Platinum for Resistance Thermometry

EFFECTS OF SURFACE CONTAMINATION

Recognition of the virtues of the platinum resistance thermometer as a practical means of accurate temperature measurement has been slow. Recently, however (perhaps largely on account of improvements in electrical measuring instruments), it has been finding wider use in the laboratory and in industry. In particular, it offers many attractions as an instrument for measuring very low temperatures. It seems likely that the range of temperature over which it will be employed to define temperature on the International Practical Temperature Scale will be extended from the present limits of between 90°K (−183°C) and 900°K (627°C) to the whole of the long range from 20°K (−253°C, the boiling point of hydrogen) to 1336°K (1063°C, the melting point of gold).

It is thus of special interest to be able to understand the exact mechanism by which changes in temperature can affect the resistivity of platinum. In the past it has been common to base theories of conduction on the simple view that any expression for resistivity can be separated into two terms, one independent of temperature and the other temperature dependent. This is known as Matthiessen's Rule, and may be written simply

$$R = R_0 + f(T)$$

where R and R_0 represent the resistance at temperature T and at 0°K respectively.

In a recent paper D. R. Lovejoy, of the Division of Applied Physics, National Research Council, Ottawa, describes (*Canadian J. Physics*, 1964, **42**, (11), 2264) how an analysis of a very large volume of experimental data collected during the calibration of resistance thermometers reveals that the resistance characteristics of thermometric grade platinum wire show, in fact, considerable deviations from Matthiessen's Rule. An important practical consideration that emerges is that various batches of thermometric grade platinum having the same value of temperature coefficient of resistivity measured between 0 and 100°C can have significantly different values of resistivity at temperatures below about −180°C.

In the paper a theoretical study is presented in an endeavour to find the causes of these deviations. It is known that positive deviations from Matthiessen's Rule result whenever two or more groups of carriers which contribute additively to the conductivity are affected by a change of temperature to a different degree by the two scattering mechanisms (photo scattering and impurity scattering).

The results of tests on three batches of 30, 59 and 33 thermometers respectively are analysed and it is shown that the variations can all be explained by the 2-electronic band theory of Sondheimer and Wilson if it is considered that the thermometer wire in fact consists of parallel bands which vary in impurity concentration. The model finally set up to reconcile the calibration data postulates that the wire consists simply of a virtually pure core of platinum, surrounded by two regions of contamination. These regions comprise:

(1) A heavily contaminated surface skin extending to a depth of about 10 atomic layers. This accounts for variations in resistivity near 700°K.

(2) A sub-surface layer about 200 atoms thick in which the impurity level averages about 0.1 per cent. This accounts for variations in the resistivity in the region of 90°K.

By making these assumptions it is shown that the observed variations in parameters A, alpha, B and C in the Callendar Van Dusen equation can be satisfactorily accounted for, and in addition it is possible to explain the variations in resistivity below 90°K.

From this work it follows that the surface contamination normally present on the wire of an average platinum resistance thermometer is the major cause of error in resistance thermometry at low temperatures. If this can be prevented there seems no reason why these instruments should not be used with confidence and the readings extrapolated below 90°K to an accuracy of better than a few millidegrees K.

The results also serve to indicate the steps that can undoubtedly be taken to improve the reliability of platinum thermometers in this respect. It is pointed out that the simple step of increasing the wire diameter alone and thereby reducing the proportion by which surface effects can influence resistivity is not a satisfactory solution and can raise more problems than it would solve. There is, however, very great hope that considerable improvements can be made by scrupulous attention to cleanliness at all stages in handling the wire and fabricating the thermometers. It is particularly hopeful to note that even now many of the best commercial thermometers show excellent performance at low temperatures.

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Thermal Conductivity of Pure Platinum

The thermal conductivity of pure platinum was recently found by Powell and Tye (1) at the National Physical Laboratory, working for the first time on substantial solid specimens, to remain surprisingly constant within 0.5 per cent of 0.73w cm^{-1}°C^{-1} over the range 0 to 950°C. Several other investigators have since examined the thermal conductivity of platinum and some of their results were reported at the Thermal Conductivity Conference at the National Physical Laboratory last July.

At first sight the conclusions of Powell and Tye are not fully supported by this further work. Thus K. H. Bode (2) of Physikalische-Technische Bundesanstalt, Braunschweig, obtained a value rising from 0.7025 to 0.7100 between 0 and 100°C using as test piece a massive cylindrical specimen. The platinum, however, contained 135 to 150 p.p.m. of impurities and its density was only 21.32 g/ml compared with 21.5, the NPL figure.

J. J. Martin and P. H. Sidles (3) of Iowa State University measured the thermal diffusivity of two specimens, one of high purity (99.999 per cent) and the other less pure (99.9 per cent) at temperatures up to 927°C and from their results calculated values of thermal conductivity. Unexpectedly the purer sample had the lower thermal conductivity at high temperatures. The figures obtained for the purer sample were, however, certainly not constant, being 5 per cent lower at room temperature than the value found by Powell and Tye, and 10 per cent higher at 877°C.

Finally, M. J. Wheeler (4) of the Hirst Research Centre of the General Electric Company Limited, at Wembley, measured thermal diffusivity from 907° to 1477°C using a modulated beam technique. The calculated values of thermal conductivity agree reasonably well with those of Powell and Tye around 1100°C but tend to rise at higher temperatures.

On the whole this new evidence does not seem to be of sufficient weight to overthrow the conclusion of Powell and Tye that the thermal conductivity is sensibly constant from room temperature to around 900°C. On the other hand, it is possible that there may very well be an inflexion around 800 to 900°C, the thermal conductivity tending to rise at higher temperatures.

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References

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3 J. J. Martin and P. H. Sidles, Contribution 1614 from Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
4 M. J. Wheeler, *Brit. J. of App. Physics*, 1965, **16**, (3), 365