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MAGNESIUM ACTIVITY IN LIQUID In–Mg ALLOY FROM VAPOUR PRESSURE MEASUREMENTS

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ABSTRACT

The activity of magnesium in liquid In–Mg alloys at 900 K has been determined by measuring its vapour pressure with a torsion-effusion apparatus. The results indicate a large negative deviation from ideality. Partial molar thermodynamic properties of magnesium have been derived.

INTRODUCTION

Apparently the only magnesium activities in In–Mg alloy are those derived from EMF measurements by Slaby and Terpilowski [1,2] and by Nebell [3]. Data of the partial molar enthalpies of this element are also derived by these authors and from calorimetric measurements by Ehrlich [4]. It was considered useful to carry out vapour pressure measurements of magnesium over different In–Mg alloys by using a torsion-effusion apparatus in order to obtain new direct values of its activity and to derive mixing thermodynamic properties.

EXPERIMENTAL

Some In–Mg alloys were prepared using spectrographically pure elements. Appropriate weights of the two metals were introduced into a stainless steel crucible with a tantalum liner, evacuated, sealed, melted by heating up to 1000 K and quenched. The homogeneity and composition of some alloys so obtained were checked by chemical analysis. Since the fugacity of indium is negligible at the covered temperature, in all the cases the exact composition of the studied sample was checked at the end of each run by weighing and analyzing the residue when the magnesium was completely vaporized from the alloy.

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The activity of magnesium in these alloys was determined by the torsion-effusion method. The basis of this technique and the experimental procedure have been described elsewhere [5]. The vapour pressure of the sample is determined by the cell deflection measurements (α) through the relation

$$P = \alpha K$$

where K takes into account the constant of the torsion filament, the cell parameters and the pressure unit. A typical cell is illustrated in Fig. 1. In order to test that thermodynamic equilibrium conditions exist inside the

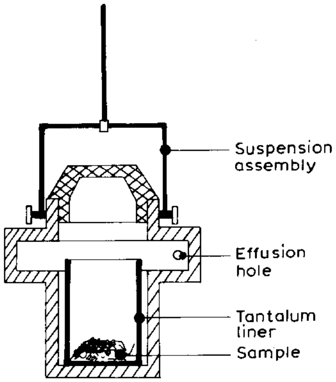

Fig. 1. Torsion effusion cell.

TABLE 1

Torsion angles of the effusion cell as a function of temperature

Exp.	Cell	Composition (at.% Mg)	ΔT (K)	$\log \alpha = A - B \times 10^3/T$	
				A	B
2.01	A	48	815–878	10.49	7.83
2.03	(pyrophillite)	52	816–883	10.67	7.83
2.04		80	813–874	10.78	7.50
2.02, 2.05		100	743–858	10.90 [a]	7.42 [a]
3.00	C	61	794–885	11.02	8.00
3.04	(graphite)	66	776–876	10.68	7.52
3.03		70	780–875	10.93	7.75
3.01		100	735–853	10.92	7.50
4.01	B	64	796–862	11.03	7.75
4.02	(graphite)	68	772–860	11.20	7.75
4.05		81	799–856	11.25	7.67
4.00, 4.03		100	741–834	11.43 [a]	7.75 [a]

[a] Average of two runs.

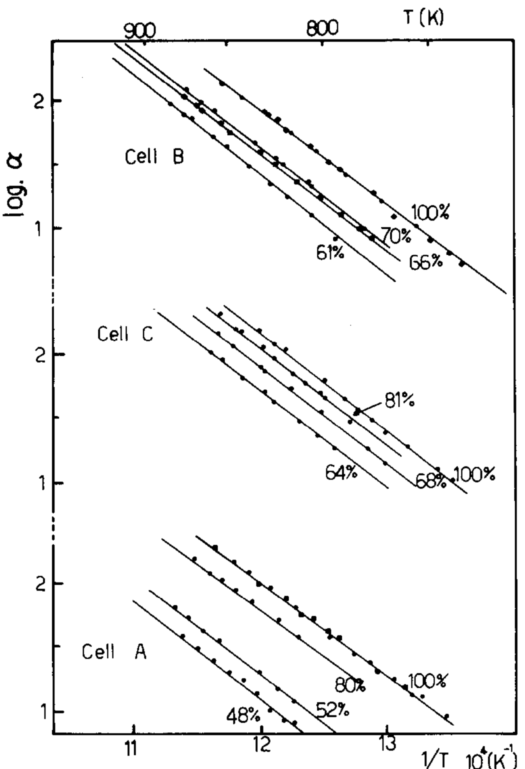

Fig. 2. Plots of log α vs. 1/*T*.

TABLE 2

Torsion angles determined from quantitative vaporization, and their temperature dependence

Exp.	Initial composition (at.% Mg)	*T* (K)	Torsion angles					
			33 (at.% Mg)	21 (at.% Mg)	15 (at.% Mg)	12 (at.% Mg)	10 (at.% Mg)	6 (at.% Mg)
5.02	52	670	46	22	14	10	7	
5.03	48	674	43	22	14	11	8	
5.06	19	694			22	16	12.5	8
5.07	40	616	16	6.5	4	3		
5.08	24	676		24	18	11	8	5
5.11	37	651		16	10	7	5	3
5.12	19	685			17	12	10	6
5.14	34	640		11	7	5	3.5	2

log α vs. 1/*T* equations:

alloy 21 (at.% Mg) $\log \alpha = 9.92 - 8.1 \times 10^3/T$

alloy 15 (at.% Mg) $\log \alpha = 10.04 - 8.4 \times 10^3/T$

alloy 12 (at.% Mg) $\log \alpha = 9.81 - 8.3 \times 10^3/T$

alloy 10 (at.% Mg) $\log \alpha = 10.09 - 8.7 \times 10^3/T$

alloy 6 (at.% Mg) $\log \alpha = 10.59 - 9.4 \times 10^3/T$

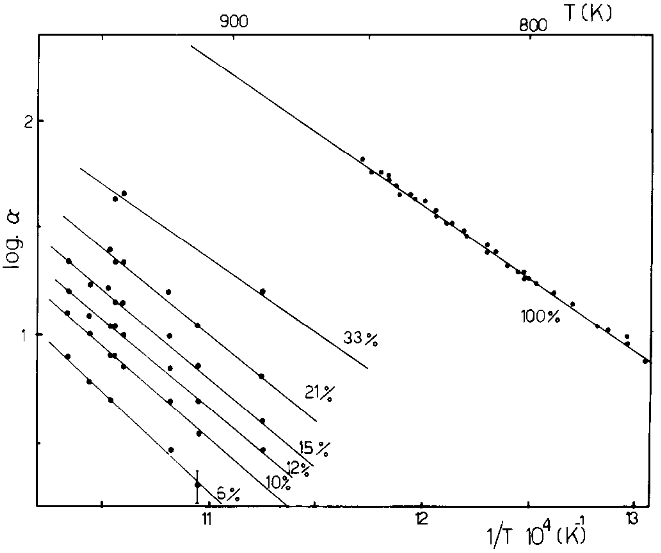

Fig. 3. Plots of log α vs. $1/T$ measured during the magnesium quantitative vaporizations.

used cells, the absolute vapour pressures of some pure elements (lead and magnesium) were measured and compared with those selected by Hultgren et al. [6]. The results obtained were in good agreement within the associated experimental errors.

In our investigation, using the same cell in the study of pure magnesium and its alloys, the activity of this element is derived directly from the ratio of the torsion angles measured at the same temperature, and analyzing the alloy and the pure element. In this way most of the systematic errors associated with the K constant are eliminated.

With this technique the alloys at composition 48–81 at.% of magnesium were studied by using three cells with different orifice areas of the effusion holes, and the results are plotted in Fig. 2. The constants of the log α vs. $1/T$ equations in the experimental temperature range as obtained by least-squares treatment of the results are summarized in Table 1. In each experiment only the initial points were taken into account so that variation in the composition of the sample was negligible.

Quantitative vaporizations of the magnesium were also carried out following the procedure described previously [7]. At the end of each experiment, carried out at constant temperature, the area obtained by plotting the deflection angles vs. time is proportional to the amount of magnesium evaporated according to the Knudsen equation [8]. From this area, knowing the initial composition and the amount of alloy, the deflection angles corresponding to the prefixed composition of the alloy can be derived. In our case, the deflection angles of the cell at the vaporization steps which correspond to the prefixed compositions of the residue equal to 33, 21, 15, 12, 10 and 6 at.% of magnesium, were measured in the temperature range 616–694 K. These quantitative vaporizations were carried out at not too high temperatures and by using an appropriate initial amount in order to realize a sufficient α–time integration area for reliable determinations of the values at the prefixed compositions. The results obtained with this procedure are reported in Table 2 and plotted in Fig. 3.

Although it is difficult to determine accurately the errors associated with these results, their evaluation leads to a very small uncertainty in the composition (~ 0.5 at.%) and a larger one in the torsion angle (~ 5%). By least-squares treatment of the data the log α vs. $1/T$ equations for each composition were derived and are reported in Table 2.

In some experiments self-calibrations were made at the end of the quantitative vaporizations of the magnesium by heating the cell to a higher temperature and measuring the pure indium vapour pressure. The purpose of these calibrations was chiefly to verify the reliability of the temperature measurements.

RESULTS AND DISCUSSION

The magnesium activities in liquid In–Mg alloys were determined at 900 K, the temperature intermediate between the ranges covered in the two sets of vaporization experiments. The activity values were calculated from

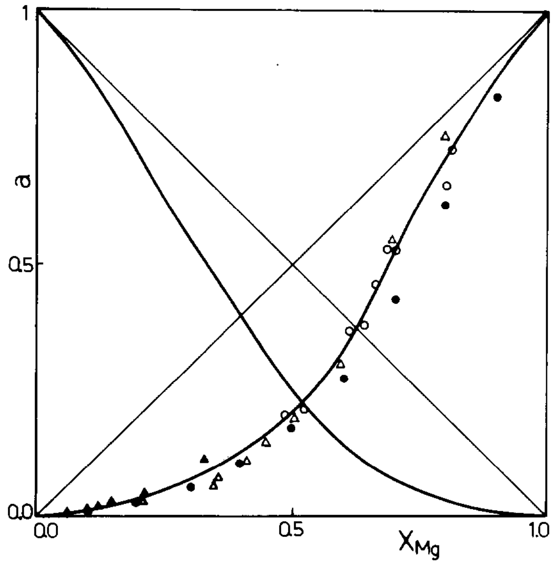

Fig. 4. Magnesium and indium activities in liquid alloys. Δ, Nebell [3] (923 K); ●, Slaby and Terpilowski [2] (923 K); ○, our data (900 K); ▲ our data (900 K), quantitative vaporizations.

the constants reported in Tables 1 and 2 by the equation

$$a_{\mathrm{Mg}} = \exp(A_x - B_x/T)\exp(B^0/T - A^0)$$

where, for each alloy, the A^0 and B^0 values for the pure element were those determined using the same cell employed for the studied alloy.

For the indium-rich alloys studied by quantitative vaporizations the values $A^0 = 10.45$ and $B^0 = 7.4 \times 10^3$ (average of six determinations) were used. In particular for the alloy 33 at.% Mg, the value $a = 0.115$ was evaluated at 900 K from the lines reported in Fig. 3.

The results so obtained are drawn in Fig. 4, together with those reported in the literature at 923 K, the melting point of pure magnesium. In good agreement with Nebell's data, and in substantial agreement with Slaby and Terplowski's results, the activities of magnesium alloyed with the indium show that this solution exhibits a large negative deviation from Rault's law.

The activity of indium has been derived in the usual way by graphic integration of the Gibbs–Duhem equation. The value $\beta = \ln \gamma_{\mathrm{Mg}}/(1 - X_{\mathrm{Mg}})^2$ necessary for this integration was calculated by the relation

$$\beta = (A_x - A_0) - (B_x - B_0)/T(1 - X_{\mathrm{Mg}})^{-2}$$

In our case it was found that this parameter is practically constant ($\beta = 2.8 \pm 0.2$) in the composition range studied. The activities of both components and the magnesium partial molar free energy values at 900 K are summarized in Table 3 at 0.1 molar fraction intervals across the system.

Partial molar enthalpies of magnesium were also derived from the slopes of the torsion–temperature equations and are plotted, with the estimated

TABLE 3

Magnesium activity and partial molar thermodynamic functions in liquid In–Mg alloys at 900 K

Mg(solid) → Mg(liquid alloy)

X_{Mg}	a_{Mg}	a_{In}	$\Delta\bar{G}_{\mathrm{Mg}}$ (kJ mole^{-1})	$\Delta\bar{G}^{\mathrm{ex}}_{\mathrm{Mg}}$ (kJ mole^{-1})	$\Delta\bar{H}_{\mathrm{Mg}}$ (kJ mole^{-1})	$\Delta\bar{S}_{\mathrm{Mg}}$ (J mole^{-1} K^{-1})	$\Delta\bar{S}^{\mathrm{ex}}_{\mathrm{Mg}}$ (J mole^{-1} K^{-1})
0.00	0.000	1.000	∞	24	-25 ± 8	∞	−0.9
0.10	0.009	0.875	35.2	17.2	−18.4	18.7	−1.3
0.20	0.035	0.715	25.1	12.0	−13.4	13.0	−1.5
0.30	0.075	0.543	43.0	10.4	−8.8	11.8	1.8
0.40	0.130	0.384	15.3	8.3	−5.9	10.5	2.7
0.50	0.205	0.248	11.8	6.6	−3.3	9.4	3.7
0.60	0.325	0.146	8.4	4.6	−0.4	8.9	4.6
0.70	0.530	0.076	4.8	2.1	1.7	7.1	4.1
0.80	0.715	0.034	2.5	0.9	4.2	7.4	5.6
0.90	0.870	0.010	1.0	0.2	6.7	8.6	7.7
1.00	1.000	0.000	0.0	0.0	8.8	9.7	9.7

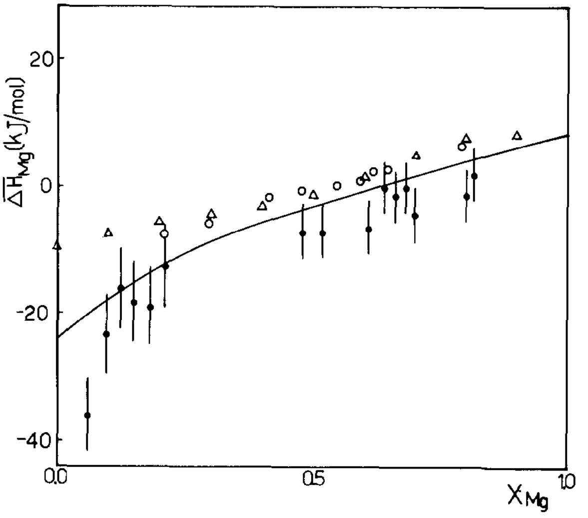

Fig. 5. Magnesium partial molar enthalpy of mixing in In–Mg alloy. △, Ehrlich [4]; ○, Nebell [3]; ● our data.

errors, in Fig. 5, with the literature data opportunely corrected for the magnesium heat of fusion, $\Delta H_{\mathrm{fus}} = 9$ kJ mole^{-1}, because at 900 K the studied reaction is

Mg(solid) → Mg(liquid alloy)

Even if our results are not particularly meaningful taking into account the uncertainties associated to the slopes, these are lower than those reported in the literature and we feel that the enthalpy of mixing at infinite dilution, $\overline{\Delta H}^{0}_{\mathrm{Mg}} = -10$ kJ mole^{-1}, extrapolated by Ehrlich can be taken as an upper limit. Therefore we propose -25 kJ mole^{-1} as the most probable value of $\overline{\Delta H}^{0}_{\mathrm{Mg}}$. In order to complete the partial molar thermodynamic functions, using the $\overline{\Delta H}_{\mathrm{Mg}}$ values derived from the selected curve in Fig. 5, $\overline{\Delta S}_{\mathrm{Mg}}$ and $\overline{\Delta S}^{\mathrm{ex}}_{\mathrm{Mg}}$ were derived and are reported in Table 3.

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