A THERMODYNAMICAL STUDY OF THE LIQUID TERNARY SYSTEM ZINC-CADMIUM-TIN

(III) THE SYSTEM ZINC-CADMIUM-TIN

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(Received October 30, 1953)

Since Darken[1] has clarified recently a thermodynamical treatment of ternary systems, Elliott and Chipman,[2] and Mellgren[3] have published thermodynamic studies of some liquid ternary alloys.

In the following, the author describes his procedure of electromochemical study on the Zn-Cd-Sn system, of which compositions are represented by straight lines crossing the ternary field from the pure component of Zinc to the point having a constant ratio of Cadmium to Tin at the binary Cd-Sn system.

The thermodynamical treatment for ternary system recently developed by Darken for computation of partial molal quantities is based on the following equation:

$$\Delta\overline{X}_{Zn} = \Delta X + (1 - N_{Zn})[\partial X/\partial N_{Zn}]N_{Sn}/N_{Cd} \tag{1}$$

where ΔX represents any extensive property; free energy and entropy etc.

Dividing through by $(1 - N_{Zn})^2$ and integrating the equation (1) along the line of constant N_{Sn}/N_{Cd} from $N = 0$ to $N = N_{Zn}$,

$$\Delta X^E = (1 - N_{Zn})\left[\int_0^{N_{Zn}} \frac{\Delta X^E_{Zn}}{(1-N_{Zn})^2}\, dN_{Zn} + \Delta X^E_{\text{binary Cd-Sn}}\right]_{N_{Sn}/N_{Cd}}. \tag{2}$$

Integrating the equation (1) from $N = 1$ to N_{Zn}

$$\Delta X^E = (1 - N_{Zn})\left[\int_1^{N_{Zn}} \frac{\Delta X^E_{Zn}}{(1-N_{Zn})^2}\, dN_{Zn}\right]_{N_{Sn}/N_{Cd}} + N_{Sn}[\Delta X^E_{Sn}]_{N_{Zn}=1} + N_{Cd}[\Delta X^E_{Cd}]_{N_{Zn}=1}. \tag{3}$$

The bracketed quantities of the last two terms refer to infinitely dilute solutions in component zinc of the systems Zn-Sn and Zn-Cd. The standard state is chosen as a pure component in each case (i.e. $\Delta\overline{F}^E_i = 0$ at $N_i = 1$).

The two constants $(\Delta X^E_{Sn})_{N_{Zn}=1}$ and $(\Delta X^E_{Cd})_{N_{Zn}=1}$ are determinable from measurements on the two binary systems Zn-Cd and Zn-Sn, respectively.

Thus ΔX^E may be evaluated at all compositions provided $\Delta\overline{X}^E_2$ is known at all compositions.

Since an attainable accuracy of values $\frac{\Delta X^E_{Zn}}{(1-N_{Zn})^2}$ decreases with increasing N_{Zn}, the equation (2) integrated with $N_{Zn} = 0$ as the lower limit was adopted in calculation to obtain the reliable data for ΔF^E. The values of ΔF^E at the lower limit

were derived from measurements on the Cd-Sn binary system reported in a previous paper.[4]

Experiment

Two master binary alloys with the atomic ratio of Cadmium to Tin of 2:1 and 1:2 were prepared by melting the mixtures of the two components having the known composition under an eutectic cover of potassium and lithium chlorides at 600° C in hard glass tube. To avoid an uncertainties associated with segregation, the alloy used as a sample was taken from every part of the solidified block which was quenched from the molten alloy.

The experimental procedure and equipment were the same as described in the previous report.[5]

Experimental Results

Nine successful runs were performed on the master alloys with the ratio of Cadmium to Tin of 2:1 and eight runs on those of 1:2.

Experimental results were recorded in Table 1 and 2.

A relationship between e.m.f. and temperature was almost linear as those in the binary systems.

TABLE 1. Experimental Results for the Ternary System Zn-Cd-Sn ($N_{Sn}/N_{Cd}=2$)

$N_{Zn}=0.0908$			$N_{Zn}=0.1954$			$N_{Zn}=0.3172$		
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$
539	62.80		582	42.16		560	26.13	
523	60.87		550	39.47		528	24.02	
490	56.23	134.3	505	35.95	79.4	490	21.76	61.8
446	49.83		476	33.62		459	19.98	
			456	31.98		429	17.86	
$N_{Zn}=0.4675$			$N_{Zn}=0.5941$			$N_{Zn}=0.7021$		
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$
571	16.28		559	10.69		584	8.11	
547	15.18		541	10.13		565	7.69	
512	13.86	36.4	495	8.88	29.1	530	7.00	20.5
471	12.53		479	8.38		507	6.52	
446	11.56		450	7.51		450	5.43	
$N_{Zn}=0.7957$			$N_{Zn}=0.8264$			$N_{Zn}=0.8989$		
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$
582	5.83		498	3.33		549	2.82	
560	5.55		489	3.27		512	2.59	
545	5.38	12.6	450	3.11	5.4	504	2.41	6.0
498	4.79		440	3.02		481	2.29	
472	4.48		430	2 97		444	2.03	

TABLE 2. Experimental Results for the Ternary System Zn-Cd-Sn ($N_{Sn}/N_{Cd}=1/2$)

$N_{Zn}=0.0721$			$N_{Zn}=0.1522$			$N_{Zn}=0.2358$		
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$
547	68.20		546	42.20		575	32.73	
509	63.28		505	38.58		533	29.68	
472	58.50	129.0	487	36.78	88.0	511	28.08	71.8
466	57.78		463	34.92		495	26.95	
457	56.52		442	33.02		465	24.78	
$N_{Zn}=0.3462$			$N_{Zn}=0.4585$			$N_{Zn}=0.6699$		
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$
586	22.82		571	16.13		566	7.82	
566	21.89		538	14.83		538	7.49	
512	19.18	49.1	497	13.32	37.4	486	6.84	13.3
467	16.96		479	12.66		469	6.66	
456	16.46		456	11.73				
$N_{Zn}=0.7759$			$N_{Zn}=0.8828$					
T °C	E mV	$\frac{dE}{dT}\times10^3$	T °C	E mV	$\frac{dE}{dT}\times10^3$			
568	5.78		545	3.55				
546	5.54		531	3.37				
508	5.15	10.3	513	3.25	6.0			
478	4.82		467	3.04				
447	4.48		447	2.90				

Treatment of the experimental results and determination of temperature gradients of the electromotive force for partial molal quantity of Zinc were carried out as mentioned above. It was assumed that the effect of segregation was negligible by reason of that activity lines were obtained smoothly. For purpose of graphical calculation of molal quantities, it is convenient to plot such functions as $\Delta F^E_{Zn}/(1-N_{Zn})^2$ and $\Delta \bar{S}^E_{Zn}/(1-N_{Zn})^2$ against N_{Zn} as shown in Fig. 1 and 2. The curve in the vicinity of $N_{Zn}=1$ was got by extrapolating smoothly from the range in which the experimental precison is sufficient, i.e., discordant points near $N_{Zn}=1$ should be disregarded in drawing of the curve, since, although the function $\bar{F}^E_2/(1-N_2)^2$ is probably finite at all compositions as discussed in the paper by Darken, the precise evaluation thereof in the vicinity of $N_2=1$ requires a very high degree of experimental accuracy.

The values of ΔF^E and ΔS^E were obtained with aid of a graphical integration, compiled in Table 3 and 4, and plotted in Fig. 3 and 4.

It was observed that at the point of which excess entropy equals to zero, the free energy lines at 500° C were crossing with those at 600° C. Through the equation $\Delta F^E=\Delta H-T\Delta S^E$, we can also immediately calculate the heats of mixing ΔH.

Those data will be found in Table 3 and 4, and Fig. 5.

Let us focus now our attention on a feature of a_{Zn} in the ternary system Zn-Cd-Sn.

TABLE 3. Thermodynamic Functions for the Ternary System Zn-Cd-Sn ($N_{Cd}/N_{Sn}=1/2$)

N_{Zn}	a_{Zn}		ΔF^E (cal)		$\Delta\bar{S}_{Zn}$	ΔS^E	ΔH
	500°C	600°C	500°C	600°C	(cal/°C)	(cal/°C)	(cal)
0.1	0.189	0.167	303	264	5.60	0.367	587
0.2	0.350	0.320	374	328	3.80	0.413	693
0.3	0.490	0.450	426	380	2.90	0.429	758
0.4	0.606	0.560	463	419	2.27	0.437	801
0.5	0.695	0.656	480	438	1.74	0.431	813
0.6	0.770	0.734	469	432	1.28	0.406	783
0.7	0.822	0.801	429	395	0.90	0.361	708
0.8	0.870	0.856	350	321	0.58	0.296	579
0.9	0.925	0.920	218	175	0.26	0.191	366

TABLE 4. Thermodynamic Functions for the Ternary System Zn-Cd-Sn ($N_{Cd}/N_{Sn}=2$)

N_{Zn}	a_{Zn}		ΔF^E (cal)		$\Delta\bar{S}_{Zn}$	ΔS^E	ΔH
	500°C	600°C	500°C	600°C	(cal/°C)	(cal/°C)	(cal)
0.1	0.213	0.185	328	284	5.00	0.380	622
0.2	0.390	0.354	412	365	3.46	0.374	701
0.3	0.521	0.483	475	427	2.57	0.354	749
0.4	0.620	0.584	514	466	1.97	0.326	766
0.5	0.696	0.667	526	481	1.50	0.294	753
0.6	0.769	0.733	508	469	1.10	0.255	705
0.7	0.820	0.802	459	433	0.77	0.209	621
0.8	0.865	0.860	366	352	0.48	0.157	487
0.9	0.920	0.918	215	208	0.22	0.089	284

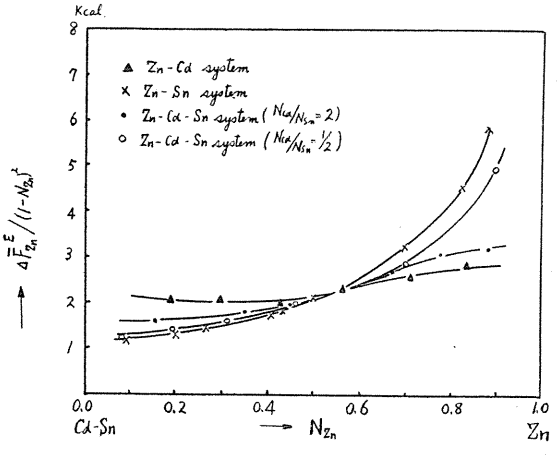

FIG. 1. Excess free energy function of zinc at 500° C.

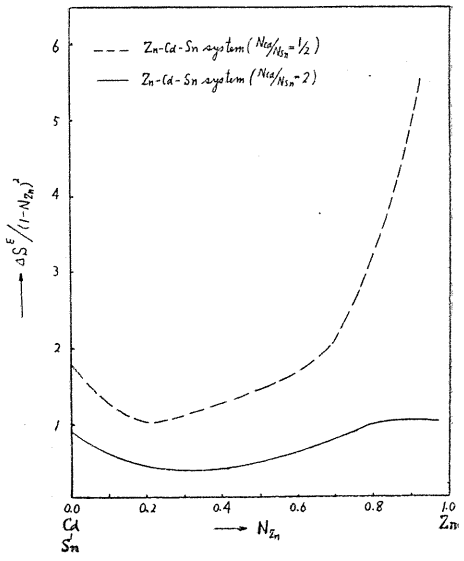

FIG. 2. Excess entropy function of zinc at 500° C. $\Delta S^E/(1-N_{Zn})^2$ calculated from values on a line drawn smoothly through experimental $\Delta\bar{S}_{Zn}$ against N_{Zn}.

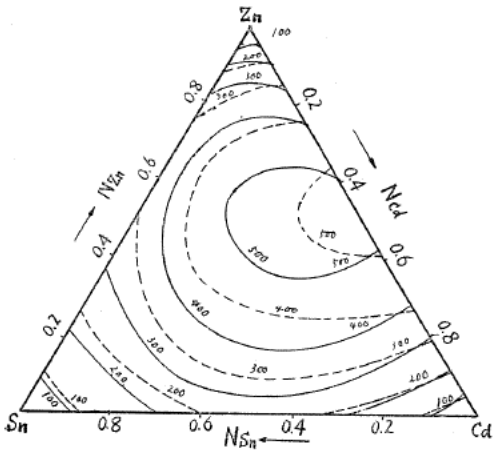

FIG. 3. Excess molal free energy surface (ΔF^E) at 500° and 600° C. ——: 500° C, ----: 600° C.

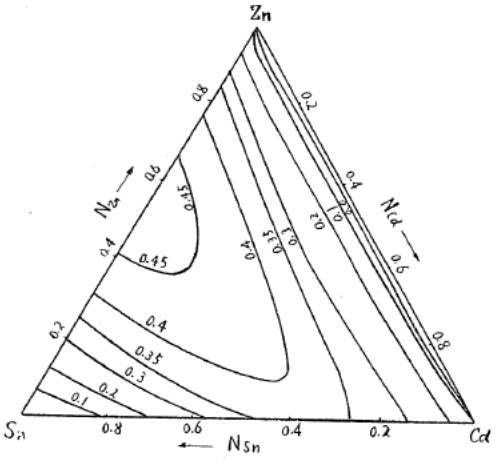

FIG. 4. Excess molal entropy surface (ΔS^E).

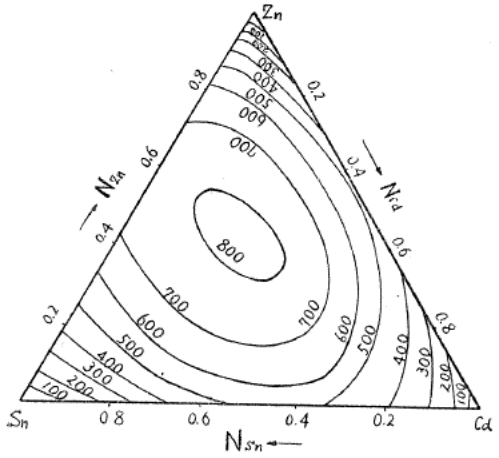

FIG. 5. Molal heat of mixing surface (ΔH).

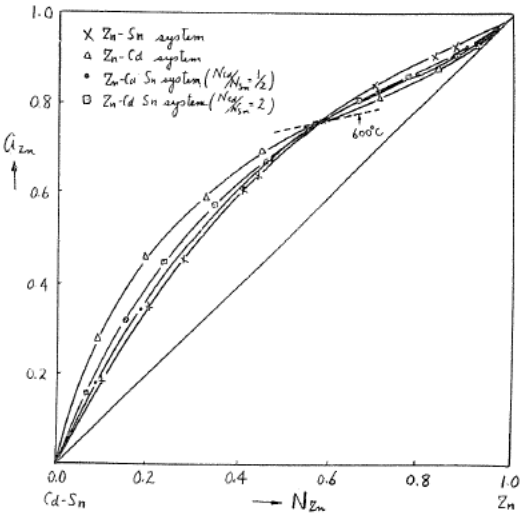

FIG. 6. Activity of zinc in the ternary field at 500° C. ---- locus of intersected point for various temperatures.

As shown in Fig. 6, it is interesting that each line of a_{Zn} in the ternary system at $N_{Zn} = 0.57$ intersects at one point.

A locus of the intercepting point, obtained by extrapolating the experimental data to temperatures above and below 500° C, was indicated with dotted line. Halla and Herdy[6] have pointed out also the same phenomenon for the ternary system Pb-Na-Hg as in this investigation.

In the case of a_{Sn} and a_{Cd}, activity curves are crossing complicatedly as shown in Fig. 7 and 8. The relations between the molal free energy at N_{Zn}

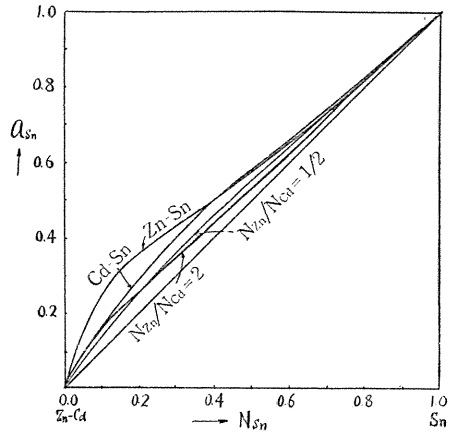

Fig. 7. Activity of Tin in the ternary field at 500° C.

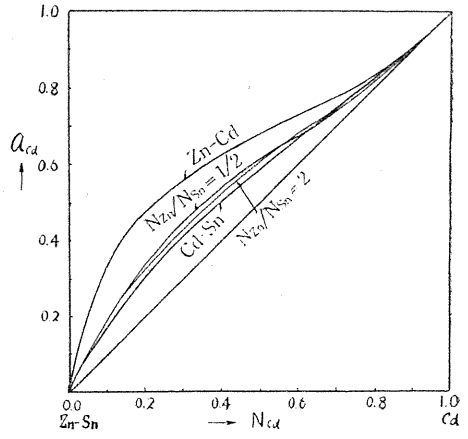

FIG. 8. Activity of Cadmium in the ternary field at 500° C.

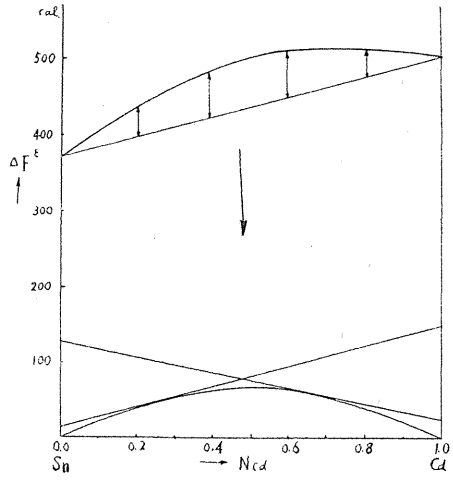

FIG. 9. Diagrammatic representation for calculation of a_{Cd} and a_{Sn} in $N_{Zn}=0.57$.

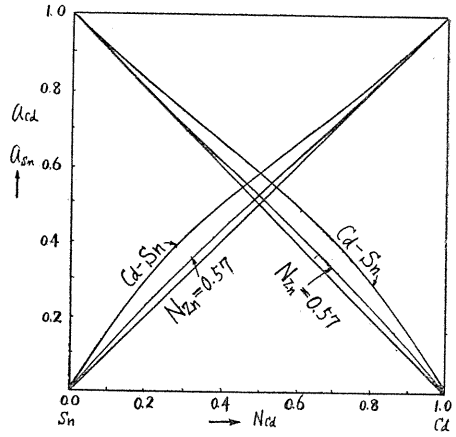

FIG. 10. Activities of Tin and Cadmium on $N_{Zn}=0.57$ line in the ternary field at 500° C.

= constant and N_{Cd} were plotted in the upper portion of Fig. 9 and the distances indicated by arrows were replotted in the lower portion of the same figure.

The tangent to these lines at any point cuts two ordinates of $N_{Cd}=0$ and $N_{Sn}=0$ at the points corresponding to the values of the partial free energies of Cadmium and Tin respectively referred to each binary solution of $N_{Zn}=$ constant as the standard state. From this cutting points, a_{Sn} and a_{Cd} for any composition were obtained and shown in Fig. 10.

a_{Cd} and a_{Sn} in Fig. 7 and 8 were deduced from the similar one with the equation (1) by the same slope intercept method as used above. The values of the right-hand side expressions in the equation (1) may be obtained from the right-

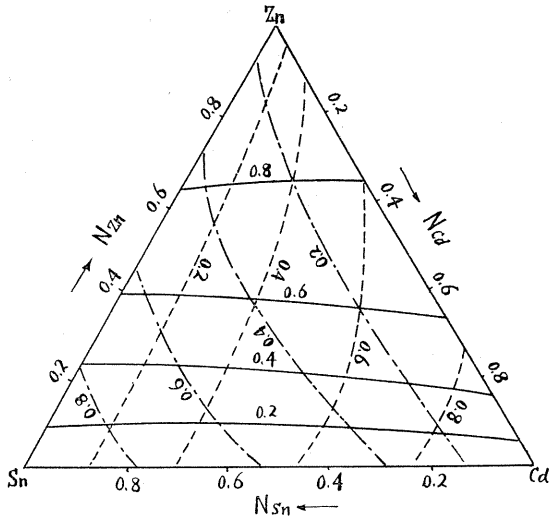

FIG. 11. Isoactivity line at 500° C. Activity lines: —— zinc; —·— Tin; ---- cadmium.

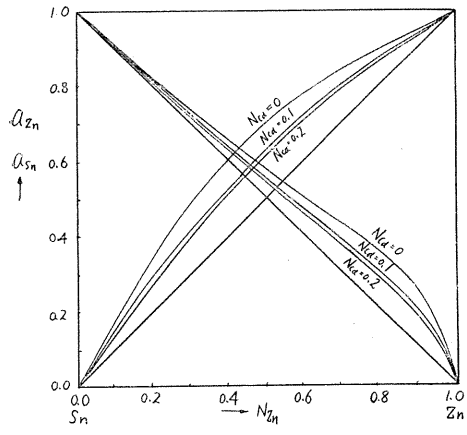

FIG. 12. Effect of cadmium on activities of zinc and Tin.

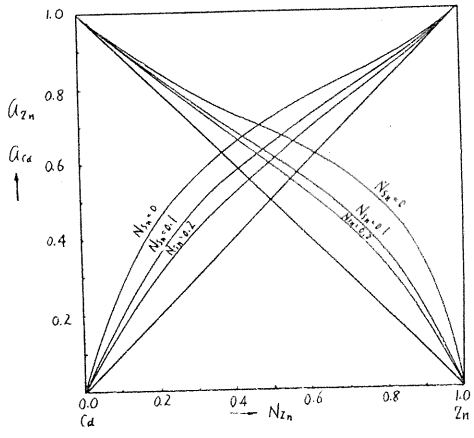

FIG. 13. Effect of Tin on activities of zinc and cadmium.

hand ordinate intercepts of tangents on the curves of ΔF^E versus N_{Cd} and those of ΔF^E versus N_{Sn} for the constant ratio of N_{Zn}/N_{Sn} and N_{Zn}/N_{Cd}, respectively.

Activity surfaces for the three components of the ternary system were depicted by isoactivity line in Fig. 11.

Effects of Cadmium and Tin on activities of the other components in the system Zn-Sn-Cd were respectively obtained by the slope intercept method mentioned in Fig. 9. As shown in Fig. 12 and 13, Tin has almost the same negative effect as Cadmium on the activities of the other components in the ternary system.

The surfaces of excess molal free energies ΔF^E and excess molal heats of mixing ΔH were all positive for the system investigated.

It was also found that all the surfaces of excess molal quantities for the ternary system Zn-Cd-Sn incline smoothly from one side of the ternary field to the other.

Summary

The thermodynamic properties of the liquid ternary system Zinc-Cadmium-Tin were investigated by the electromotive force method. It was shown that the thermodynamic quantity surfaces inclines smoothly from the one side of the ternary field to the other and each curve of a_{Zn} for the binary and the pseudo-binary systems intersects at one point.

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