which it is used; therefore, in order to control its constancy, it is necessary to take its reading occasionally at some known temperature, as the ice or steam point. Well-shielded, pure platinum wound on a frame that does not contaminate the wire will change its constants with use less than does impure platinum, so that it is highly desirable to use only the purest of platinum in the construction of pyrometers. Even with pure platinum, however, in work of great precision, it is necessary to recalibrate occasionally, and when temperatures above 1000° C. are measured frequently this operation becomes very onerous. Great care has to be exercised, and this should be especially emphasized for industrial as well as scientific installations, to secure a proper insulation of all electrical circuits.

Methods of Measurement. — It is evident that most of the ordinary methods for the measurement of resistance may be used in platinum thermometry, but in practice only a few of these methods have been applied to temperature measurements, although there is a tendency at the present time, in the solution of specific-temperature problems, to take advantage of the peculiarities of less usual methods both for work of high precision in the laboratory and for industrial applications. Thus, in addition to the ordinary slide-wire and dial Wheatstone bridge methods, the Kelvin double bridge is sometimes used with pyrometers of very low resistance, for which this method is particularly adapted. Potential terminal and differential galvanometer methods are also used in precision work, and for industrial practice several deflection methods have been developed for the direct reading of temperatures on a galvanometer scale.

Compensation for Pyrometer Leads. — There is one characteristic in the measurement of a resistance coil used as a pyrometer that distinguishes it from an ordinary resistance measurement, namely, that in the case of the pyrometer coil there is a region of great temperature gradient from the coil to the measuring apparatus, so that it becomes imperative to eliminate the variable resistance of the leads to the pyrometer coil — a resistance that varies both with the depth of immersion of the coil and with its temperature. There are several ways of effecting the necessary compensation of this variable lead resistance, and they will be described under the several headings.

Three-lead Thermometer. — This was the form originally given to the instrument by Siemens in 1871, and it is used in the construction of apparatus suitable for industrial use by Siemens and Halske and by Leeds and Northrup.

In the Siemens method (Fig. 67), the thermometer coil P forms one arm of a Wheatstone bridge, of which the others are r_1, r_2, and R, when from the principle of the bridge, if the galvanometer G remains undeflected, $P = R\frac{r_2}{r_1}$, neglecting the leads.

The compensation for the variable resistance of the thermometer leads is effected in the following manner: The lead aa', of the same material as the thermometer coil P to avoid thermoelectric effects at their junction, is constructed to be as exactly equal as possible electrically to the similar lead bb'. The lead

aa' is in the P arm of the bridge and the lead bb' is put in the R arm by means of the auxiliary lead $c'b$ of the same material as P.

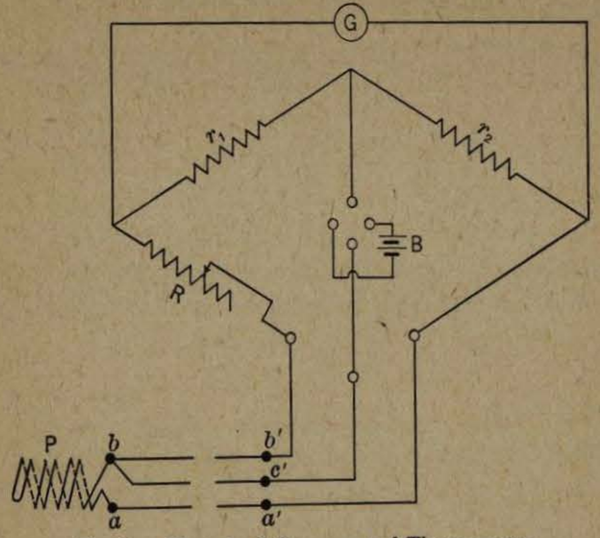


Fig. 67. Three-lead Compensated Thermometer.

This lead $c'b$ may be put in the battery circuit as shown, or in the galvanometer circuit if preferred. It is not necessary to adjust $c'b$ to any particular resistance, so that fine wire may be used for it. With this arrangement, therefore, the resistance of the thermometer remains apparently constant for a given temperature whatever its depth of immersion and whatever the temperature gradient along the leads aa', bb', so long as it is the same for both.

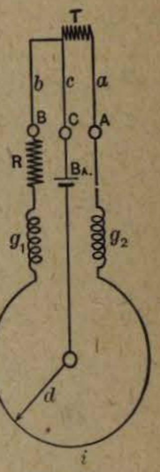


Fig. 68. Use of Differential Galvanometer.

The three-lead compensated thermometer may also be used with a differential galvanometer. Fig. 68 shows the principle of such an arrangement for an instrument of Leeds and Northrup. The slider d is set on the slide wire i in such a position that the current from B divides equally between the circuits $b + R + g_1$ and $T + a + g_2$, of which g_1 and g_2 are the two differential galvanometer coils. If the resistance