

A THERMODYNAMICAL STUDY OF THE LIQUID
TERNARY SYSTEM ZINC-CADMIUM-TIN (II)
THE SYSTEMS ZINC-CADMIUM AND ZINC-TIN

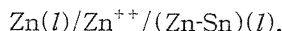
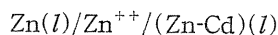
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In the following, the same electromotive force method as used in a previous investigation¹⁾ was adopted to obtain informations for free energies, heats of mixing and entropies of the binary solutions of zinc-cadmium and Zinc-Tin.

For the two systems, reversible galvanic cells take the form

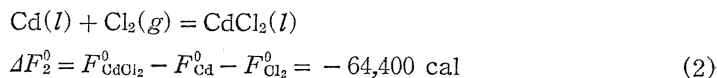
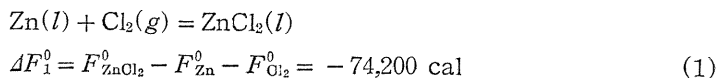


In the experimental operations, the following troubles will be generally expected; a formation of pyrosols in the electrolyte, reactions between metal and metallic chloride, hydrolysis of electrolyte, absorption²⁾ of one of constituents into the alloy at the alloy-electrolyte interface, and a liquid junction potential in the Tungsten-metal and metal-electrolyte interfaces.

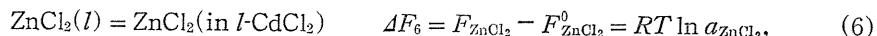
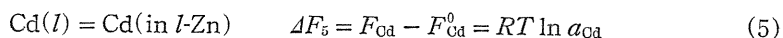
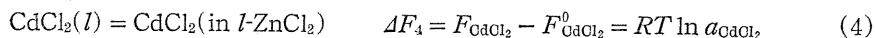
It has been reported that solubility of zinc in zinc chloride at 500°C is of the order of 9×10^{-4} g atom/mol.³⁾ Since, in the present case, mole fraction of zinc chloride in the electrolyte are small, the effect caused by dissolution of zinc in zinc chloride is negligible.

It will be seen that the absorption at the interface would have practically no effect on the composition of the alloy as shown in the system Cu-S.⁴⁾

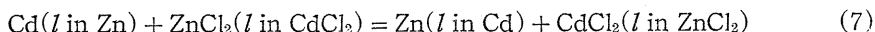
According to thermodynamical calculations⁵⁾ at 500°C,



in which F^0 represents the standard free energy.



where a and F denotes the activity and the molal free energy of the respective substances, and R denotes the gas constant. In the reaction



the equilibrium condition at constant temperature and pressure is defined by the equation:

$$\Delta F = F_{\text{Zn}} + F_{\text{CdCl}_2} - F_{\text{Cd}} - F_{\text{ZnCl}_2} = 0. \quad (8)$$

From the equations (3), (4), (5) and (6) at equilibrium state

$$\Delta F^0 = F_{\text{Zn}}^0 + F_{\text{CdCl}_2}^0 - F_{\text{Cd}}^0 - F_{\text{ZnCl}_2}^0 = -RT \ln \frac{a_{\text{Zn}} \cdot a_{\text{CdCl}_2}}{a_{\text{Cd}} \cdot a_{\text{ZnCl}_2}}. \quad (9)$$

By subtracting (1) from (2)

$$\Delta F^0 = -RT \ln K_1 = -RT \ln \frac{a_{\text{Zn}} \cdot a_{\text{CdCl}_2}}{a_{\text{Cd}} \cdot a_{\text{ZnCl}_2}} = 9,800 \text{ cal} \quad (10)$$

where K_1 is the equilibrium constant of the reaction mentioned above. Therefore, we obtain

$$K_1 = \frac{a_{\text{Zn}} \cdot a_{\text{CdCl}_2}}{a_{\text{Cd}} \cdot a_{\text{ZnCl}_2}} = 1.69 \times 10^{-3}. \quad (11)$$

According to Jellinek and Siewers's experimental data⁶⁾ at 500°C,

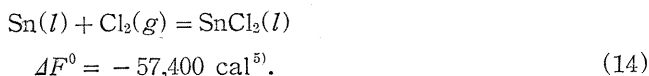
$$K_1' = \frac{N_{\text{Zn}} \cdot N_{\text{CdCl}_2}}{N_{\text{Cd}} \cdot N_{\text{ZnCl}_2}} = 2.848 \times 10^{-3}. \quad (12)$$

Where K_1' is average equilibrium value for systems containing above 80 weight per cent of cadmium and below 17 weight per cent of zinc, and N is weight per cent of the respective substances. It is probable from the following considerations that activity of LiCl-ZnCl₂ system would small positive, from heat of fusion of ZnCl₂ and activity of LiCl-systems, and yet activity of ZnCl₂ in the electrolyte would negative because of negative deviation of KCl-systems.

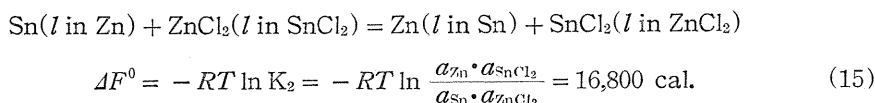
However, if $a_{\text{Zn}} = a_{\text{Cd}}$ and $a_{\text{ZnCl}_2} = 0.08$, we obtain from the equation (11)

$$a_{\text{CdCl}_2} = 1.35 \times 10^{-4}. \quad (13)$$

Similarly,



From the equations (1) and (14)



Therefore,

$$K_2 = \frac{a_{\text{Zn}} \cdot a_{\text{SnCl}_2}}{a_{\text{Sn}} \cdot a_{\text{ZnCl}_2}} = 1.77 \times 10^{-5}. \quad (16)$$

If $a_{\text{Zn}} = a_{\text{Sn}}$ and $a_{\text{ZnCl}_2} = 0.08$, we obtain

$$a_{\text{SnCl}_2} = 1.42 \times 10^{-6}. \quad (17)$$

It may be understood from these thermodynamic calculations and the experimental

values, that the amount of CdCl_2 and SnCl_2 which can exist in the chloride phase is generally very small.

Let us consider on a feature of binary chloride mixtures by calculating B from solubility curves of phase diagram⁷⁾ and heat of fusion⁸⁾ using the following relation

$$RT \ln \frac{a_1}{N_1} = T \cdot \frac{\Delta H_m}{T_m} - \Delta H_m - RT \ln N_1 = BN_2^2, \quad (18)$$

where N_1 , a_1 , ΔH_m and T_m denotes content on liquidus line, activity referred to undercooling liquid chloride as standard state, heat of fusion and melting point of component 1, respectively, and B is constant.

1) MgCl_2 -systems show a tendency of regular solution, KCl - and NaCl -systems show comparatively it and other systems show not well it. KCl - and NaCl -systems show negative deviation from ideality regardless of evidence of compound formation in the solid state.

2) Activity deviations of the chloride systems of the alkali metal are approximately proportional to value of heat of fusion of other component, but other systems show not this regulation necessarily.

3) Degree of controlling of those features are also corresponding to above mentioned special character (strength of tendency to regular and of regulation of activity deviation) of one component in two.

It is supposed that the electrolyte used in this experiment is nearly regular solution from the above considerations.

Experiment

The electromotive force measurements were carried out in H-cells of a type shown in Fig. 1.

Leads were tungsten wires sealed in Pyro capillaries.

The electrolyte was composed from the fused eutectic mixture of KCl and LiCl to which about 8 weight per cent of zinc chloride was added.

An average weight of each alloy and pure metal used as electrodes was about 5 g.

To prevent the hydrolysis in the electrolyte during this determination, ammonium chloride was added to the chloride solution with a small quantity of zinc metal in a hard glass test tube, and then the clear molten solution obtained was used as the electrolyte.

The actual procedure was analogous to that in the case of Cd-Sn sys-

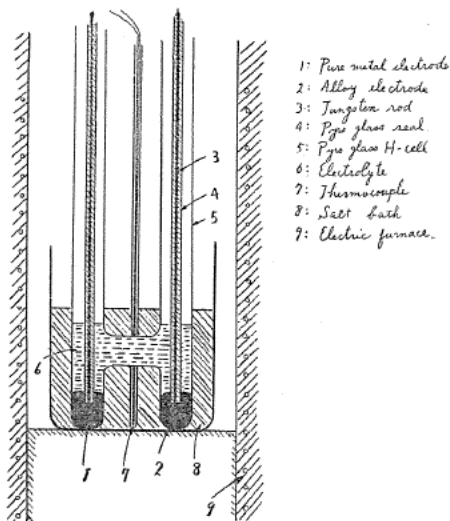


FIG. 1. Cell for e.m.f. measurements.

tem in the previous paper.

In a period of 24 to 30 hours, some independent measurements with regard to temperature and electromotive force were carried out. The electromotive force was reproducible within the limit of 0.05 millivolt.

After each run, the cell was destroyed. Weight of each alloy sample was determined and compared to the original weight. 0.4 weight per cent of the original weight was lost. It seemed in this measurement that the irreversible effect by the liquid junction introduces no error.

Experimental Results

Experimental results for the various runs were shown in Table 1 and 2. The relationship between e.m.f. and temperature was almost exactly linear in the measurement range of temperature.

This implies that the corresponding heats of mixing are independent of the temperature.

From these data, the activities for each component of the alloy were calculated and plotted versus mole fraction of zinc in Fig. 2 and 3. The activity curves in the two systems studied show relatively large departure from ideality.

TABLE 1. Experimental Results for the System Zn-Sn

$N_{Zn}=0.0993$			$N_{Zn}=0.2033$			$N_{Zn}=0.2799$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
577	66.63	133.6	571	41.88	94.5	523	27.80	76.8
542	61.85		547	39.59		513	27.00	
500	56.27		518	36.90		503	26.21	
482	53.96		484	33.65		495	25.55	
458	50.79		452	30.67		444	21.60	
$N_{Zn}=0.4059$			$N_{Zn}=0.4361$			$N_{Zn}=0.5827$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
520	17.70	56.5	515	16.04	50.9	533	10.13	37.3
505	16.85		503	15.37		527	9.93	
495	16.28		495	14.87		505	9.18	
488	15.83		487	14.41		476	7.95	
446	13.57		476	13.90		451	7.05	
$N_{Zn}=0.7023$			$N_{Zn}=0.8260$			$N_{Zn}=0.8745$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
541	6.38	19.5	524	3.63	11.4	525	2.72	8.2
504	5.61		514	3.50		495	2.41	
479	5.12		503	3.33		479	2.31	
466	4.90		476	3.06		456	2.06	
434	4.24		453	2.77				

TABLE 2. Experimental Results for the System Zn-Cd

$N_{Zn}=0.0896$			$N_{Zn}=0.1943$			$N_{Zn}=0.3250$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
530	44.53	99.4	562	30.59	71.3	579	22.10	52.6
519	44.47		526	27.88		562	21.20	
492	41.84		516	27.05		527	19.23	
470	39.61		486	25.18		479	16.78	
457	38.34		440	21.94		456	15.58	
$N_{Zn}=0.4415$			$N_{Zn}=0.5670$			$N_{Zn}=0.7097$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
572	14.58	30.0	584	10.91	20.5	568	7.58	13.4
550	13.82		560	10.41		540	7.18	
525	13.14		520	9.64		520	6.91	
470	11.50		460	8.41		479	6.35	
450	10.81		437	7.87		448	6.00	
$N_{Zn}=0.8341$			$N_{Zn}=0.8467$			$N_{Zn}=0.9233$		
T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$	T °C	E mV	$\frac{dE}{dT} \times 10^3$
537	4.65	8.1	571	4.03	5.7	560	2.83	5.0
523	4.56		529	3.79		547	2.69	
513	4.44		489	3.54		535	2.59	
466	4.05		459	3.32		501	2.44	
458	3.99					474	2.32	

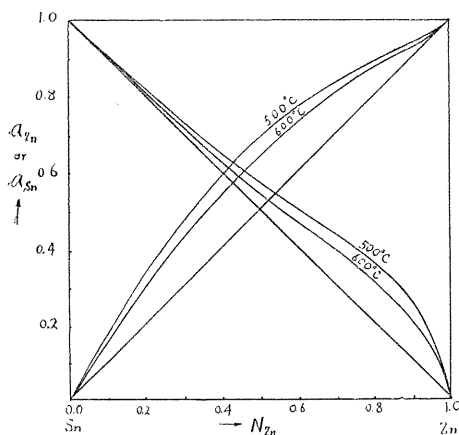


FIG. 2. Activities of zinc and tin in the system Zn-Sn at 500° and 600° C.

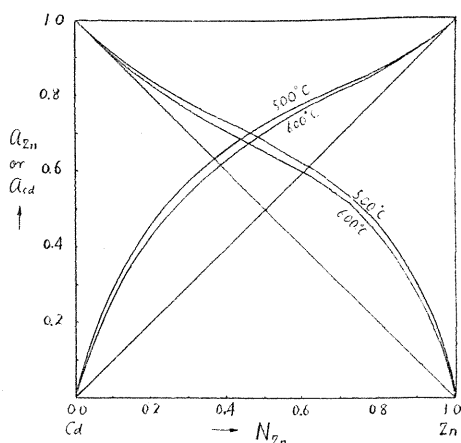


FIG. 3. Activities of cadmium and zinc in the system Zn-Cd at 500° and 600° C.

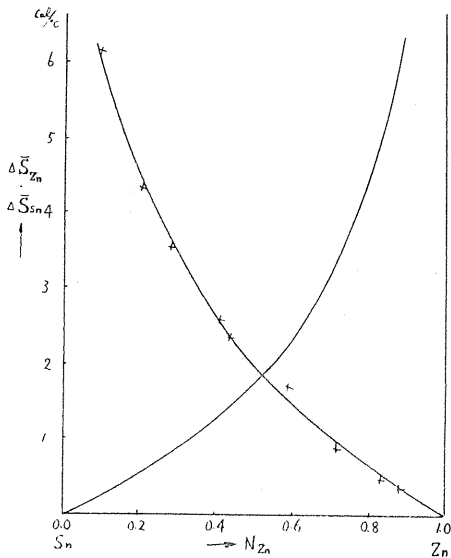


FIG. 4. Partial molal entropies of zinc and tin in the system Zn-Sn.

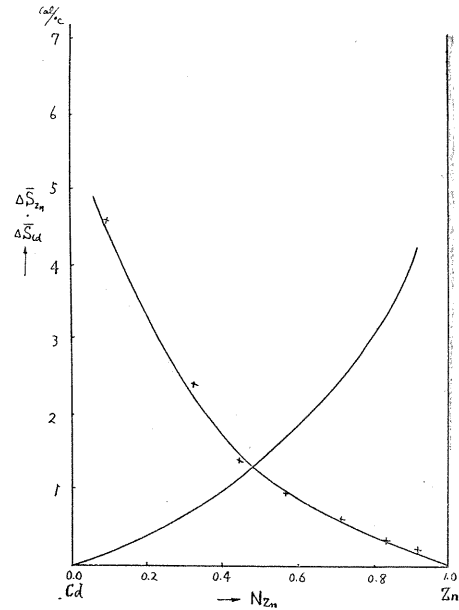


FIG. 5. Partial molal entropies of zinc and cadmium in the system Zn-Cd.

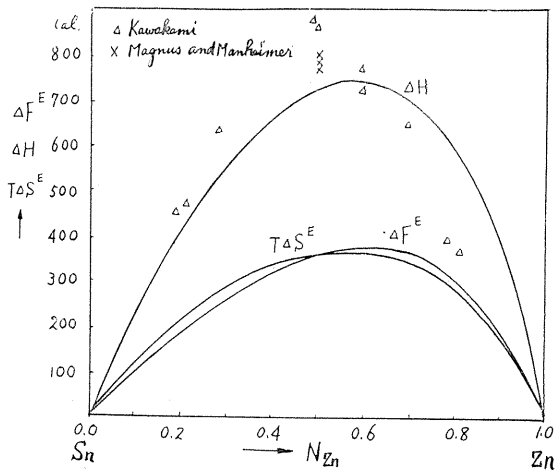


FIG. 6. Thermodynamic functions in the system Zn-Sn at 500° C.

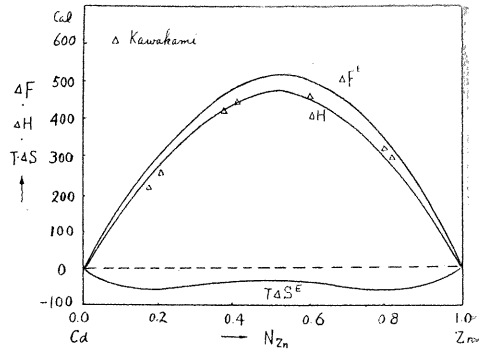


FIG. 7. Thermodynamic functions in the system Zn-Cd at 500° C.

Regarding to partial molar entropy $\Delta \bar{S}$, excess molar free energy ΔF^E , heat of mixing ΔH and excess molar entropy ΔS^E , the values computed for the both systems were given in Fig. 4, 5, 6 and 7.

Based on this set of experimental data, the thermodynamic functions for round figures of atomic fractions were determined by graphical interpolation of the smooth curve drawn through the experimental points. The corresponding

TABLE 3. Thermodynamic Functions for the System Zn-Sn

N_{Zn}	a_{Zn}		a_{Sn}		ΔF^E (cal)		$\Delta \bar{S}_{Zn}$ (cal/°C)	$\Delta \bar{S}_n$ (cal/°C)	ΔS^E (cal/°C)	ΔH (cal)
	500°C	600°C	500°C	600°C	500°C	600°C				
0.1	0.186	0.155	0.910	0.903	111	81	6.05	0.24	0.18	246
0.2	0.344	0.300	0.818	0.810	194	158	4.45	0.50	0.28	407
0.3	0.483	0.435	0.730	0.720	264	227	3.36	0.85	0.39	567
0.4	0.596	0.545	0.647	0.630	314	265	2.58	1.26	0.45	663
0.5	0.692	0.645	0.571	0.540	351	288	1.95	1.75	0.47	737
0.6	0.775	0.735	0.500	0.460	373	308	1.42	2.37	0.46	731
0.7	0.843	0.818	0.428	0.385	363	319	0.97	3.22	0.44	704
0.8	0.892	0.880	0.362	0.310	316	284	0.62	4.45	0.39	619
0.9	0.939	0.920	0.256	0.215	203	167	0.29	6.50	0.26	400

TABLE 4. Thermodynamic Functions for the System Zn-Cd

N_{Zn}	a_{Zn}		a_{Cd}		ΔF^E (cal)		$\Delta \bar{S}_{Zn}$ (cal/°C)	$\Delta \bar{S}_{Cd}$ (cal/°C)	ΔS^E (cal/°C)	ΔH (cal)
	500°C	600°C	500°C	600°C	500°C	600°C				
0.1	0.297	0.268	0.910	0.904	182	200	4.35	0.14	-0.071	127
0.2	0.456	0.427	0.834	0.830	304	314	3.30	0.33	-0.076	245
0.3	0.570	0.538	0.781	0.762	414	423	2.40	0.60	-0.059	368
0.4	0.660	0.632	0.730	0.705	488	492	1.70	0.96	-0.061	441
0.5	0.725	0.702	0.676	0.650	517	522	1.20	1.38	-0.052	477
0.6	0.771	0.760	0.620	0.590	500	515	0.88	1.85	-0.057	456
0.7	0.816	0.807	0.560	0.530	452	469	0.62	2.32	-0.068	399
0.8	0.860	0.854	0.470	0.440	351	364	0.40	2.95	-0.084	286
0.9	0.915	0.917	0.327	0.304	205	222	0.20	3.90	-0.074	148

functions were shown in Table 3 and 4.

In the case of the system Zn-Cd, small as it was, the value of the excess entropy was negative.

A comparison between the heats of mixing calculated from the results of this investigation and the values obtained calorimetrically by Kawakami,⁹⁾ and Magnus and Mannheimer,¹⁰⁾ was shown in Fig. 6 and 7.

Summary

The thermodynamic properties of the liquid systems Zn-Cd and Zn-Sn were investigated by the electromotive force method. It was shown that the value of the excess molal entropy in the system Zn-Cd was negative, and the excess molal free energy and the heats of mixing were all positive for the both systems.

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