Platinum Metal Thermocouples

NEW INTERNATIONAL REFERENCE TABLES

By T. J. Quinn and T. R. D. Chandler

National Physical Laboratory, Teddington, Middlesex

As a result of a remarkable piece of international collaboration between three national standards laboratories and seven United States and United Kingdom manufacturers, new reference tables have now been completed for platinum : 10 per cent rhodium-platinum and platinum: 13 per cent rhodium-platinum thermocouples. These new tables take into account the changes in the temperature scale resulting from the introduction of the International Practical Temperature Scale of 1968 (IPTS-68) and also provide reference tables which will be common to both U.S. and U.K. manufacturers and users of thermocouples.

The changes in the temperature scale (1) when IPTS-68 was introduced highlighted the problem hitherto of the two conflicting reference tables for rhodium-platinum thermocouples. One table was based on work done in 1933 at the National Bureau of Standards (NBS) by Roeser and Caldwell (2) and was published as NBS 561, and the other was based on work done at the National Physical Laboratory (NPL) in 1950 by C. R. Barber (3) and was published in the United Kingdom as BS 1826. These tables differed from one another as a result of differences in both the realisation of the temperature scales in the original calibrations and in the compositions of the platinum and rhodium-platinum wire. Since the original measurements were made, particularly those in 1933, there have been substantial improvements in the purification of both platinum and rhodium and thus, in order to continue to meet the old tables, changes were made in the composition of the alloy arms of the thermocouples. The result was that differences between thermocouples made to meet NBS 561 and those made to meet BS 1826 have become quite substantial. It has been clear for some time that it was uneconomic for manufacturers to have to make material of nominally the same composition to these two specifications.

In September 1967 an informal meeting took place at the NBS between representatives of the NBS, National Research Council of Canada (NRC) and the NPL. At this meeting it was agreed that the introduction of the IPTS-68 would provide an excellent opportunity to unify the reference tables for platinum thermocouples. It was agreed that a joint approach should be made by the three national laboratories to all the U.S. and U.K. manufacturers with a view to carrying out a programme of research leading to new reference tables. This was welcomed by the manufacturers, many of whom had been aware of and had encouraged the proposals discussed at this meeting, and it was agreed that the terms of reference for the project would be as follows:

(i) Each of four American and three British manufacturers would contribute 24 metres of pure platinum wire and 12 metres each of 10 per cent rhodium-platinum and 13 per cent rhodium-platinum wire.

(ii) Each of the three types of wire would have nominal diameter 0.5 mm and be supplied in a continuous length.

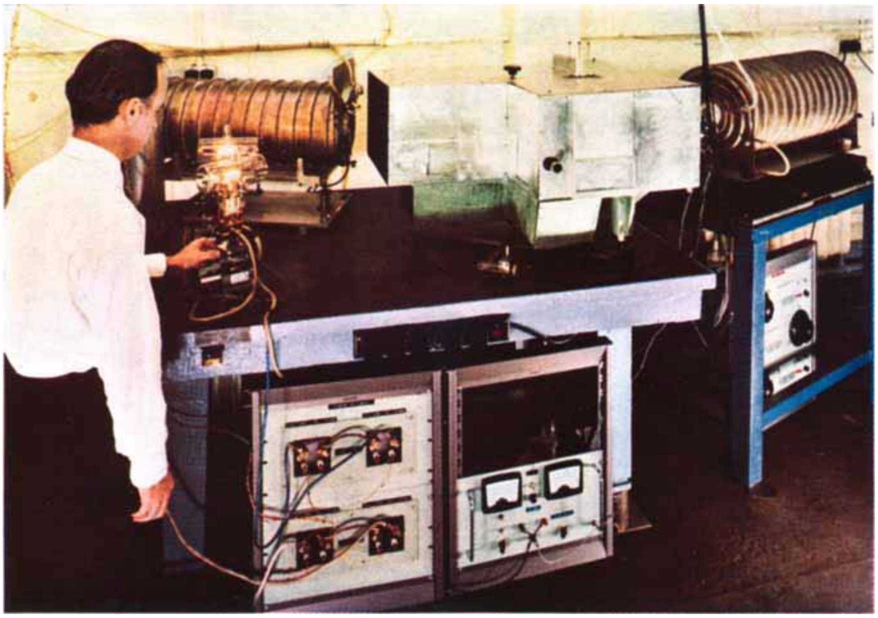

Fig. 1 Experimental work at the National Physical Laboratory to provide the data for new reference tables for platinum : 10 per cent rhodium-platinum and platinum : 13 per cent rhodium-platinum thermocouples above the gold point was carried out using the NPL photoelectric pyrometer. The standard lamps and furnace are seen here also and the furnace containing a gold point black-body as a reference is on the right

(iii) The pure platinum wires should have a steam point to ice point resistance ratio not less than 1.3924.

(iv) The two alloy wires would contain as closely as possible 10 per cent rhodium and 13 per cent rhodium respectively, rather than have the rhodium contents adjusted to match particular specified e.m.f.s of the gold point. It was generally acknowledged that this would lead to slightly higher values of e.m.f. for given temperatures than in existing tables.

It was decided also to split the experimental work among the three national laboratories in the following way:

(i) The materials would be collected and the thermocouples assembled by NBS, then half of the completed thermocouples would be sent to NRC.

(ii) NBS and NRC would perform primary calibrations on some and comparison calibrations on all of their thermocouples from 0°C to the gold point.

(iii) A selected number of thermocouples from each of the NBS and NRC groups would then receive primary calibrations at NPL from the gold point to the platinum point against a photoelectric optical pyrometer using a suitable black-body cavity. Enough calibrations would be done at the gold point to ensure agreement with the NBS and NRC calibrations.

(iv) The thermocouples retained by NBS and NRC would be intercompared from the gold point to the platinum point and also be compared with those from NPL upon their return.

(v) NBS and NRC would ensure agreement with the NPL by a limited number of high temperature calibrations obtained by measuring palladium and platinum points by the wire method.

The Reference Tables

This work has now been completed and the new reference tables were presented at the

Table I

The New Platinum : 10% Rhodium-Platinum Reference Table Defined by Sets of Polynomial Functions

Temperature Range	Polynomial
−50°C to 630.74°C	$E=\sum_{i=0}^{6} a_i t_{68}^i$ µV where $a_0=0$ $a_1=5.399578$ $a_2=1.251977\times10^{-2}$ $a_3=-2.244822\times10^{-5}$ $a_4=2.845216\times10^{-8}$ $a_5=-2.244058\times10^{-11}$ $a_6=8.505417\times10^{-15}$
630.74°C to 1064.43°C	$E=\sum_{i=0}^{2} g_i t_{68}^i$ µV where $g_0=-298.245$ $g_1=8.237553$ $g_2=1.645391\times10^{-3}$
1064.43°C to 1665°C	$E=\sum_{i=0}^{3} b_i(t^*)^i$ µV where $t^*=(t_{68}-1365)/300$ $b_0=13943.439$ $b_1=3639.869$ $b_2=-5.028$ $b_3=-42.451$
1665°C to 1767.6°C	$E=\sum_{i=0}^{2} c_i(t^*)^i$ µV where $t^*=(t_{68}-1715)/50$ $c_0=18113.083$ $c_1=567.954$ $c_2=-12.112$ $c_3=-2.812$

Table II

The New Platinum : 13% Rhodium-Platinum Reference Table Defined by Sets of Polynomial Functions

Temperature Range	Polynomial
−50°C to 630.74°C	$E=\sum_{i=0}^{7} d_i t_{68}^i$ µV where $d_0=0$ $d_1=5.289139$ $d_2=1.391111\times10^{-2}$ $d_3=-2.400524\times10^{-5}$ $d_4=3.620141\times10^{-8}$ $d_5=-4.464502\times10^{-11}$ $d_6=3.849769\times10^{-14}$ $d_7=-1.537264\times10^{-17}$
630.74°C to 1064.43°C	$E=\sum_{i=0}^{3} h_i t_{68}^i$ µV where $h_0=264.180$ $h_1=8.046868$ $h_2=2.989229\times10^{-3}$ $h_3=-2.687606\times10^{-7}$
1064.43°C to 1665°C	$E=\sum_{i=0}^{3} e_i(t^*)^i$ µV where $t^*=(t_{68}-1365)/300$ $e_0=15540.414$ $e_1=4235.777$ $e_2=14.693$ $e_3=-52.214$
1665°C to 1767.6°C	$E=\sum_{i=0}^{3} f_i(t^*)^i$ µV where $t^*=(t_{68}-1715)/50$ $f_0=20416.695$ $f_1=668.509$ $f_2=-12.301$ $f_3=-2.786$

5th Symposium on "Temperature" held in Washington in June 1971.* These new reference tables, unlike the old ones, have been produced by means of agreed sets of polynomial functions fitted to the results of the experimental work. These functions are listed in Tables I and II and skeleton reference tables derived from them appear in Tables III and IV. The differences between the new tables and the old are shown in Figs. 2 and 3, which also clearly indicate the differences between the NBS 561 and BS 1826 tables.

* The Proceedings of the 5th Symposium on "Temperature Measurement and Control in Science and Industry" are to be published in 1972.

Table III

Skeleton Reference Table for Platinum : 10 per cent Rhodium-Platinum (Type S) Thermocouples

Temperatures in Degrees Celsius (IPTS–68) **Reference Junction at 0°C**

Temp.	0	10	20	30	40	50	60	70	80	90
	Absolute E.M.F. in Microvolts									
0	0	−53	−103	−150	−194	−236				
0	0	55	113	173	235	299	365	432	502	573
100	645	719	795	872	950	1029	1109	1190	1273	1356
200	1440	1525	1611	1698	1785	1873	1962	2051	2141	2232
300	2323	2414	2506	2599	2692	2786	2880	2974	3069	3164
400	3260	3356	3452	3549	3645	3743	3840	3938	4036	4135
500	4234	4333	4432	4532	4632	4732	4832	4933	5034	5136
600	5237	5339	5442	5544	5648	5751	5855	5960	6064	6169
700	6274	6380	6486	6592	6699	6805	6913	7020	7128	7236
800	7345	7454	7563	7672	7782	7892	8003	8114	8225	8336
900	8448	8560	8673	8786	8899	9012	9126	9240	9355	9470
1000	9585	9700	9816	9932	10048	10165	10282	10400	10517	10635
1100	10754	10872	10991	11110	11229	11348	11467	11587	11707	11827
1200	11947	12067	12188	12308	12429	12550	12671	12792	12913	13034
1300	13155	13276	13397	13519	13640	13761	13883	14004	14125	14247
1400	14368	14489	14610	14731	14852	14973	15094	15215	15336	15456
1500	15576	15697	15817	15937	16057	16176	16296	16415	16534	16653
1600	16771	16890	17008	17125	17243	17360	17477	17594	17711	17826
1700	17942	18056	18170	18282	18394	18504	18612			

Table IV

Skeleton Reference Table for Platinum : 13 per cent Rhodium-Platinum (Type R) Thermocouples

Temperatures in Degrees Celsius (IPTS–68) **Reference Junction at 0°C**

Temp.	0	10	20	30	40	50	60	70	80	90
	Absolute E.M.F. in Microvolts									
0	0	−51	−100	−145	−188	−226				
0	0	54	111	171	232	296	363	431	501	573
100	647	723	800	879	959	1041	1124	1208	1294	1380
200	1468	1557	1647	1738	1830	1923	2017	2111	2207	2303
300	2400	2498	2596	2695	2795	2896	2997	3099	3201	3304
400	3407	3511	3616	3721	3826	3933	4039	4146	4254	4362
500	4471	4580	4689	4799	4910	5021	5132	5244	5356	5469
600	5582	5696	5810	5925	6040	6155	6272	6388	6505	6623
700	6741	6860	6979	7098	7218	7339	7460	7582	7703	7826
800	7949	8072	8196	8320	8445	8570	8696	8822	8949	9076
900	9203	9331	9460	9589	9718	9848	9978	10109	10240	10371
1000	10503	10636	10768	10902	11035	11170	11304	11439	11574	11710
1100	11846	11983	12119	12257	12394	12532	12669	12808	12946	13085
1200	13224	13363	13502	13642	13782	13922	14062	14202	14343	14483
1300	14624	14765	14906	15047	15188	15329	15470	15611	15752	15893
1400	16035	16176	16317	16458	16599	16741	16882	17022	17163	17304
1500	17445	17585	17726	17866	18006	18146	18286	18425	18564	18703
1600	18842	18981	19119	19257	19395	19533	19670	19807	19944	20080
1700	20215	20350	20483	20616	20748	20878	21006			

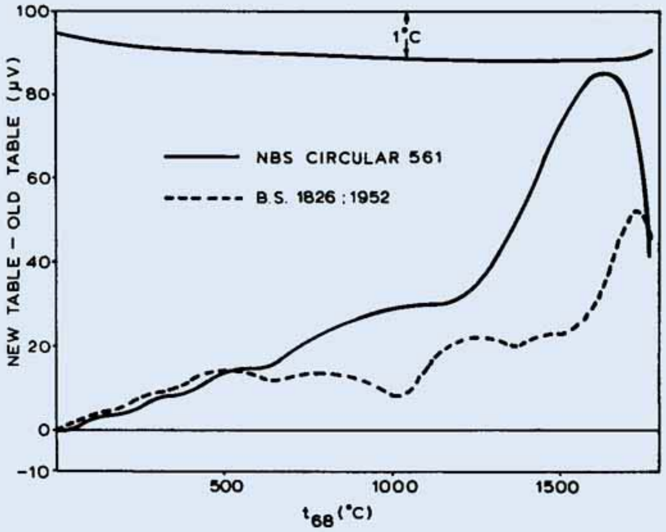

Fig. 2 Differences between the new reference table and NBS 561 and BS 1826 (adjusted to IPTS-68) for Pt : 10% Rh-Pt

Experimental Work

The experimental work carried out at NPL that provided the data for the new reference tables above the gold point was undertaken using the NPL photoelectric pyrometer (Figure 1). This was used to measure the temperature of a black-body

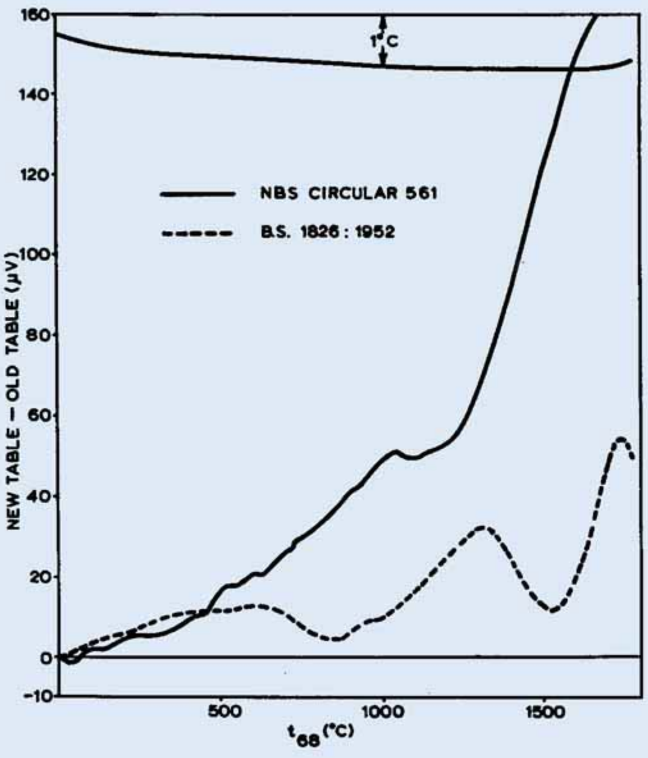

Fig. 3 Differences between the new reference table and NBS 561 and BS 1826 (adjusted to IPTS-68) for Pt : 13% Rh-Pt

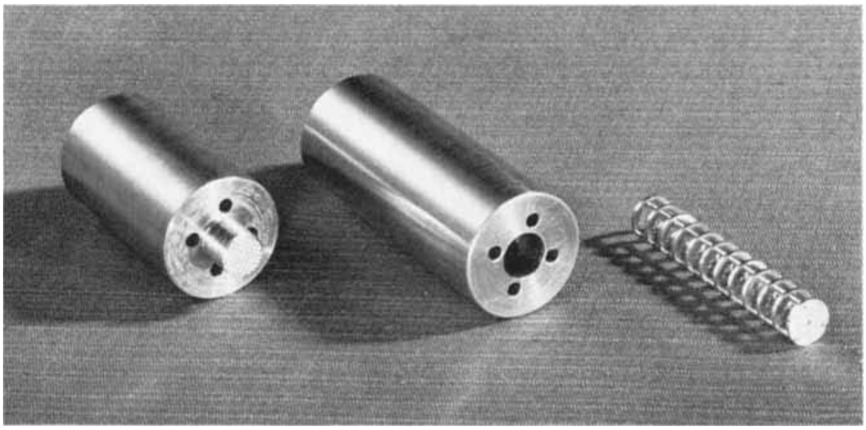

Fig. 4 The platinum black-body constructed by Johnson Matthey before assembly and use

cavity which could accommodate up to four thermocouples at a time. The cavity used from the gold point up to 1748°C was made from solid platinum and was loaned to NPL for this work by Johnson Matthey. It is illustrated in Figs. 4 and 5. Using a furnace wound with pure rhodium ribbon and 40 per cent rhodium-platinum wire internal end heaters, a temperature uniformity, at about 1500°C, of within 0.3 deg C was achieved over the whole length of the block.

It was found that the reproducibility of platinum : 13 per cent rhodium-platinum thermocouples was significantly better than that of platinum : 10 per cent rhodium-platinum thermocouples over the whole temperature range. For example, the mean gold point e.m.f. determined by NPL for eight platinum : 13 per cent rhodium-platinum thermocouples was 0.4 microvolts above the NBS and NRC mean ingot value, while that of the platinum : 10 per cent rhodium-platinum thermocouples was 2 microvolts higher. A difference in behaviour of this sort can be reasonably accounted for by the fall in slope, between 10 per cent rhodium and 13 per cent rhodium, of the e.m.f./composition curve for rhodium-platinum alloys. It would seem reasonable therefore to hope that in due course the platinum : 13 per cent rhodium-platinum thermocouple would supersede the platinum: 10 per cent rhodium-platinum thermocouple in general use, particularly if the IPTS-68 between 630.74°C and 1064.43°C is eventu-

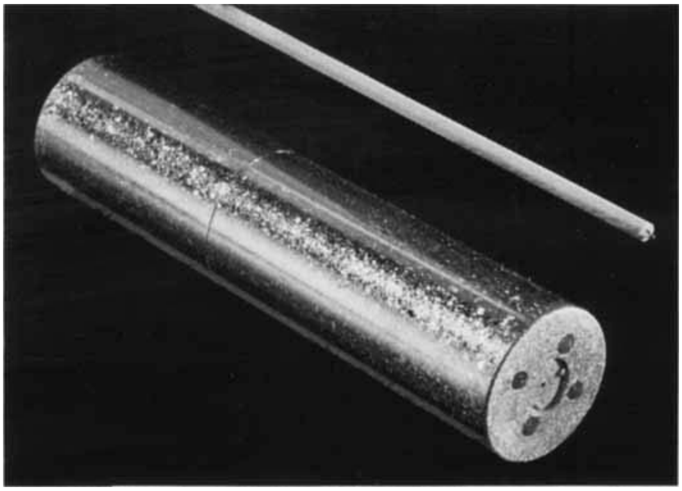

Fig. 5 The platinum black-body after prolonged use at temperatures up to 1748°C. One of the thermocouples used for this work is also shown

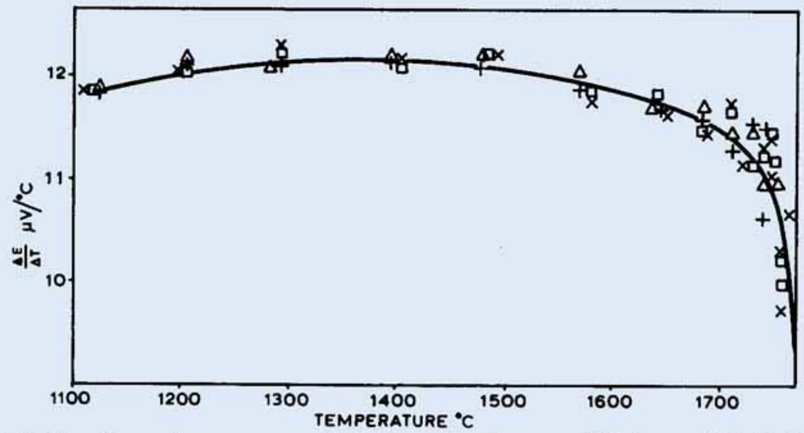

Fig. 6 Experimental measurements of the thermoelectric power of platinum : 10% rhodium-platinum thermocouples

+ A5 □ A8 × D4 △ D5

ally defined in terms of the platinum resistance thermometer rather than the platinum: 10 per cent rhodium-platinum thermocouple.

To cover the range between 1748°C and the melting point of platinum further measurements were made using a black-body cavity made from alumina. It was found with this cavity that there is a significant drop in the thermoelectric power both of platinum : 10 per cent rhodium-platinum and platinum : 13 per cent rhodium-platinum thermocouples above 1700°C. Figures 6 and 7 show the results of these high temperature measurements of thermoelectric power. The change in slope of the thermoelectric power/temperature curve above about 1100°C can be accounted for qualitatively by the effects of the increasing concentration of lattice vacancies at high temperatures. The drop above 1700°C, however, seems too steep to be accounted for solely by lattice defects; there must be another factor which is becoming important. One such factor could be the conductivity of the alumina refractory which is increasing at a significant rate at these temperatures.

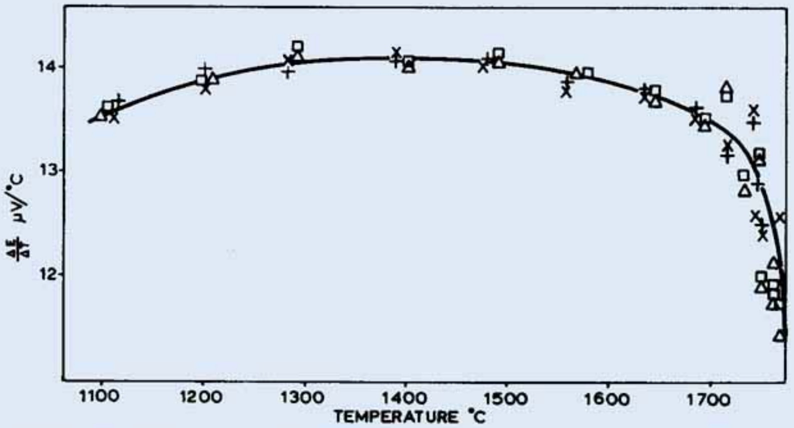

Fig. 7 Experimental measurements of the thermoelectric power of platinum: 13% rhodium-platinum thermocouples

+ A14 □ A17 × D14 △ D15

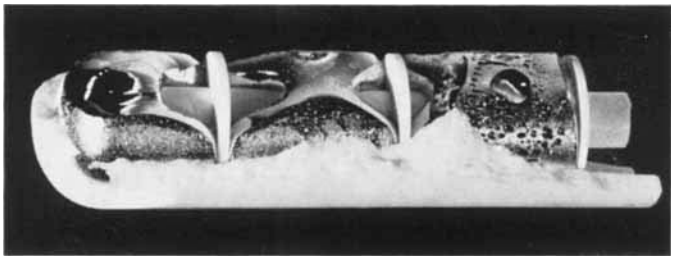

Fig. 8 An ingot of platinum after melting. Neither the alumina crucible nor black-body were damaged during heating or cooling from room temperature to the melting point. The crucible was broken after the measurement so that the melted platinum could be examined

The Freezing Point of Platinum

It became apparent during the course of this work that a temperature of 1772°C (IPTS-68) for the freezing point of platinum would not be consistent with the results of measurements made in the two black-bodies from the gold point upwards. The e.m.f./temperature curve thus obtained showed that the temperature at which the platinum arm of the thermocouple melted was some 4 deg C below 1772°C. A similar result was obtained from platinum wire-point measurements made at NRC. That the freezing point of platinum was lower than the previously accepted value was subsequently confirmed at NPL by measurements made with the photoelectric pyrometer using substantial ingots of pure platinum (4). Three series of measurements were made, two ingots being supplied by Engelhard (U.K.) and one by Johnson Matthey. There was no significant difference found between the results from the three ingots, nor between the melts and the freezes. The final value for the freezing point of platinum was found to be 1767.6±0.3°C (IPTS-68).

The authors are pleased to acknowledge the generous assistance given by Johnson Matthey & Co Ltd, throughout this work by the supply of the platinum and rhodium-platinum wire, the construction and loan of the platinum black-body, the machining and loan of one of the ingots of platinum used for the melting point work, and for spectrographic analysis of pieces of the platinum before and after melting.

Much of the impetus behind this work, together with invaluable advice and encouragement during its execution, came from the late C. R. Barber of NPL.

References

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2 W. F. Roeser and H. T. Wensel, *J. Res. Nat. Bur. Stds.*, 1933, **10**, 275
3 C. R. Barber, *Proc. Phys. Soc.*, 1950, **B63**, 492
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Iron-Rhodium Resistance Thermometers

Cryogenic engineering is becoming much more important as work with liquid gases and on the applications of superconductivity increases. Special thermometers are needed at these very low temperatures because although platinum resistance thermometers are satisfactory for use down to 20 K they cannot be used below 10 K.

The use of 0.5 atomic per cent iron-rhodium alloy as a resistance thermometer material at very low temperatures was proposed by Professor B. R. Coles of Imperial College, London in 1964 (*Phys. Lett.*, 1964, **8**, (4), 243–244). Tests have since shown that it is suitable for use between 0.35 and 40 K. It is now available from Johnson Matthey Metals in the form of wire 0.13 mm diameter in either a hard-worked or an annealed condition.

The rate of increase of resistance of the wire varies somewhat over the range of temperature from 0.35 up to 40 K. Calibration is therefore necessary and this should take place in the position in which the instrument is to be used.

Strong magnetic fields occur in work on superconduction but the iron-rhodium alloy remains virtually unaffected so that the change in resistance per deg K is small and predictable. At temperatures in the liquid helium range a one per cent change in the resistance is produced by a field of 10 kOe. The change in resistance per deg K is not altered by work-hardening. Accuracy of $\pm 10^{-3}$deg K in the range is possible with 20 cm of 0.13 mm diameter wire used with conventional potentiometric measuring equipment.