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THE ACTIVITY OF ZINC IN SOLID Al–Zn ALLOYS

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ABSTRACT

The activities of zinc in solid Al–Zn alloys in the temperature range 625–696 K were determined by means of a multiple rotating Knudsen source coupled with a mass spectrometer.

Thermodynamic properties, free energies, enthalpies and entropies of mixing, were calculated at 660 K and compared with previous values.

INTRODUCTION

The Al–Zn system has been the object of study by many researchers under the thermodynamic profile. Almost all the data reported in the literature are thermodynamic quantities relative to the liquid system[1–3]. The only data concerning the solid system are those selected by Hultgren[4] and refer to the measurements of Al activity by means of the e.m.f.[5,6]. Apparently, no direct measurements of the activity of zinc for the solid Al–Zn system are reported in literature, therefore, we thought it useful to perform some measurements of this parameter using a multiple rotating Knudsen cell coupled with a mass spectrometer.

EXPERIMENTAL PROCEDURE

A Bendix time-of-flight mass spectrometer, Model 3015, was utilized together with a multiple-rotating molecular source formed by a cylindrical block of graphite in which five housings have been drilled closed with lids having a knife-edged central effusion hole, 1 mm in diameter. Heating of the block was accomplished by radiation of a tungsten filament and its temperatures were measured using a calibrated Pt/Pt–10% Rh thermocouple placed in a small housing drilled to the centre of the cap of the block. Details of the experimental procedure and of the method are reported in a previous work[7].

Samples of Al–Zn alloys were prepared by sealing in quartz ampoules under argon atmosphere intimate mixtures of weighted amounts of spectrographic pure elements; the ampoules were subsequently heated for 2 h at a temperature above the melting point of aluminum. The composition of the prepared alloys and their homogeneity were then checked by chemical and metallographic analyses.

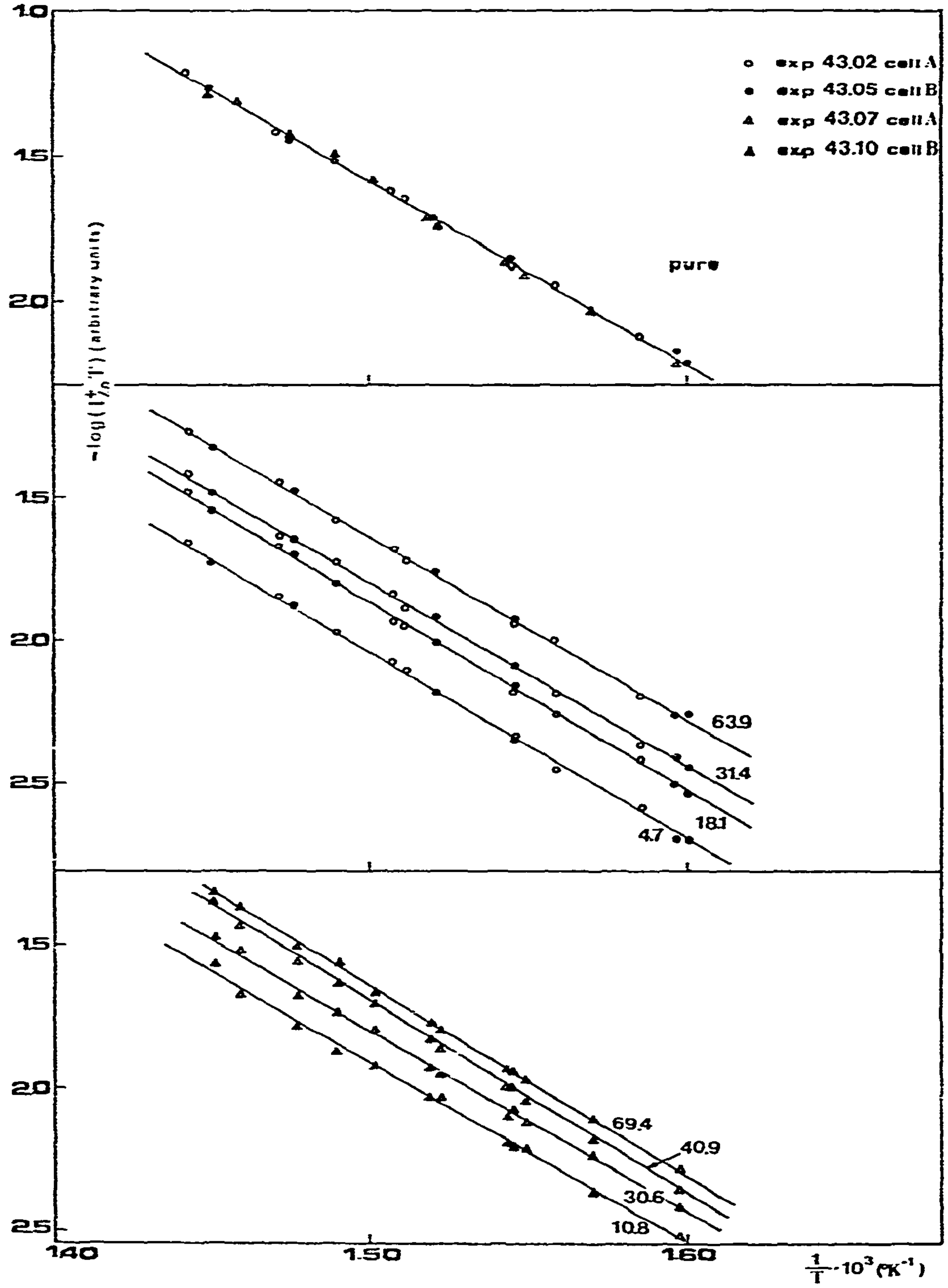


Fig. 1. Plots of log ($I^+_{Zn}T$) vs. $1/T$ for zinc pure and for zinc in Al–Zn alloys.

RESULTS

Aluminum-zinc alloys of eight compositions varying from 0.047 to 0.694 at.-% zinc were studied in four sets of experiments carried out in the temperature range 625–696 K by using two different rotating cells. During the vaporization of the alloys samples, Zn(g) was the only species observed in the vapor phase, and, therefore, Zn^+ was the only ion species measured. In order to warrant the constancy of the composition of each single alloy during the measurements of the Zn^+ intensity, only the initial values measured in each vaporization were taken into account for the thermodynamic calculations.

TABLE 1

ROTATING CELLS CALIBRATION COEFFICIENT VALUES (γ_i)

Exp.	*Cell*	*Point No.*	*1*[a]	*2*	*3*	*4*	*5*
43.01	A	6	1.000	1.067	0.978	1.019	1.001
43.03		4	1.000	1.065	0.984	1.016	1.007
43.08		4	1.000	1.071	0.981_5	1.015	1.009
		Average	1.000	1.068	0.981	1.017	1.006
43.04	B	7	1.000	1.009	1.003	0.988	1.012
43.06		5	1.000	1.013	1.010	0.982	1.015
43.09		4	1.000	1.008	1.009	0.980	1.017
		Average	1.000	1.010	1.007	0.983	1.015

[a] Reference cell.

TABLE 2

$\log(I^+_{Zn}T) = A + B/T$, IN ARBITRARY UNITS, AS A FUNCTION OF TEMPERATURE FOR VARIOUS COMPOSITIONS IN THE Al-Zn SYSTEM

Mol % zinc	*$\log(I^+_{Zn}T) = A + B/T$*	
	A	*B*
100	8.007 ± 0.021	-6398 ± 59
4.7	7.691 ± 0.055	-6488 ± 87
10.8	7.785 ± 0.053	-6461 ± 177
18.1	7.893 ± 0.072	-7507 ± 83
30.6	7.814 ± 0.048	-6406 ± 65
31.8	7.758 ± 0.051	-6303 ± 90
40.9	7.779 ± 0.039	-6342 ± 83
63.9	7.932 ± 0.067	-6381 ± 96
69.4	7.923 ± 0.049	-6369 ± 123

The Zn^+ ion intensities measured during the vaporization of the alloys are plotted as $\log [I_{Zn}^+ T]$ vs. $1/T$ in Fig. 1. The intensity values have been corrected by a calibration factor γ_i which accounts for the possible differences in the geometry of effusion holes and their non-perfect alignment during the rotation of the thermostating block. Values of the γ_i factors were determinated by loading, before each vaporization, the four crucibles with an amount of pure zinc and by recording the Zn^+ ion intensity corresponding to each crucible. The γ_i values are reported in Table 1. A summary of the equation constants obtained by a least square treatment of the experimental results is shown in Table 2. In all cases the errors associated to the constants are standard deviations.

THERMODYNAMIC CALCULATIONS AND CONCLUSIONS

The agreement found between the $\Delta H_T^\circ = 29.3 \pm 0.3$ kcal mol^{-1}, or $\Delta H_{298}^\circ = 29.8 \pm 0.3$ kcal mol^{-1} (where the reported error represents the standard deviation) associated to the vaporization of pure zinc obtained by a second-law treatment of our data and the selected value ($\Delta H_{298} = 31.17 \pm 0.10$ kcal mol^{-1}) reported by Hultgren[4], could be considered an indication of thermodynamic equilibrium conditions within the effusion cells.

The Zn activities in the alloys at different compositions can be calculated at a given temperature T, in the investigated temperature range from the ion intensity–temperature equation given in Table 2 using the relation:

$$a_x = \exp (A_x + B_x/T)/\exp (A_0 + B_0/T) \qquad (1)$$

where A_0, A_x, B_0 and B_x are the constants reported in Table 2, for pure zinc and the Zn in the alloy at a composition x, respectively. The points reported in Fig. 2 are the zinc activity values so evaluated at the average temperature of 660 K. According to the phase diagram[4], from 0.66 to 0.98 N_{Zn} we have considered the activity of Zn to be constant, owing to the existence of a gap of miscibility.

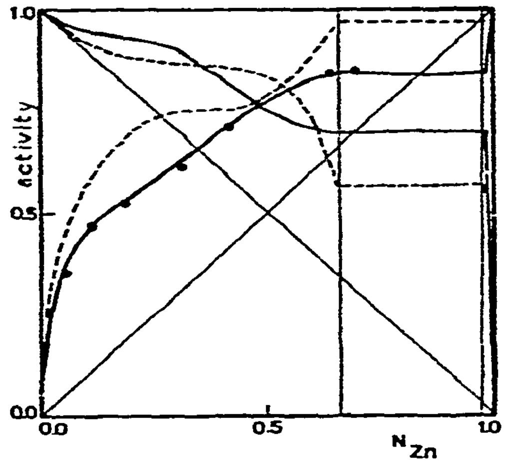
The activities of the component aluminum, at various compositions of the alloy, have been calculated in the usual way by a graphical integration of the Gibbs–Duhem equation. The values of $\alpha = \ln \gamma_{Zn}/N_{Al}^2$ necessary for this integration were evaluated for the investigated alloys by using the relation[8]:

$$\alpha = [\ln (A_x + B_x/T) - \ln (A_0 - B_0/T) - \ln N_{Zn}](1 - N_{Zn})^{-2} \qquad (2)$$

The activity values of both components so calculated at 660 K are given in Table 3 at 0.1-mol fraction intervals across the system and are reported in Fig. 2 (solid line). In Table 3 are also reported the free energies, the enthalpies and the entropies of mixing. The ΔH_{mix} are evaluated by graphic integration of the relation[8]:

$$\Delta H_{mix} = (1 - N_{Zn}) \int_{N_{Zn}=0}^{N_{Zn}=N_{Zn}} \frac{4.576(B_0 - B_x)}{(1 - N_{Zn})^2} \, dN_{Zn} \qquad (3)$$

The entropy values, ΔS_{mix} have been then calculated from the Gibbs–Helmholtz



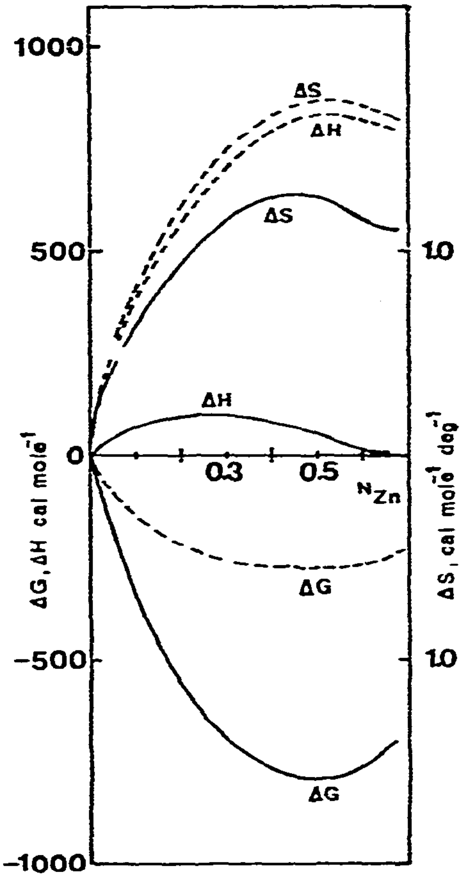


Fig. 2. Activity of zinc and aluminum in solid alloys vs. zinc atomic fraction at 660 K (sketched line are referred to the values selected by Hultgren).

Fig. 3. Excess quantities of mixing in the Al–Zn system at 660 K ———, this work; – – –, selected by Hultgren.

TABLE 3

THERMODYNAMIC ACTIVITIES AND FREE ENERGY, ENTHALPY, AND ENTROPY OF MIXING IN THE Al–Zn SYSTEM AT 660 K

N_{Zn}	a_{Zn}	a_{Al}	ΔG_{mix} (*cal mol*$^{-1}$)	ΔH_{mix} (*cal mol*$^{-1}$)	ΔS_{mix} (*cal mol*$^{-1}$ *K*$^{-1}$)
0.00	0.00	1.00	0.00	0.00	0.00
0.10	0.47	0.95	−367	62	0.65
0.20	0.55	0.93	−536	90	0.95
0.30	0.61	0.90	−671	92	1.16
0.40	0.70	0.83	−768	75	1.28
0.50	0.79	0.75	−790	46	1.27
0.60	0.84	0.70	−747	13	1.15
0.66*	0.85	0.68	−719	−2	1.10

* Phase boundary.

equation. A summary of the results is reported in Fig. 3. A comparison of one data with those selected by Hultgren[4] obtained from the aluminum thermodynamic data at 653 K (sketched line of Fig. 2) shows that our zinc activity values are not in agreement with those reported by Hultgren. In particular, they deviate in defect, especially for the alloys with high zinc content in the proximity of the miscibility gap. However, our activity values seem to be more reliable as they are based on direct measurements.

As regards the thermodynamic data of mixing, especially the values for ΔH_{mix} the uncertainty which could be attached to the derived values is rather high. This degree of uncertainty is, however, to be expected if one considers the limited temperature range covered by the measurements. Therefore, we feel that further experimental work is necessary for the establishment of ΔH_{mix} for the system Al–Zn using a more direct technique (e.g., calorimetry).

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