A Rhodium-Platinum Thermocouple for High Temperatures

A REFERENCE TABLE FOR THE "SIX-THIRTY" COUPLE

The thermocouple formed by two rhodium-platinum alloys containing 6 per cent and 30 per cent of rhodium respectively was first introduced in Germany some thirteen years ago by Degussa of Hanau for temperature measurements in molten steel. Since then it has been widely used in other high temperature applications; J. A. Stevenson (1), for example, has recently given an account of its use in the control of glass melting furnaces in Russia.

The "Six-Thirty" thermocouple, as it is commonly known, was developed because the standard platinum : 10 per cent rhodium-platinum and platinum : 13 per cent rhodium-platinum thermocouples were found to have limitations when used much above 1500°C. The pure platinum limb becomes extremely weak mechanically and is very susceptible to contamination by rhodium from the alloy limb. The "Six-Thirty" thermocouple overcomes these disadvantages by the use of two rhodium-platinum alloys that enable it to be used for continuous temperature measurements up to 1700°C and intermittently up to about 1800°C, the limiting temperature being the melting point of the 6 per cent rhodium-platinum limb at 1820°C.

The thermocouple is very stable under clean oxidising conditions. Walker, Ewing and Miller (2) have shown this couple to be more stable than any other rhodium-platinum alloy combination. The use of two rhodium-platinum alloys produces a lower e.m.f. output, but above 1000°C the sensitivity of the "Six-Thirty" closely approaches that of the platinum : 10 per cent rhodium-platinum thermocouple and may thus be used without any appreciable sacrifice in the accuracy of measurements. At room temperature the e.m.f. and sensitivity are so low that below 50°C cold junction correction may be neglected for all but the most precise measurements.

The growing importance of this thermocouple led to the redetermination of basic values, and new and more accurate reference tables compiled by Obrowski and Prinz of Degussa (3) were published in 1962. These tables are now regarded as standard values in Europe.

In the U.S.A. the "Six-Thirty" has become the preferred thermocouple for high temperature measurements and to facilitate its use and calibration in America reference tables have been derived by George W. Burns and John S. Gallaher (4) of the National Bureau of Standards. In a commendably detailed paper the authors describe how their test programme was conducted using thermocouples from three major American manufacturers and one from Degussa. The compositions chosen, 6.12 per cent and 29.6 per cent rhodium respectively, reflect the desire to avoid creating a new and conflicting set of standards, since these alloys had been previously found to generate e.m.f.s that conform closely to the values determined by Obrowski and Prinz.

The American reference table is therefore similar to the 1962 table and the differences between them, shown graphically in the diagram, are claimed to be less than the differences found between the couples being tested.

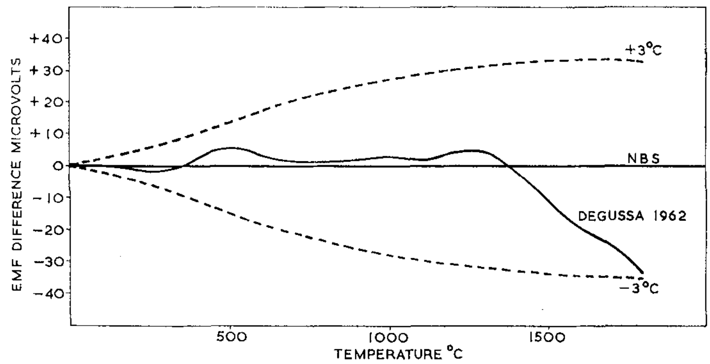
Burns and Gallaher give a full account of the techniques used to calibrate their thermocouples; these include comparison with a platinum resistance thermometer, comparison with a platinum : 10 per cent rhodium-platinum thermocouple and comparison with

Reference Table for 6 per cent Rh-Pt : 30 per cent Rh-Pt Thermocouples (Temperature in °C (IPTS 1948); electromotive force in absolute millivolts; reference junction 0°C									
t(°C)	1000	1100	1200	1300	1400	1500	1600	1700	1800
0	4.844 0.092	5.793 0.098	6.800 0.104	7.866 0.110	8.979 0.114	10.124 0.116	11.286 0.117	. 2.453 0.117	13.616 0.115
10	4.936 0.093	5.891 0.099	6.904 0.105	7.976 0.110	9.093 0.113	10.240 0.116	11.403 0.116	12.570 0.116	13.731 0.116
20	5.029 0.093	5.990 0.100	7.009 0.105	8.086 0.110	9.206 0.114	10.356 0.115	11.519 0.117	12.686 0.117	13.847
30	5.122 0.094	6.090 0.100	7.114 0.106	8.196 0.111	9.320 0.114	10.471 0.116	11.636 0.117	12.803 0.116	
40	5.216 0.095	6.190 0.100	7.220 0.106	8.307 0.111	9.434 0.115	10.587 0.117	11.753 0.116	12.919 0.116	
50	5.311 0.095	6.290 0.101	7.326 0.107	8.418 0.112	9.549 0.114	10.704 0.116	11.869 0.117	13.035 0.117	
60	5.406 0.096	6.391 0.101	7.433 0.108	8.530 0.111	9.663 0.115	10.820 0.116	11.986 0.117	13.152 0.116	
70	5.502 0.096	6.492 0.102	7.541 0.108	8.641 0.113	9.778 0.115	10.936 0.117	12.103 0.117	13.268 0.116	
80	5.598 0.097	6.594 0.103	7.649 0.108	8.754 0.112	9.893 0.116	11.053 0.116	12.220 0.116	13.384 0.116	
90	5.695 0.098	6.697 0.103	7.757 0.109	8.866 0.113	10.009 0.115	11.169 0.117	12.336 0.117	13.500 0.116	
100	5.793	6.800	7.866	8.979	10.124	11.286	12.453	13.616	

an optical pyrometer. A large number of e.m.f. determinations were also carried out on each limb of the thermocouples under test, the e.m.f.s being measured with respect to platinum reference wires. In addition a study was made of the effect of variations in the rhodium content on the temperature-e.m.f. relationship. The results of this and other parts of the test programme are shown concisely in graph form.

After averaging the results of the calibrations three quartic equations were derived with the aid of an IBM 7094 digital computer. In common with previous investigators, Burns and Gallaher found that no equation of simple form will adequately describe the e.m.f.-temperature relationship over the entire temperature range.

The authors emphasise the arbitrary nature of their reference table, but conclude that the thermocouples used by Obrowski and Prinz had essentially the same characteristics as those of American manufacture. Thus thermocouples made to comply with the earlier table



Difference between the NBS reference table and the 1962 Degussa reference curve for the "Six-Thirty" thermocouple of Obrowski and Prinz will comply with the American table to within similar tolerances.

The authors conclude their paper with a discussion of the results obtained and a consideration of the uncertainties in the measurements. Burns and Gallaher estimate that they do not exceed $\pm 2^\circ C$ at 1400°C and about ± 3 or 4°C at 1750°C.

It is interesting to note that the American results are based almost entirely on comparison techniques, whereas Obrowski and Prinz used the fixed melting point technique. If criticism of this paper may be made it is that the value of the work would have been given more weight if more than one set of batches from each manufacturer had been tested. Apart from this one reservation the authors have presented an extremely competent and valuable paper and the publication of these tables underlines the international recognition of the "Six-Thirty" thermocouple as an accurate, sensitive and stable sensor for the measurement of high temperatures.

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References

1 J. A. Stevenson, *Platinum Metals Rev.*, 1966, **10**, 128–131

2 B. E. Walker, C. T. Ewing and R. R. Miller, *Rev. Sci. Instrum.*, 1962, **33**, (10), 1029–1040

3 W. Obrowski and W. Prinz, Archiv Eisenhüttenwesen, 1962, **33**, (1), 1–4; *Platinum Metals Rev.*, 1962, **6**, 96–97

4 George W. Burns and John S. Gallaher, *J. Res. NBS*, 1966, **70C**, (2), 89–125

Platinum Metal Electrocatalysts for Fuel Cells

A high proportion of the papers dealing with fuel cell developments presented at the Fifth International Power Sources Symposium at Brighton in September again focused attention on the use of platinum metals as electrocatalysts. Among these contributions was an analysis by A. L. Harrison and G. R. Lomax of Electrical Power Storage of the economic factors determining the role that fuel cells will play in the future as electricity generating devices. This gave some quantitative expression to the most likely areas of fuel cell application, which might include power generation for radio repeater stations, submarines, marine buoys and certain electric vehicles such as fork lift trucks. A 1 kW hydrogen-air fuel cell battery employing a supported palladium catalyst and equipped with full instrumentation to record all aspects of its successful operational life of 2000 hours was also described in detail by M. I. Gillibrand and J. Gray of the same company. Such a battery has also been built into an electrically driven factory truck.

Recent advances in internal reforming methanol-air cells were described by C. G. Clow, J. G. Bannochie and G. J. W. Pettinger of Energy Conversion Limited. Such systems reform methanol with water to yield hydrogen in a reaction chamber immediately adjacent to a silver-palladium membrane that acts as the anode. The hydrogen thus formed diffuses through the anode to the potassium hydroxide electrolyte side, and is consumed as the fuel. A bi-porous nickel cathode is employed, and an integrated unit to provide 6 kW was described. In order to make more economical use of the silver-palladium alloy, a tri-foil developed by Johnson Matthey and consisting of a nickel/silver-palladium alloy/nickel "sandwich" having an overall thickness of 0.005 inch with the alloy thickness of about 0.00003 inch formed the basis of a new "window" electrode structure for such a cell. This development consists of electrolytically removing small windows of nickel on the tri-foil, leaving the thin silver-palladium membrane exposed but supported mechanically by the surrounding nickel overlay.

Activation of Raney-nickel anode electrocatalysts by small amounts of platinum or palladium was demonstrated by M. Jung and H. H. V. Döhren of Varta AG, Germany, to provide a satisfactory technique for providing highly active anodes with low polarisations. Platinum loadings as low as 0.58 mgm/cm^2 proved effective.

A contribution from the U.S.S.R. by V. S. Bagotzky described the mechanism and kinetics of cathodic oxygen reduction on platinum electrodes. Different forms of chemisorbed oxygen, as well as some penetration by oxygen into the upper atomic layers of the metal, could be demonstrated.

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