

## Bibliographie

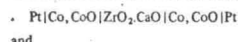
- Banus, M. D., et Nye, S. D., 1964, *Rev. Sci. Instr.*, **35**, 1319-23.  
 Bradley, C. C., 1969, *High Pressure Methods in Solid State Research* (Butterworths, London).  
 Contré, M., 1963, Etude systématique d'un appareil générateur de hautes pressions en milieu solide, HP 63 R1, Communication privée, 4 Avril.  
 Deaton, B. C., et Graf, R. B., 1963, *Rev. Sci. Instr.*, **34**, 45.  
 Drickamer, J. G., et al., 1964, *Rev. Sci. Instr.*, **35**, 29-33.  
 Hall, H. T., Barnett, J. D., et Merrill, W., 1963, *Science*, **139**, 111.  
 Hall, H. T., Merrill, L., et Barnett, J. D., 1964, *Science*, **146**, 1297.  
 Houck, J. C., et Hutton, U. O., 1962, dans *High Pressure Measurement, Proceedings of the A.S.M.E. Symposium, New York City, November, 1962*, Eds. A. A. Giardini et E. C. Lloyd (Butterworths, Washington), p.221.  
 Jamieson, J. C., 1961, dans *Progress in Very High Pressure Research*, Eds. F. P. Bundy, W. R. Hibbard, Jr., et H. M. Strong (Wiley and Sons, New York), pp.10-14.  
 Jamieson, J. C., et Lawson, A. W., 1962a, dans *Modern Very High Pressure Techniques*, Ed. R. H. Wentorf (Butterworths, London), pp.70-92.  
 Jamieson, J. C., et Lawson, A. W., 1962b, *J. Appl. Phys.*, **33**, 776.  
 Lees, J., 1966, dans *Advances in High Pressure Research*, Ed. R. S. Bradley, volume 1 (Academic Press, London), pp.2-78.  
 Lloyd, E. C., Hutton, V. O., et Johnson, D. P., 1959, *J. Res. Nat. Bur. Std.*, **63C**, 59.  
 Weir, C. E., van Valkenburg, A., et Lippincott, E., 1962, dans *Modern Very High Pressure Techniques*, Ed. R. H. Wentorf (Butterworths, London), pp.51-69.  
 Zeitlin, A., 1961, *Ultra-high Pressure Apparatus*, Internal Report, E.S.C.O., New York.  
 Zeitlin, A., et Brayman, J., 1962, dans *High Pressure Measurement, Proceedings of the A.S.M.E. Symposium, New York City, November, 1962*, Eds. A. A. Giardini et E. C. Lloyd (Butterworths, Washington), pp.301-20.

## E.m.f. measurements on cobalt-copper alloys

W.A.Dench and O.Kubaschewski

Division of Materials Applications, National Physical Laboratory, Teddington, Middlesex  
 Received 17 July 1969

**Abstract.** E.m.f. measurements have been made at 750 to 1275°C employing a solid electrolyte of stabilized zirconia in cells of the type:



It is shown that in this case a precision of  $\pm 0.2$  mV (10 cal per g-ion oxygen) can be achieved. The results, in conjunction with solubility data from X-ray measurements at 900-1000°C reported in the literature, enabled the thermodynamic properties of the solid solutions of copper in cobalt to be evaluated and the phase boundary extended to higher and lower temperatures.

## Introduction

It has been pointed out (Kubaschewski, 1968) that the accuracy attained in thermochemical experiments is lagging behind the demands made by applied metallurgical thermodynamics, which mostly consists in the calculation of phase boundaries in binary and multicomponent metallic systems. For various reasons (Kubaschewski, 1968) the methods employed are operated at high temperatures—at present 500-2000°C. Since the strain energies, interface and surface energies, and impurity effects may add up to a total of, say, 5-10 cal g-atom<sup>-1</sup>, the best accuracy one should strive to attain is  $\pm 10$  cal per g-atom of metallic material.

In calorimetry, the most powerful apparatus to date for the determination of heats of reaction is the high-temperature Calvet calorimeter (Calvet and Prat, 1955) which attains and even exceeds this accuracy. The methods most widely employed for the determination of free energies of reaction are determinations of electromotive forces and vapour pressures. Repeated considerations and discussions in the team of the present authors have led to the conclusion that a substantial improvement in the accuracy of the vapour pressure methods can at present not be envisaged, whereas there seem to be good prospects for an improvement of the e.m.f. methods.

For high-temperature e.m.f. work the use of solid electrolytes has recently come to the fore. Solid glass was used as early as 20 years ago (Kubaschewski and Huchler, 1948). More recently, solid oxide electrolytes, such as solid solutions of CaO in ZrO<sub>2</sub> and of Y<sub>2</sub>O<sub>3</sub> in ThO<sub>2</sub>, have been extensively explored and applied (Alcock, 1968). Experimental accuracies of  $\pm 1$  mV are often justifiably claimed. This corresponds to about  $\pm 50$  cal per g-ion oxygen. The present work is an attempt to increase this accuracy to 10 cal, i.e.,  $\pm 0.2$  mV. For the investigation the eutectic alloy system copper-cobalt was selected because the stability of CoO permits the use of a zirconia electrolyte and because the solid solubilities are of the order of a few percent (Hansen and Anderko, 1958) so that the total e.m.f.'s to be measured were expected to be relatively small—less than, say, 20 mV. The earlier work on the phase diagram has been reviewed by Hansen and the solubilities have been redetermined by Old and Haworth (1966).