

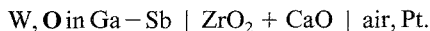
Determination of Oxygen Activity in Gallium-Antimony Liquid Solutions**

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The activity of oxygen occurring at low concentrations in liquid Ga—Sb solutions was studied by means of the galvanic cell with zirconia solid electrolyte:



The coulometric titration technique was employed. The activity coefficient of oxygen was determined over the whole composition range as a function of temperature in the interval 1 123 K—1 223 K. From the experimental results *Wagner's* parameter h was deduced as: $h_{\text{GaSb}} = 7\,730 \text{ J/g atom O}$. Values of oxygen activity coefficients in ternary gallium-indium-antimony alloys were predicted.

(*Keywords: Liquid metals; Oxygen activity; Solid electrolyte; Coulometric titration*)

Bestimmung der Sauerstoffaktivität in flüssigen Gallium-Antimon-Lösungen

Es wurde die Aktivität des in flüssigen Ga—Sb-Lösungen in niedrigen Konzentrationen anwesenden Sauerstoffs mittels einer galvanischen Zelle mit festem Elektrolyt: W, O in Ga—Sb|ZrO₂ + CaO|Luft, Pt untersucht. Als Elektrolyt wurde mit Calciumoxid stabilisiertes Zirkoniumoxid benutzt. Es wurde dabei die coulometrische Titrierung angewendet. Der Aktivitätskoeffizient von Sauerstoff wurde als Funktion der Temperatur in einem Bereich von 0 bis 100 At% Sb ermittelt. Auf Grund von experimentellen Daten wurde der *Wagnersche* Parameter zu $h = 7\,730 \text{ J/g Atom O}$ ermittelt. Die Werte der Sauerstoff-Aktivitätskoeffizienten in ternären Gallium-Indium-Antimon-Legierungen wurden berechnet.

Introduction

The application of galvanic cells with solid electrolytes based on zirconia in the early studies of oxygen partial pressures was limited to

** Dedicated to Prof. Dr. Kurt L. Komarek on the occasion of his 60th birthday.

systems, where these pressures were not lower than 10^{-10} Pa. This limit of applicability was suggested during the studies of conductivity of solid electrolytes by *Steele* and *Alcock* [1]. However, further investigations provided the evidence that the range of oxygen pressures under which the ionic conductivity is predominant is considerably wider. It was found [2] that the purity of materials and the method of fabrication exert a strong influence on the range of ionic domain. The limit of electronic conductivity of zirconia allows to measure the *Gibbs* free energy of formation of gallium oxide [3]. However, no attempt was made to measure the oxygen potential below the saturation limit in gallium.

Growing interest in the properties of oxygen in such metals, as indium and gallium, which can be used as a solvent in liquid phase epitaxial growth of semiconducting materials, gave the impulse to check the possibility of using zirconia based electrolytes in case of Ga–O dilute solutions. Though thoria-yttria solid electrolytes show ionic conductivity at low oxygen pressures, they are hardly available commercially. The recent study on the influence of gallium and arsenic on the activity of oxygen dissolved in liquid indium [4] had shown that working with zirconia reliable results can be obtained at oxygen pressures as low as 10^{-15} Pa. The following study [5] concerned with arsenic-oxygen interaction in liquid gallium demonstrated that calcia stabilized zirconia solid electrolyte can be successfully used for oxygen potential measurements in liquid gallium above 1073 K. The obtained results are almost identical with those measured with $\text{ThO}_2 + \text{Y}_2\text{O}_3$ electrolyte [6]. The aim of the present work is to determine the activity coefficients of oxygen in liquid gallium-antimony alloys over the temperature range 1123 K – 1223 K. The data available in the literature regard the oxygen activities only in the pure liquid constituents. Oxygen solubility in gallium was studied by *Foster* and *Scardefield* [7]. The oxygen activity in liquid gallium was investigated by *Jacob* and *Alcock* [8] with the use of an isopiestic technique, and by *Heshmatpour* and *Stevenson* [6] who applied the electrochemical method with a thoria-yttria solid electrolyte. Oxygen activity in liquid antimony was studied by *Isecke* and *Osterwald* [9], *Otsuka* and *Kozuka* [10], *Fitzner* [11], and by *Heshmatpour* and *Stevenson* [6], who all used the coulometric titration technique. *Jacob* and *Mani Matthew* [12] used a combination of the isopiestic and electrochemical method to determine the oxygen activity in liquid antimony. No data are known on the oxygen activity in liquid Ga–Sb alloys.

Experimental

Solid electrolyte tubes made of $\text{ZrO}_2 + 15$ pct CaO, outer diameter 8 mm and inner diameter 5 mm with one end closed were produced by Degussa (Federal Republic of Germany). Gallium, 99.9999% purity was delivered by the Institute

of Electronic Materials (Poland). Antimony, 99.995% purity was made in the Skawina Aluminium Plant (Poland).

A coulometric titration technique was employed for the determination of oxygen activity in liquid alloys. The equipment and procedure were described in details previously [13]. A schematic diagram of experimental arrangement of the cell:



is presented in Fig. 1. The tube of solid electrolyte contained about 3 g of metallic alloy of chosen composition. A tungsten wire acted as electric contact with the metal electrode. The outer part of the solid electrolyte tube coated with platinum paste worked as an air reference electrode and was connected to the electric system with a platinum wire. The electric circuit contained the potentiostat and charge meter (integrator), both produced by Radelkis (Hungary), type OH-404, and the digital voltmeter V 544, made by Meratronik (Poland). Purified argon was passed through the cell just above the surface of the liquid metal, and caused the preliminary adjustment of oxygen concentration in the metal, which was usually at the level 0.01 at · pct or less. After the equilibrium EMF of the cell E_1 was recorded, the preselected additional potential ΔE was applied by the poten-

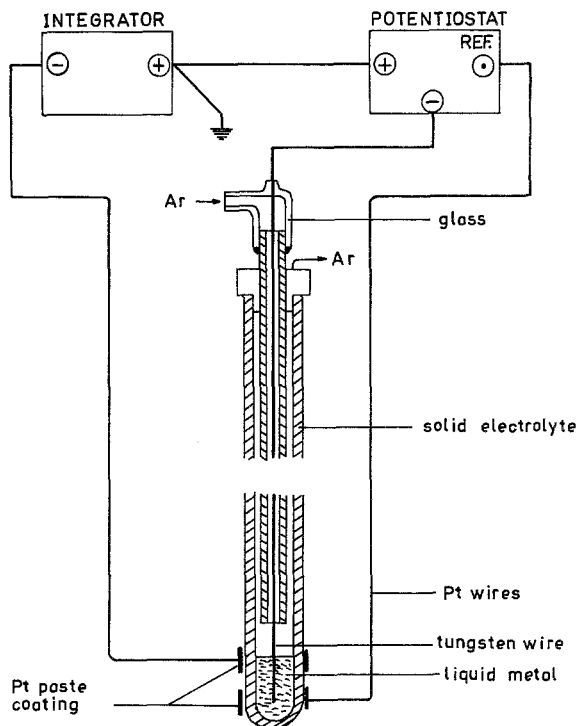


Fig. 1. Schematic diagram of the experimental arrangement

tiostat. The resulting current passed through the cell in such a direction, that oxygen was pumped out of the metal.

The decrease in oxygen concentration resulted in an increase of the *EMF* of the cell (which could be observed after the current was stopped) and the decay of electric current. The final *EMF* value E_2 and the electric charge Q were recorded. The experimental run was repeated several times at the same temperature, then the temperature was changed.

The initial equilibrium oxygen concentration C_1 (atomic pct.) corresponding to the *EMF* value E_1 was calculated from the formula:

$$C_1 = 100 \cdot \frac{M}{W} \cdot \frac{Q}{2F} \left\{ 1 - \exp \left[\frac{-2(E_2 - E_1)F}{RT} \right] \right\}^{-1} \quad (1)$$

where M is the average atomic weight of the alloy, W is the sample weight, Q is the electric charge transferred through the cell, F is the *Faraday's* constant and R is the gas constant. *EMF* values of the cell were corrected for the thermoelectric force of platinum-tungsten junction. Then, the oxygen activity coefficient γ_0 was calculated from the relationship:

$$\ln \gamma_0 = -\frac{2E_1F}{RT} + \ln \sqrt{0.21} \quad (2)$$

Eqs. (1) and (2) are correct under the assumption of *Henry's* law valid over the range of oxygen concentration covered by the experiments. The above equations were derived by *Otsuka* and *Kozuka* [10].

Results

Experiments were carried out for the alloys containing 10, 20, 40, 60 and 80 at · pct gallium. For each alloy composition runs were performed at 1 123 K, 1 173 K, and 1 223 K, with an exception of 60 at · pct gallium alloy, where the conductivity of the solid electrolyte tube was unexpectedly small at the temperature 1 123 K. For this alloy the measurements were also done at 1 273 K, as with increasing temperature the conductivity of the tube also increased. The obtained results are presented in Fig. 2, where the $\ln \gamma_0$ values were plotted against reciprocal temperature. The respective equations describing the temperature dependence – obtained from a least-square fit – are as follows:

$$N_{\text{Ga}} = 0.1 \quad \ln \gamma_0 = 19.45 - 43\,166 \frac{1}{T} \quad (3)$$

$$N_{\text{Ga}} = 0.2 \quad \ln \gamma_0 = 22.40 - 48\,867 \frac{1}{T} \quad (4)$$

$$N_{\text{Ga}} = 0.4 \quad \ln \gamma_0 = 16.70 - 42\,396 \frac{1}{T} \quad (5)$$

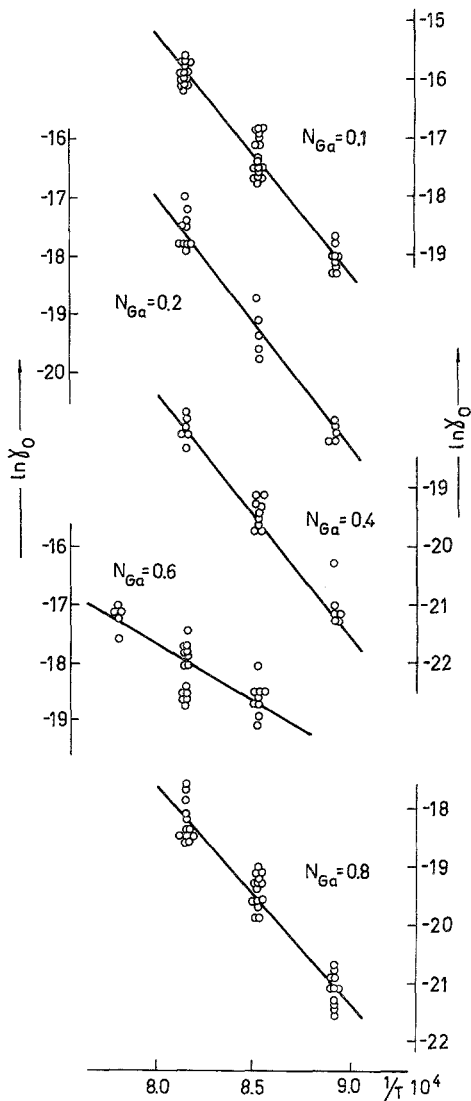


Fig. 2. Experimental results; straight lines correspond to Eqs. (3)–(7)

$$N_{Ga} = 0.6 \quad \ln \gamma_0 = -1.48 - 20217 \frac{1}{T} \quad (6)$$

$$N_{Ga} = 0.8 \quad \ln \gamma_0 = 13.09 - 38300 \frac{1}{T} \quad (7)$$

The description of the composition dependence of the oxygen activity coefficient in a liquid binary alloy can be achieved by means of *Wagner's* model [14]:

$$\ln \gamma_{0(\text{Ga-Sb})} = \frac{1}{2} (\ln \gamma_{0(\text{Ga})} + \ln \gamma_{0(\text{Sb})}) - \ln \left\{ \sum_{i=0}^z \binom{z}{i} \left(\frac{1 - N_{\text{Ga}}}{\Phi} \right)^{z-i} (N_{\text{Ga}} \cdot \Phi)^i \exp \left[\frac{(z-i) i h}{2 RT} \right] \right\} \quad (8)$$

where $\Phi = \left(\frac{\gamma_{0(\text{Sb})}}{\gamma_{0(\text{Ga})}} \right)^{\frac{1}{2z}}$ and z denotes the number of metallic atoms

which surround the oxygen atom in the first coordination shell. The value of $z = 6$ was accepted in the calculations.

The parameter h in equation (8) was obtained by a non-linear regression fit of $\ln \gamma_0$ values calculated from equations (3)–(7) for the temperature 1173 K. The values of $\ln \gamma_0$ of pure antimony and pure gallium at this temperature were accepted after *Fitzner* [11] and *Wypartowicz* and

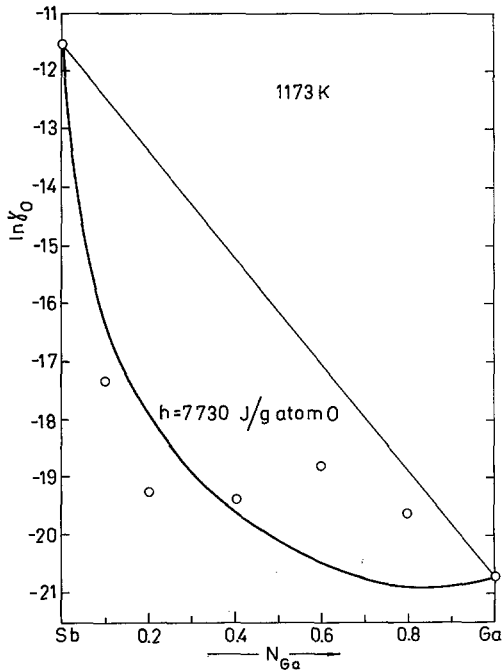


Fig. 3. Comparison of $\ln \gamma_0$ values determined experimentally at 1173 K and deduced from *Wagner's* model

Fitzner [5], respectively. The calculated plot of $\ln \gamma_0$ vs. the metallic alloy composition obtained from *Wagner's* model (8) is compared in Fig. 3 with the experimental results. The obtained scatter of $\ln \gamma_0$ values around the composition $N_{Ga} = 0.6$ is apparently connected with observed changes in conductivity of the zirconia tube. Thus, it is rather due to experimental errors than to solution behaviour. The obtained value of $h_{GaSb} = 7730 \text{ J/g atom 0}$ may be used in characterization of the oxygen activity coefficient in ternary Ga – In – Sb solutions. *Kapoor* [15] extended *Wagner's* model for ternary solutions. For Ga – In – Sb one obtains:

$$\ln \gamma_0 = - \ln \left\{ \sum_{a=0}^z \sum_{b=0}^{z-a} \left(\frac{z!}{a! b! c!} \right) \left[N_{Ga} \gamma_{O(Ga)}^{-\frac{1}{z}} \right]^a \left[N_{In} \gamma_{O(In)}^{-\frac{1}{z}} \right]^b \left[N_{Sb} \gamma_{O(Sb)}^{-\frac{1}{z}} \right]^c \exp \left[\left(ab \cdot h_{GaIn} + bc \cdot h_{GaIn} + bc \cdot h_{InSb} + ac \cdot h_{GaSb} \right) \frac{1}{2 RT} \right] \right\} \quad (9)$$

where: $a + b + c = z$

The meaning of other symbols is analogous as in equation (8). The calculation of $\ln \gamma_0$ in ternary solutions Ga – In – Sb regards the tem-

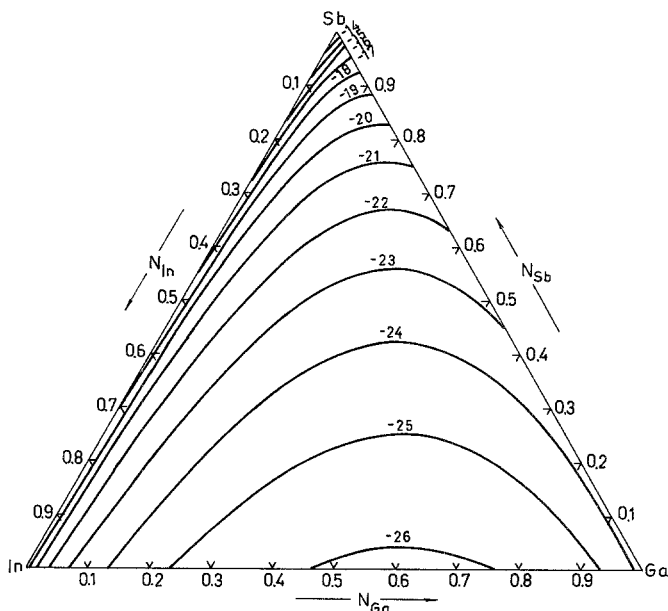


Fig. 4. Activity coefficient of oxygen in liquid ternary Ga – In – Sb solutions at 1073 K

perature 1073 K. The value of parameter $h_{\text{GaIn}} = 9757 \text{ J/g atom O}$ and the value of $\ln \gamma_0$ in pure indium (-19.41) were obtained from a study of *Wypartowicz and Fitzner* [4]. The parameter $h_{\text{InSb}} = 3355 \text{ J/g atom O}$ was determined by *Fitzner* [16]. The value of $\ln \gamma_0$ in pure gallium (-23.62) was taken from [5], while $\ln \gamma_0$ in pure antimony (-12.81) was evaluated from references [9]–[12].

The results of the calculations are presented in Fig. 4.

Discussion

Earlier experiments showed that the oxygen solubility in liquid gallium can be measured by a coulometric titration technique using $\text{ZrO}_2 + \text{CaO}$ tubes above 1073 K. This fact extended the number of systems which could be studied with this technique. As a first one Ga–Sb–O solutions were investigated. The obtained results were interpreted with *Wagner's* model, using the value of $h = 7730 \text{ J/g atom O}$. The scatter of the results observed for compositions $N_{\text{Ga}} = 0.8$ and 0.6 in the $\ln \gamma_0$ vs. N_{Ga} curve could be attributed to the possible onset of electronic conductivity in the

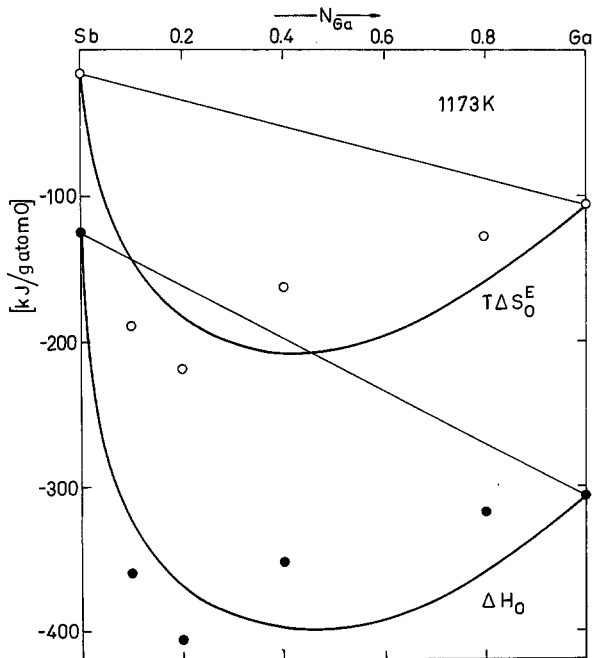
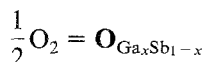


Fig. 5. Enthalpy and excess entropy of oxygen dissolution in liquid binary Ga–Sb alloys; solid lines are tentative and do not correspond to any particular model

electrolyte. It may have happened that the oxygen potential had fallen with the alloy composition into the electronic domain. Investigations of $\ln \gamma_0$ were carried out in the temperature range 1 123 K–1 223 K. It allows to derive the enthalpy and entropy of solution terms for the reaction:



as a function of alloy composition. They are shown in Fig. 5. It is clear, that a big heat effect is partially compensated by the $T \Delta S_0^E$ term. No particular model can be suggested to describe this behaviour. The results obtained for $N_{\text{Ga}} = 0.6$ were not taken into account because of the change of the conductivity of zirconia tube observed for this particular composition. Despite of the scatter of the experimental results, the value of the h_{GaSb} parameter can be derived. This fact enables the prediction of oxygen behaviour in multicomponent systems which comprise binary Ga – Sb contribution. As an example $\ln \gamma_0$ iso-lines in ternary Ga – In – Sb liquid alloys were predicted.

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