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THERMODYNAMIC INVESTIGATION OF Cu—Sn ALLOYS WITH SOLID STATE GALVANIC CELLS

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ABSTRACT

An experimental apparatus for the measurement of the EMF of galvanic cells with solid state electrolytes and with separate gas chambers around the electrolytes is described. This provides the possibility of a more precise determination of the thermodynamic values for solid alloys. Measurements on alloys from the copper-rich solid solution region of the Cu—Sn system resulted in a linear temperature dependence of the measured EMF values with very little scatter. The partial free energies of mixing and the integral mixing enthalpies obtained using the published value of Petot-Ervas et al. [10] for the formation enthalpy difference of the oxides NiO and SnO_2 agree well with the literature data, which were determined by other methods.

INTRODUCTION

Increasingly, thermodynamic properties of solid alloys are being investigated by measurement of the EMF of galvanic cells with ionic conducting solid state electrolytes [1]. In particular the oxygen-ion conducting mixed oxides ZrO_2—CaO and ThO_2—Y_2O_3 have been used. The investigations have frequently been carried out using the experimental procedure introduced by Rapp and Maak [2], in which the electrodes are in the same gas chamber. Measurements carried out by us [3] with this arrangement have shown that, depending upon the oxygen partial pressure difference between the electrodes or the electrodes and the protective atmosphere, respectively, mixed potentials were measured which did not correspond to thermodynamic equilibrium. This resulted in a slight but measurable drift of the EMF values over a long time period (24 h).

In order to prevent interactions between the electrodes and the protective atmosphere, as well as between the electrodes through the protective atmosphere, an apparatus with separate gas chambers over the electrodes was built. The protective atmosphere is thus adjusted so that its oxygen partial pressure is optimum at the respective electrodes. In addition the apparatus was so designed that up to 3 solid-state cells could be measured simultaneously. The first experiments have been carried out on copper-rich solid solutions in a Cu—Sn system. One of the authors [4] had earlier made measurements in this system with solid-state cells within a single gas chamber.

The values of the partial free energies of mixing of tin so obtained differ by as much as 27 kJ mole^{-1} from the values obtained by Alcock and Jacob [5] using a gas—solid equilibrium method.

EXPERIMENTAL PROCEDURE

A solid-state cell which has the following schematic arrangement was used for the experiments

$$- \,|A + A_2O_z|\ \text{solid } O^{2-} \text{ conductor } |A\text{—}B \text{ alloy} + A_2O_z| \,+ \qquad (1)$$

A_2O_z is the stable oxide of component A at the measurement temperature and z the valency of A. The solid-state cell consists of co-existing electrodes, for which an equilibrium stabilization is required both between the two components in the electrode and between electrode and electrolyte. The two electrodes, in general, have different oxygen partial pressures. Thus a pressure equalization occurs across the electrolyte by transport of O^{2-} ions and with it a charge displacement. The work to transfer $z \times F$ charges is equal to $z \times F \times$ (EMF) where F is the Faraday constant. This work per mole corresponds, for isothermal and reversible transfer, to the partial free energy of mixing for component A

$$\overline{\Delta G_A} = -z \times F \times (\text{EMF}) \qquad (2)$$

In order to make a rapid restoration of the equilibrium possible, high test temperatures are required. Often the element, A, no longer exists in the solid state, so that a solid reference electrode, such as Ni + NiO, can be used at this temperature in place of $A + A_2O_z$. The EMF^0 values measured with Ni—NiO as the reference electrode can be converted into the EMF values which one will obtain with cell (1). If one refers the free energy of formation of the oxides NiO and A_2O_z respectively to one mole of oxygen, the following results:

$$\text{EMF} = \text{EMF}^0 + \frac{\Delta G^F_{\text{NiO}} - \Delta G^F_{A_2O_z}}{4F} \qquad (3)$$

The experimental apparatus with separated gas chambers around the electrodes is shown in Fig. 1. The separation of the gas chambers results from the use of a flat, one-end closed electrolyte tube of ThO_2—Y_2O_3 which serves as the electrolyte and simultaneously supports the cell. Since the outer gas chamber is not sub-divided the same comparison electrode must be used for all three cells. The inner electrode is kept pressed against the electrolyte tube by a spring over an Al_2O_3 tube. The spring pressure can be adjusted with a screw. In addition, each electrode is sprayed through the Al_2O_3 tube with the protective gas adapted for that electrode. The outer electrode is pressed against the electrolyte using a nickel wire fixed with two springs around a small Al_2O_3 plate. Again the contact pressure is variable. The protective gas inlet is also in the outer gas chamber in the immediate vicinity of the electrodes. The apparatus was sealed vacuum-tight by a water-cooled brass top and a bottom plate with a closed-end quartz tube. Lid, top and quartz tube

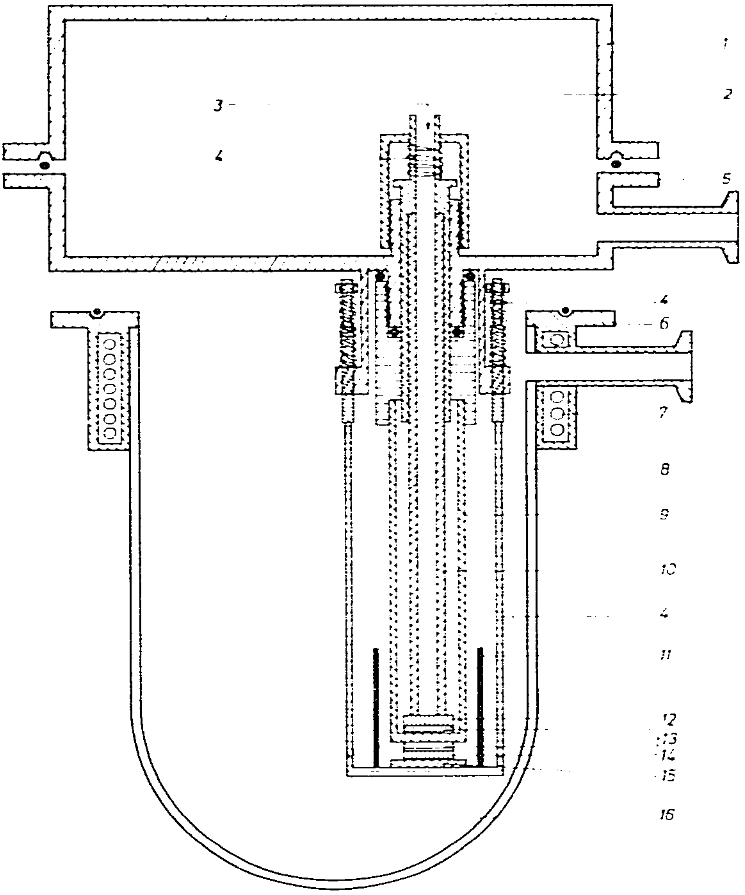

Fig. 1. Design of the equipment for the EMF measurements. 1, Top; 2, inner gas chamber; 3, protective gas; 4, pressure mechanism; 5, brass top; 6, base plate; 7, water cooling coils; 8, quartz tube; 9, electrolyte tube; 10, carborundum tube; 11, Ni-shield; 12, electrode with Pt-contact; 13, small electrolyte plate; 14, comparison electrode with Pt-contact; 15, carborundum disc; 16, outer gas chamber.

(Fig. 1) were attached to an adjustable guide rail in a vertical furnace. The EMF of the cell was measured with platinum wires and platinum contacts. The test temperature was measured by a platinum/platinum—rhodium thermocouple near the cell. The thermocouple was calibrated at the melting points of tin, cadmium, zinc, silver and gold. The test apparatus was shielded from the furnace by a grounded thermax tube. A further shielding of the cell by a grounded hollow Ni-cylinder is found in the Ni—NiO electrode gas chamber. Through electronic regulation of the furnace a temperature precision of better than ±0.5 degrees was guaranteed. The individual temperature steps and the test time could be preset with a temperature programmer so that the measurement program could proceed without interruption. The EMF was measured with an electrometer with an input resistance of 10^{14} Ω. The measured EMF was recorded simultaneously on a strip-chart recorder in order to demonstrate easily its constancy over long periods.

The comparison electrodes of nickel and nickel oxide were thoroughly mixed in a ratio of 3 : 1 and pressed into cylinders of 6 mm diameter and

1—3 mm thick. After sintering the powder compact at 1300 K for a sinter time of 24 h the sample surfaces were cut and polished in order to provide intimate contact with the electrolyte and the platinum contacts. The contact problems were minimized by pressing the powder mixture directly onto the electrolyte.

The copper—tin alloys were melted in an argon purged induction furnace. The homogeneous compact alloys were filed to a powder. Metallic chips from the file were removed from the resulting powder by a strong magnet. Alloy and oxide powders were mixed and pressed in the same way as the comparison electrodes.

Electrolytes prepared from ThO_2—Y_2O_3 or ZrO_2—CaO with 15 mole percent Y_2O_3 or CaO, respectively, employing the procedure of Alcock and Steele [6] were mostly used. A summary of the purity of the materials is given in Table 1. In addition, commercial ThO_2—Y_2O_3 solid solutions obtained from the firm zircoa in tube and pellet form were used. These contained 13 mole percent Y_2O_3. The oxygen partial pressure of the utilized electrodes lies within the pressure region of pure O^{2-} ion conductivity for the electrolyte [7,8]. The cell did not operate differently when using different ThO_2—Y_2O_3 electrolytes.

The apparatus was evacuated by a diffusion pump and purged several times with argon. The equipment was slowly heated to 600 K under vacuum. At this temperature the equipment was flooded with argon. Pure argon (99.999%), which was further purified with a zirconium getter at about 1000 K, then flowed through the system at a very slow velocity. The oxygen partial pressure in the protective gas was adjusted by choosing the temperature for gas cleaning and the flow velocity such that the electrodes were neither oxidized nor reduced. The oxygen partial pressure in the protective gas was more precisely adjusted for each electrode by placing additional electrode material in the gas stream before the electrode to produce an oxygen partial pressure in the gas approximately equal to the equilibrium oxygen pressure of the electrode. The measurements were started at the highest experimental temperature for each alloy. A constant EMF occurred for most alloys within 5 h of the attainment of the maximum temperature. The experimental tem-

TABLE 1

Purity of the substances used

Substance	Purity
Ni	Puriss.
Cu	99.999% min.
Sn	99.999% min.
NiO	99.998% min.
Cu_2O	Purum
SnO_2	Purum
Y_2O_3	99.99%
ThO_2	99.9%
$CaCO_3$	Puriss.
ZrO_2	99.9%

perature was then changed in steps of 20 to 50 degrees and the EMF values recorded. In order to guarantee that the cells were in equilibrium, the experimental temperature cycles were carried out several times. For the same reason the flow velocity of the protective gas was changed for a short time period and the cell was displaced from equilibrium by a short-time application of a reverse potential of several hundred millivolts.

EXPERIMENTAL RESULTS

The EMF of the cell

$$|\mathrm{Ni, NiO}|\mathrm{ZrO_2 + CaO}|\mathrm{ThO_2 + Y_2O_3}|\mathrm{ZrO_2 + CaO}|\mathrm{Cu, Cu_2O}| \quad (4)$$

was measured to test the experimental apparatus. The EMF values obtained, which deviate by less than 0.5 mV from the least-squares line, are shown in Fig. 2 together with some literature values [7,9]. It is noteworthy that a time period of over 100 h existed between the first and last measured value during which no drift of the measured values could be observed.

The results of the EMF measurements on Cu—Sn solid-solutions (still referenced to Ni—NiO) are shown as a function of temperature in Fig. 3. To a good approximation it shows a linear dependence on temperature. The slopes and intercepts of the equilibrium lines are presented in Table 2.

For the evaluation of the EMF values from eqn. 3, knowledge of the formation enthalpies of NiO and SnO_2 or their difference is necessary. These values have already been determined several times. The results differ considerably. Petot-Ervas et al. [10] obtained 2 (—54496 + 18.623T ± 205) J for the difference $\Delta G^{F}_{\mathrm{NiO}} - \Delta G^{F}_{\mathrm{SnO_2}}$, if the enthalpies of formation refer respectively to one mole of oxygen, whereas Belford and Alcock [11] report 2 (—57990 + 20.991T ± 376) J and Coughlin [12] reports 2 (—51718 + 11.991T ± 2510) J for this difference.

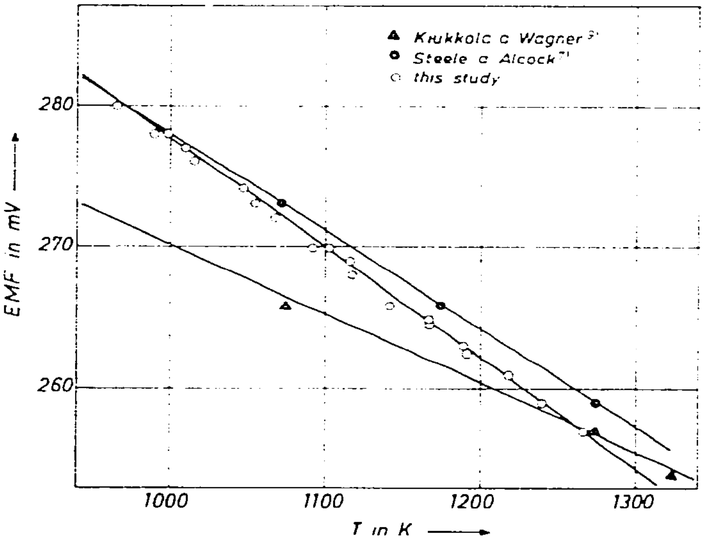

Fig. 2. Temperature dependence of the measured EMF between the electrode Ni—NiO and Cu—CuO_2 in comparison with literature data.

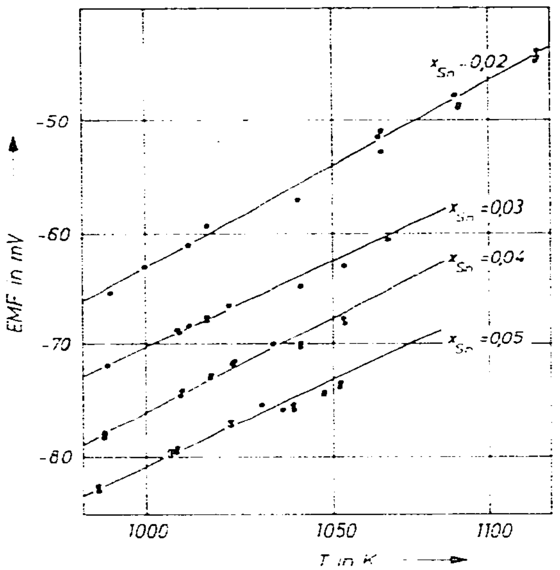

Fig. 3. Temperature dependence of the measured EMF values for Cu—Sn alloys referenced to Ni—NiO. The points shown correspond to several values.

TABLE 2

Temperature dependence of the EMF of galvanic cell (4) intercept ($T = 0^\circ C$) and slope for the equilibrium line $E = A + BT$ (T in °C)

x_{Sn}	A (mV)	B (mV deg^{-1})	Max. deviation (%)	Number of data points
0.02	−180.35	0.161346	1.7	18
0.03	−170.94	0.138506	0.5	20
0.04	−186.306	0.151535	0.6	62
0.05	−180.114	0.136617	0.6	60

DISCUSSION

The data obtained are given in Table 2. The partial free energies of mixing of tin obtained from eqn. 2 and eqn. 3 are shown together with literature data in Fig. 4 for a temperature of 1000 K. It shows that our values lie somewhat lower than those published by Alcock and Jacob [5]. At a tin concentration of $x_{Sn} = 0.05$ the difference is 3.2 kJ mole^{-1} if the value of Petot-Ervas et al. [10] is used for the difference in the formation enthalpies of the oxides. A larger difference results if the other two formation enthalpy differences mentioned above are used. Predel and Schallner [4] have used the value of Coughlin [12] for the difference in the formation enthalpies of the oxides. If one refers their results to the value of Petrot-Ervas et al. [10] the difference between our results and those of Alcock and Jacob is smaller. Nevertheless a distinct difference (≈ 27 kJ mole^{-1} at $x_{Sn} = 0.05$)

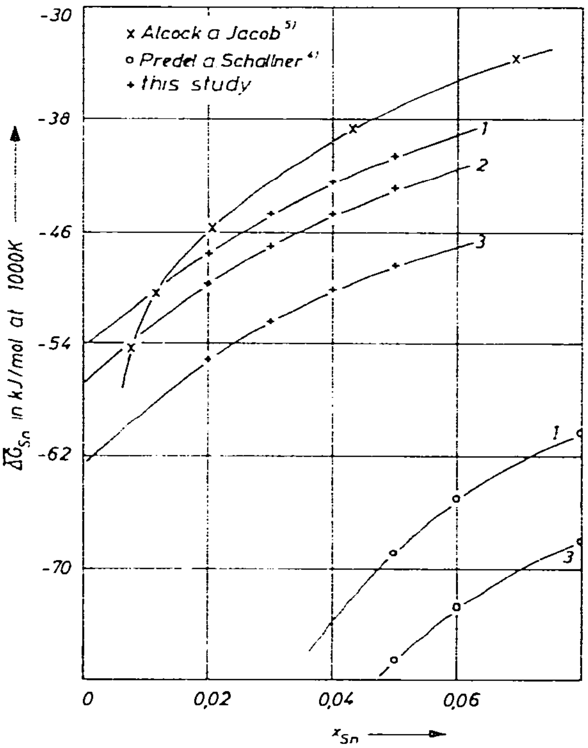

Fig. 4. Partial free energies of mixing of tin in solid Cu—Sn alloys. Difference of the oxide formation enthalpies according to: (1) Petot-Ervas et al. [10], (2) Belford and Alcock [11], (3) Coughlin [12].

remains for our results. Thus it can be implied that in the earlier measurements [4] which were carried out with a single gas chamber around the electrodes mixed potentials were measured which can be attributed to an interaction between the electrodes and the protective gas.

From the temperature dependence of the partial free energy of mixing one obtains the partial entropy of mixing and in a well-known way the integral mixing values (Fig. 5). The scatter of the formation enthalpies of the oxides indicates considerable uncertainty for the integral values.

A very good agreement exists between the value for ΔH obtained by us and the calorimetrically determined heat of formation of solid Cu—Sn alloys found by Kleppa [13] if one uses the value of Petot-Ervas et al. [10] for the difference in formation energies of the oxides NiO and SnO_2.

The reversibility of the measurements over long periods of time and the small scatter of the single values (see Fig. 3) show that EMF measurements with separated gas chambers around the electrodes are very precise experiments for the determination of thermodynamic values of solid alloys. A considerable error in the final results is caused by the low accuracy of the reported literature values for the formation enthalpies of the oxides. Differences in the free energies of formation of oxides which have been determined directly from EMF measurements with solid electrolytes using separate gas chambers, as for example is the case for the data of Petot-Ervas et al. [10], can be especially precise.

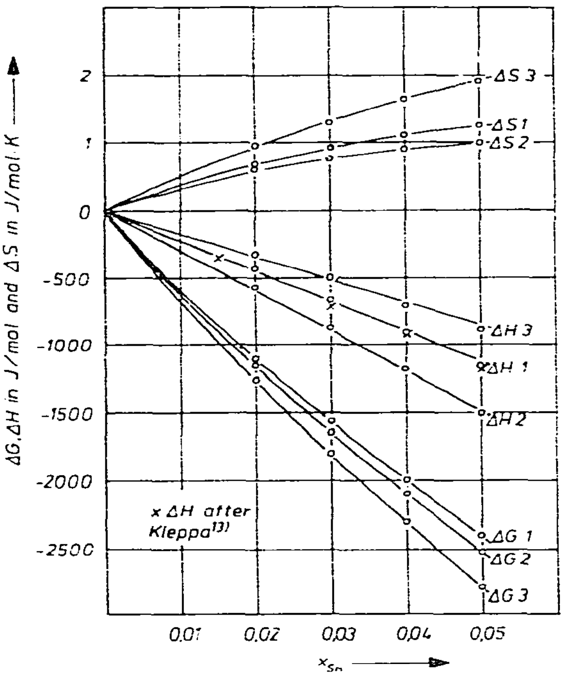

Fig. 5. Integral free energies of mixing, ΔG, integral mixing enthalpies, ΔH, and integral mixing entropies, ΔS, of solid Cu—Sn alloys at 1000 K as a function of the concentration and their dependence on the difference in the formation enthalpies of the oxides (see Fig. 4).

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