Thermochimica Acta, 37 (1980) 259—260

Note

COMMENTS ON CALORIMETRIC DETERMINATION OF EQUILIBRIUM PHASE DIAGRAMS OF INORGANIC SYSTEMS

R. CASTANET

Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S., 26 rue du 141e R.I A., 13003 Marseille (France)

(Received 28 September 1979)

I read with interest the paper by Gaune-Escard and Bros [1] published recently in Thermochimica Acta and I have essentially three comments on it.

First, the method described in this work is not original. Indeed, the paper is written as if the authors were the first ones to find and to use the direct calorimetric determination of phase boundaries. However, this method was developed forty years ago by Körber et al. [2] and I have used this kind of determination for eleven years. We published in 1971 a paper [3] entitled "Applications de la calorimétrie de flux à l'étude des diagrammes de phases" where the method of determination of the boundaries of liquid—liquid and liquid—solid regions (the solid phase can be either a pure component or an intermediate compound) was described. This method was based on calorimetric isobaric measurements of isothermal enthalpy of mixing with respect to concentration using Calvet calorimeters. The experimental procedure was the drop method.

We then applied this method to the determination of many phase boundaries of inorganic systems at 737 K, e.g. Bi—Te [4] in 1970, Ag—Te and Cu—Te [5] in 1971, Sn—Te and Pb—Te [6] in 1972, Bi—Sb—Te [7] in 1975, etc. The high-temperature phase boundaries of Ge—Te [8] (at 6 temperatures from 1028 to 1150 K), Cu—Sb [9] (at 14 temperatures from 843 to 1375 K), Tl—Te [10—11] (at 18 temperatures from 580 to 740 K), and Au—Te [12] (at 6 temperatures from 728 to 1200 K) were determined in 1976 and 1977. In the case of Tl—Te [13], Au—Te [12], and Au—Si [14], equilibrium diagrams were calculated from the measured thermodynamic functions [15] in agreement with experimental diagrams.

Now, two practical comments on the method.

(a) It enables not only liquidus lines to be determined but, in some cases, solidus lines too. For example, it was possible [6] to show that the Sn—Te compound has a narrow range of solid solubility and that the Pb—Te compound is a straight-line compound, whereas the opposite conclusion was drawn by Hansen and Anderko [16]. In the case of the solid phases of the Ag—Te system [17], we were able to determine the location at 728 K of $Ag_{1.9}Te$ ($x_{Ag} = 0.647$) compound and at 745 K that of the Ag_2Te ($x_{Ag} = 0.667$). The boundaries of the β-phase of the Cu—Sb alloys [9] at 929 K and those of the Bi_2Te_3—Sb_2Te_3 solid solutions [7] at 737 K were also determined.

(b) In order to determine the phase boundaries, it is better to measure the partial enthalpy of dissolution of one of the components than the integral enthalpy of mixing. Indeed, the partial enthalpy undergoes a jump with respect to mole fraction crossing over the phase boundary whereas the integral enthalphy undergoes only a break. The measurements of partial enthalpies are more difficult but the boundary determinations are more accurate, as I pointed out in a previous paper [18].

REFERENCES

1 M. Gaune-Escard and J.-P. Bros, Thermochim. Acta, 31 (1979) 323.
2 F. Körber, W. Oelsen and H. Lichtenberg, Mitt. Kaiser Wilhelm Inst. Eisenforsch., 19 (1937) 131.
3 R. Castanet, Y. Claire and M. Laffitte, Cah Therm. Ser. B, 1 (1971) 19.
4 M. Lafitte, R Castanet and Y. Claire, High Temp. High Pressures, 2 (1970) 317.
5 R. Castanet, Y. Claire and M Laffitte, J. Chim. Phys., 68 (1971) 1133.
6 R. Castanet. Y. Claire and M. Laffitte, High Temp. High Pressures, 4 (1972) 343.
7 R. Castanet and M. Laffitte, J. Less-Common Met., 40 (1975) 221.
8 C. Bergman and R. Castanet, Ber. Bunsenges. Phys. Chem., 80 (1976) 774.
9 E. Hayer. K.L. Komarek and R Castanet, Z. Metallkd., 68 (1977) 688.
10 R. Castanet, C. Bergman, M.-L. Michel and H.V. Kehiaian, Z. Metallkd , 68 (1977) 342.
11 H. Said and R. Castanet, Z. Metallkd , 69 (1978) 181.
12 C. Bergman and R. Castanet, Ber. Bunsenges Phys. Chem , 81 (1977) 1000.
13 R. Castanet, M. Gilbert and C. Bergman, Z. Metallkd., 69 (1978) 298.
14 R. Castanet, R. Chastel and C. Bergman, Mater. Sci. Eng., 32 (1978) 93.
15 R. Castanet, C. Bergman and H.V. Kehiaian, 4th IUPAC Int. Conf. Chem. Thermodyn. Montpellier, 26—30 August 1975.
16 M. Hansen and K. Anderko. Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
17 R Castanet and M. Laffitte. Rev. Int. Hautes Temp. Refract., 11 (1974) 103.
18 R. Castanet, Proc. CALPHAD VIII Meeting, 21—25 May 1979, Stockholm, 1979, pp. 62—82.