°C is still well within the liquid range.

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Zinc Activity Measurements in Thallium–Zinc Alloys by the Torsion–Effusion Technique

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Zinc activities in liquid Tl–Zn alloys were determined at 730 K from vapor-pressure measurements carried out by the torsion–effusion technique. The corresponding values for thallium were derived by the Gibbs–Duhem equation. Since the system shows a large miscibility gap at the operating temperature, constant activity values for both components in the alloy with variable composition were found in this range. A special procedure was used for the zinc measurements over the Tl-rich alloy out of the gap (0–18 atom % of zinc).

Activities of the components for Tl–Zn alloys are not well-known. Calorimetric data of the mixing process[1] and zinc activity data measured in two dilute solutions at 625 K by the Knudsen effusion method[2] and by a comparative vapor pressure method[3] at 1000 and 1100 K have been reported in literature. Apparently no other direct determination of activity is reported. Therefore, we thought it useful to carry out measurements of this parameter by means of a torsion–effusion technique.

Experimental Section

The principle of the technique and details of the apparatus have been described elsewhere.[4,5]

The relation between the pressure and the cell deflection is given by:

$$P = 2K\alpha/(a_1l_1f_1 + a_2l_2f_2)$$

where α is the torsion angle, K is the torsion constant of the tungsten wire (30 μm in diameter, 35 cm length) from which the cell is suspended, a_1 and a_2 are the areas of the two effusion holes, l_1 and l_2 are their respective perpendicular distance from the rotation axis, and f_1 and f_2 are the corresponding geometrical correction factors.[6] In this work cells similar to the one illustrated in Figure 1 were used. The cell constants are given in Table I. The temperature of the operating cell was measured by a calibrated chromel–alumel thermocouple placed inside an identical cell directly beneath the operating cell.

In order to check that thermodynamic equilibrium conditions existed in each of the operating cells, we measured the absolute vapor pressures of pure zinc and thallium. The corresponding heats of vaporization $\Delta H°_{298}$ obtained from second- and third-law treatments of the data (32.8 ± 0.9 and 30.9 ± 0.7 kcal mol^{-1} for zinc and 41.9 ± 1.5 and 42.2 ± 0.5 kcal mol^{-1} for thallium) were in good agreement within the experimental errors and with the values selected by Hultgren et al.[7]

Table I. Constants of the Used Cells

		cell A (graphite)	cell B (pirophyllite)	differential cells (pirophyllite)
orifice area, $\times 10^{-3}$ cm[a]	(1)	7.39 ± 0.05	7.90 ± 0.07	7.85_5 ± 0.05
	(2)	7.09 ± 0.05	8.70 ± 0.07	7.85 ± 0.05
moment arm, cm (±0.01)	(1)	0.85	0.84	0.85
	(2)	0.88	0.87	0.90
force correction factor[b]	(1)	0.464	0.558	0.521
	(2)	0.410	0.570	0.530

[a] Measured by photographic enlargement. [b] Calculated by the equation[6] $1/f = 0.0147(L/r)^2 + 0.3490(L/r) + 0.9982$, where r and L are the radius and the thickness of the effusion hole, respectively.

Three Tl–Zn alloy samples of different compositions within the miscibility gap,[8] and six thallium-rich samples outside of this range at the operating temperature 700–750 K were prepared by melting required quantities of high-purity elements under vacuum in a quartz tube. The samples were kept for several hours at about 1100 K and then quenched in a water bath. The composition and the homogeneity of the alloys were evaluated by polarographic analysis for both the constituents (Zn, Tl) by testing different portions of each sample. The error in the composition has been evaluated to be not larger than 0.1–0.2 atom % of zinc.

Particular care was taken in the preparation and in the filling of the thallium-rich samples in the assembly.

The study of this system was performed in two steps. In the first step measurements were made on pure zinc and on the three Tl–Zn alloys (35, 51, and 87 atom % of Zn) inside the miscibility gap.[8] In Table II the constants of the straight lines log α vs. $1/T$ derived by least-squares treatment of the experimental data are summarized for each sample investigated.

Only the points taken at temperatures higher than 690 K, where the two solutions are molten, were considered. One alloy (35 atom % of Zn) was also studied by using a particular cell (called "differential cell") similar to the one described in a previous article[9] in which one semicell can be rotated around its axis (see Figure 2). In the first part of the experiment two sets of measurements were carried out by using this cell with the two semicells loaded with pure zinc: in the first set the semicells were placed in the conventional way and the temperature dependence of $\alpha°$ was measured; in the second set a semicell was placed in the differential way (two orifices in the same direction) for calibration purpose. Over the entire calibration

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Table II. Torsion Angles as a Function of the Temperature for Tl-Zn Alloys

run	cell	sample (atom % of zinc)	temp range, K	no. of points	$\log = A - B/T$	
					A^a	B^a
A.01	A	51	705-765	13	10.79 ± 0.10	6407 ± 77
A.02	A	100	698-740	24	10.85 ± 0.12	6389 ± 21
A.03	A	35	700-772	14	10.82 ± 0.11	6446 ± 30
A.06	B	100	701-759	16	10.78 ± 0.09	6283 ± 29
A.07	B	87	703-758	19	10.70 ± 0.10	6309 ± 48
C.02	differential[b]	100	703-806	17	10.89 ± 0.16	6311 ± 59
C.03	differential[c]	35	705-798	18	9.79 ± 0.18	6297 ± 66

[a] The quoted errors are standard deviation. [b] The two semicells, both filled with pure zinc, are placed in conventional position. [c] The two semicells, filled with pure zinc and alloy (35 atom % of Zn), respectively, are placed in differential position (see text).

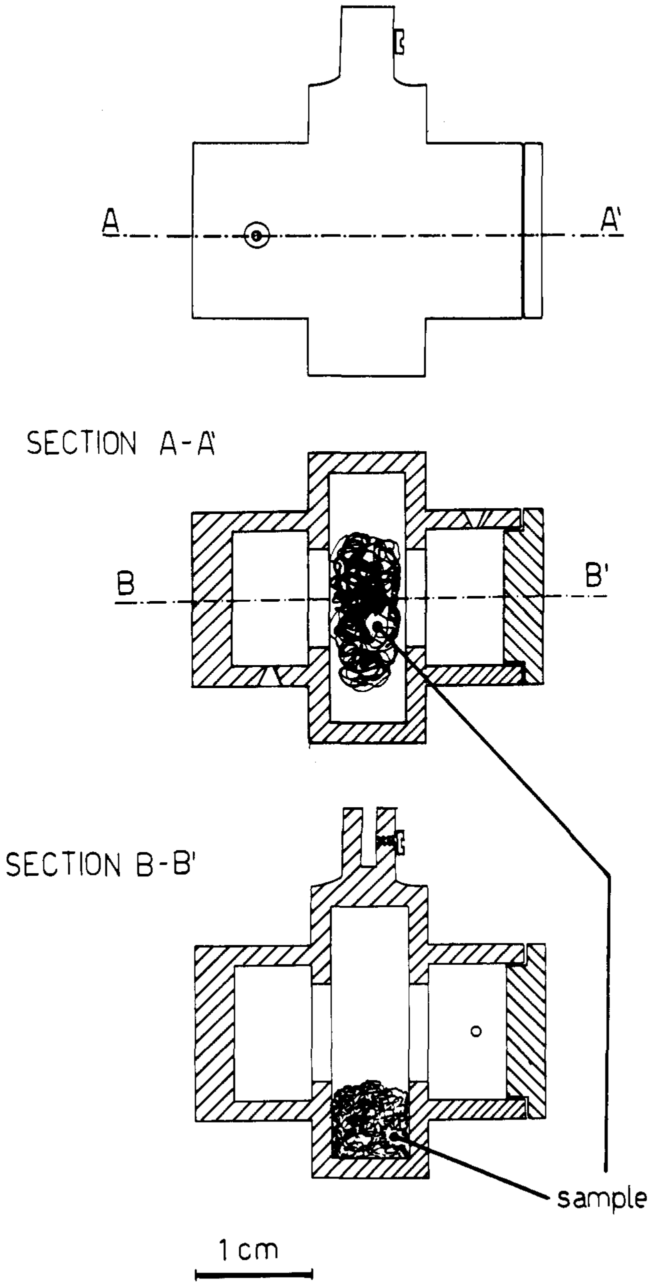

Figure 1. Schematic diagram of the torsion-effusion cell.

experiment a substancial absence of torsion angle up to 845 K showed that the force moments operating on the two semicells were practically equal. Subsequently the semicells were filled with the alloy sample and pure zinc and the differential rotation angles were measured in a temperature range where the high vapor pressure of zinc makes the conventional technique too sensitive.

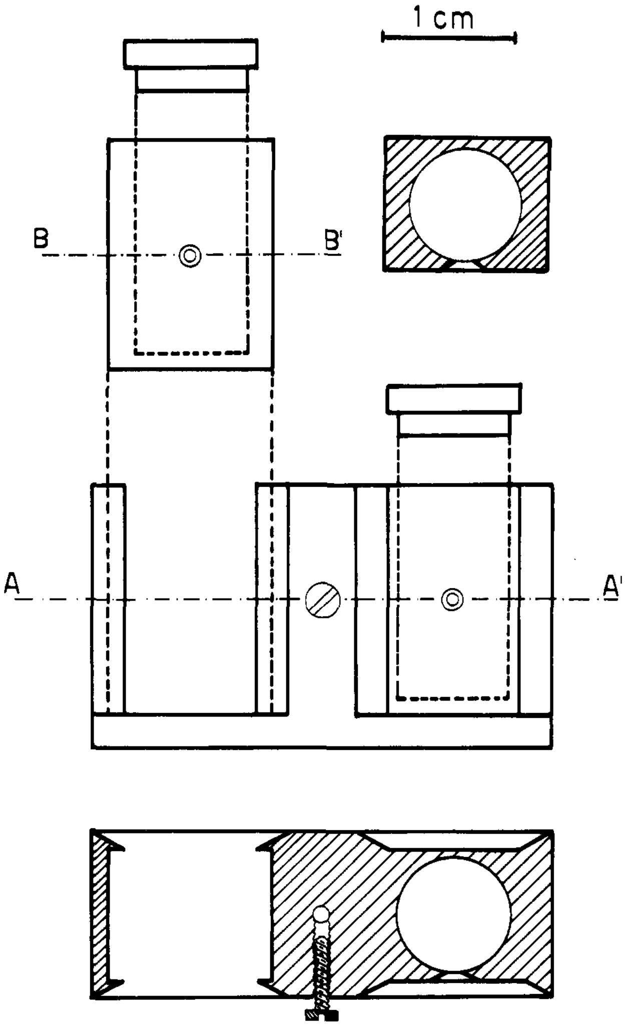

Figure 2. Schematic diagram of the "differential cell".

The experimental data treated in the usual way are reported in Table II.

The six alloys in the thallium-rich region were studied in the second part of the experiment. Since the conventional procedure leads to an appreciable variation of the compositions of the alloys because of zinc vaporization, zinc activity values for these alloys samples were determined by quantitative vaporization of this component from the alloy employing a procedure similar to that described previously.[9]

At the end of each experiment, carried out at constant temperature, the area obtained by plotting the deflection angles α vs. time is proportional to the amount of zinc evaporated according to the Knudsen equation.[10] A typical plot (run B.03) is reported in Figure 3. From this area, knowing the initial composition and the amount of the alloy, we derived the deflection angles corresponding to four prefixed compositions, 0.9, 3.1, 5.7, and 8.8 atom % of zinc.

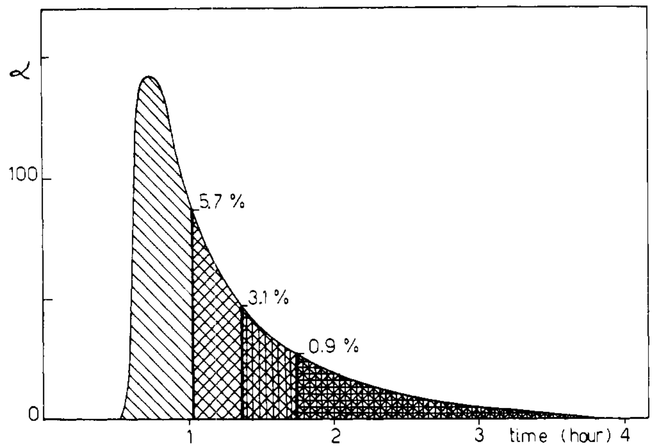

Figure 3. Plot of torsion angle vs. time determined during the zinc quantitative vaporization from the Tl-Zn alloy at 703 K (run B.03).

Table III. Zinc Vapor Pressure over Alloy Thallium-Rich Derived from Quantitative Vaporizations[a]

run	initial compn (at % of Zn)	cell[b]	T, K	P, atm × 10^4			
				8.8 (at % Zn)	5.7 (at % Zn)	3.1 (at % Zn)	0.9 (at % Zn)
B.01	11.5	A	694 ± 3	2.24	1.44	0.76	0.32
B.03	8.7	B	703 ± 2		1.74	0.93	0.54
B.04	7.3	A	717 ± 4		2.63	1.55	0.59
D.03	13.7	diff	704 ± 4	2.75	1.78	1.15	0.50
D.07	9.6	diff	728 ± 3		3.47	2.09	0.78
D.08	19.4	diff	730 ± 2	5.13	3.24	1.66	0.93

[a] The errors correspond at the maximum fluctuation of the temperature during the zinc vaporization. [b] diff = differential.

A self-calibration of the assembly was made at the end of the zinc vaporization run by heating the cell to higher temperature and measuring the torsion angle associated with the pure thallium vaporization. The average instrument constant derived in this way and that derived from the physical constants of the torsion-effusion apparatus are in substantial agreement, and this agreement showed also the reliability of the temperature measurements.

The zinc vapor pressure data at prefixed compositions are reported in Table III. The vaporization runs were performed at temperatures that were not too high in order to realize a sufficient α-time integration area to permit a reliable determination of the α values at the prefixed compositions.

Quantitative vaporizations were also carried out by employing the "differential cell" fitted with the two semicells loaded with pure zinc and alloy, respectively. In this case the experimental torsion angles correspond to the differences between the zinc fugacities of the pure element and the alloy during depletion of zinc from the sample. At the end of the zinc vaporization from the alloy, the torsion angle α° is due only to the vaporization of the pure zinc. The torsion angles corresponding to the vaporization of zinc from the alloy are derived as differences between α° and the experimental α values. A typical plot (run D.07) is reported in Figure 4. By heating the cell after the quantitative evaporation of zinc from the alloy, we made a self-calibration using the experimental torsion angles caused by the evaporation of the pure zinc and the corresponding zinc vapor pressure values.[7] The average between this calibration value and that derived from physical constants was used for the calculation of the absolute vapor pressures of zinc over the prefixed compositions. The pressure values so determined are also reported in Table III. The zinc vapor pressures over thallium-rich alloys determined with quantitative vaporization are summarized in Figure 5.

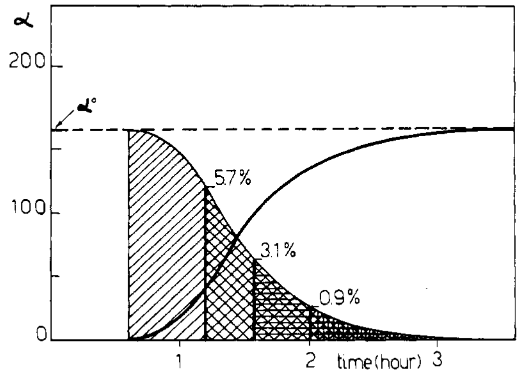

Figure 4. Plot of the differential torsion angle determined during the zinc quantitative vaporization from the Tl-Zn alloy at 728 K (run D.07)—experimental α curve (see text).

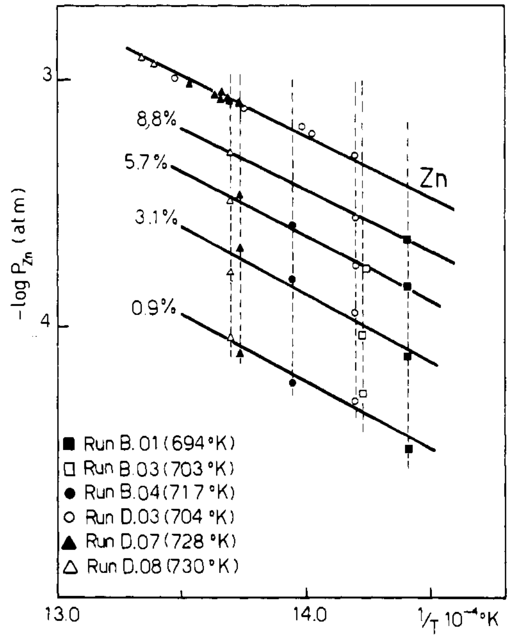

Figure 5. Plot of log α vs. $1/T$ for the alloys at prefixed composition measured during the quantitative vaporization.

Table IV. Activities of the Components of Liquid Zinc-Thallium Alloys at 730 K

atom % of Zn	a_{Zn}	a_{Tl}	$-\Delta G_{mix}$, cal/mol
2	0.15	0.98	152
4	0.32	0.96	168
6	0.44	0.94	213
8	0.57	0.93	222
10	0.68	0.91	245
12	0.78	0.90	243
13	0.80	0.90	240
20	0.80	0.90	256
50	0.80	0.90	326
90	0.80	0.90	420
99.6	0.80	0.90	442

Results and Discussion

The zinc activities in Tl-Zn alloys were calculated at the average temperature of 730 K by using the α-temperature equations reported in Table IV through the relation

$$a_{Zn} = \exp(A_x - B_x/T)/\exp(A^\circ - B^\circ/T)$$

where A_x, B_x, A°, and B° are the constants of the α-temperature equations corresponding to the alloy and the pure zinc determined by using the same cell. The values are plotted in Figure 6.

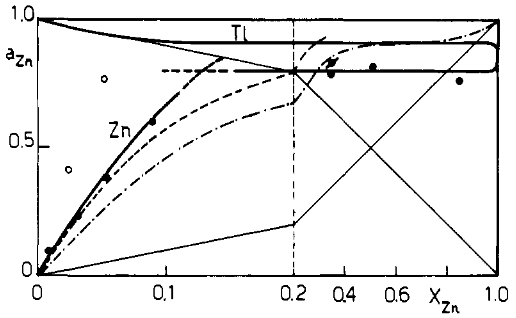

Figure 6. Thallium and zinc activity values in liquid alloy at 730 K: ● our points (solid line) (● measured in run C.03 with the differential cell); O, Niwa[2] (625 K); (---) and (- • • •) Hagiwara[3] at 1000 and 1100 K, respectively.

Table V. Zinc Activities in Thallium-Rich Alloys Measured from the Quantitative Vaporizations

atom % of Zn	P-T eq[a] (730 K)	run D.03 (740 K)	run D.07 (728 K)	run D.08 (730 K)	av
0.9	0.101	0.105	0.098	0.109	0.10
3.1	0.235	0.234	0.251	0.215	0.23
5.7	0.410	0.363	0.426	0.393	0.39
8.8	0.605	0.575		0.616	0.60

[a] Activity values calculated from the pressure–temperature equations derived from the quantitative pressure.

The zinc activity in the 35 atom % of zinc alloy was also measured by use of the differential cell and calculated at 730 K by the equation

$$a_{Zn} = (\alpha^\circ - 2\Delta\alpha)/\alpha^\circ = 1 - 2[\exp(A - B/T)]/\exp(A^\circ - B^\circ/T)$$

where the constants are reported in Table II. The value obtained with this procedure and reported in Figure 6 shows good agreement with that derived with the conventional cell.

The zinc activities in thallium-rich samples at 730 K were calculated at the prefixed compositions 0.9, 3.1, 5.7, and 8.8 atom % of zinc. These values were evaluated from the zinc pressure values derived by the least-squares treatment of all the quantitative vaporization experiments and the values reported by Hultgren[7] for the pure zinc.

The activities so determined are reported in Table V. In the same table the activity values derived from the relation $a = 1 - \alpha/\alpha^\circ$ (where α and α° are the experimental values measured at the prefixed compositions and at the end of each experiment carried out by use of the differential cell) are also reported. These values are in agreement with those derived at 730 K from the pressure–temperature equations, and their averages are reported in Figure 6. For comparison the literature data are reported in the same figure. The two zinc activities measured by Niwa et al.[2] at 625 K during the study of a ternary solution (Sn–Zn–Tl) seem to be too high, while the data reported by Hagiwara et al.[3] at 1000 and 1100 K are in better agreement with ours in particular because they show a similar trend in the activity with the variation of the alloy composition.

From the intercept of the activity curves determined inside and outside the miscibility gap the concentration of 13 ± 1 atom % of zinc as miscibility point at 730 K is derived in agreement with the value ~14 reported by Hansen.[8] The corresponding activity curve for thallium was calculated by means of the Gibbs–Duhem equation[11] and the a_i values for both components against the mole fraction of zinc are reported in Table IV.

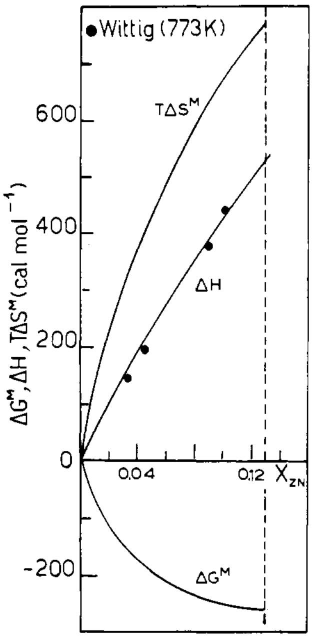

Figure 7. Mixing thermodynamic quantities of thallium-rich Zn–Tl liquid alloys at 730 K.

It is apparent from Figure 6 that the activities of both components show a large positive deviation from Raoult's law. The nonideal behavior of the alloy has to be expected considering the wide miscibility gap in the liquid field. The present data are not sufficiently accurate to permit an evaluation of the heats of mixing from the temperature coefficients of the activities since the associated errors are greater than the values. However, it seemed interesting to derive values of the mixing entropy for alloys of the thallium-rich region by using the calorimetric heat of formation at 773 K reported by Witting.[1]

The mixing entropies so determined are reported as a function of N_{Zn} in Figure 7 together with the mixing free energy and Witting's data. Our ΔS_{mix} values show a positive behavior in agreement with the findings of Hagiwara et al.[3]

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