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

(I) THE SYSTEM CADMIUM-TIN

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1. Introduction

The accumulation of data on the thermodynamic properties of liquid metallic solutions may lead eventually to a better understanding of the nature of such systems. Moreover, those data will be useful to improve metallurgical technique. In a detailed experimental study of the thermodynamic properties of liquid alloy systems, there are two methods: the electromotive force, and the vapor pressure method.

One method is to evaluate the activity of a volatile component by vapor pressure measurements and the other depends on measuring the electromotive force in reversible galvanic cell of the type $A(1)/A^{n+}/(A+B)(1)$, where A denotes the more electropositive metal, B denotes the other metal. Of the two, the electromotive force method will easily give us all the data required for a complete evaluation of the thermodynamic properties of the mixture.

Numerous investigations of the thermodynamic properties for binary mixtures have already been made, but those dealing with ternary mixtures are very few. In the present investigation, some thermodynamical values in the case of the liquid ternary system zinc-cadmium-tin were determined with the aid of e.m.f. measurements.

First, the thermodynamic properties of the cadmium-tin system were measured. It is a part of an investigation of ternary solutions which will be published later. The results are compared with the values obtained by Taylor,[1] and Chipman and Elliott,[2] and are found to agree fairly well with them.

Up to the present time, theoretical treatment of the properties of the liquid mixtures has been in a primitive state of development. The most elegant theory[3] of non-ideal solutions which has been ever appeared is that by the applicability of the law of regular solution.

But it is supposed from Matuyama's work[4] that cadmium-tin system fails to qualify as regular solutions because the volume of alloys is not additively related to the volumes of the pure constituents. Such a relation is found also in the author's experimental excess entropy data.

2. Equipment and Materials

The cell used in this investigation was the open H-shaped cell which has found extensive application in this kind of work, and was made from Pyro glass (dia. 12 mm).

Pyro glass (made in Japan) was the satisfactory cell material for use up to 600°C. The cell was shown in Fig. 1. Tungsten wires, sealed through the bottom, were welded to copper wires which were led out of the furnace and connected with the potentiometer. The tungsten wires were cleaned by electrolyzing a concentrated aqueous solution of sodium hydroxide.

The cell was washed in turn with a sulphuric acid potassium dichromate solution, dilute nitric acid, and distilled water.

The cell was dried at 150°C for several hours. During a run it was positioned in a vertical tube furnace.

Temperatures was measured with alumel-chromel thermocouple.

The metals and salts used were commercial "chemical pure" materials. The electrolyte consists of a eutectic mixture of lithium chloride and potassium chloride, and cadmium chloride of about 8 wt. per cent dried previously at 150°C for several hours. A clear electrolyte was obtained by settling the mixture of a small quantity of cadmium metal and chloride consisting of the electrolyte, in the evacuated pyro test tube at 600°C for a short time.

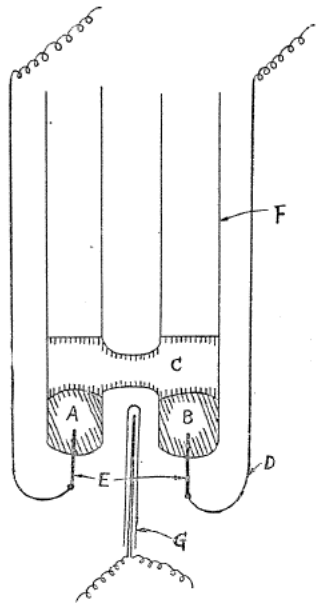

FIG. 1. Cell design.

A: Pure cadmium electrode
B: Alloy electrode
C: Electrolyte
D: Copper wire
E: Tungoten lead
F: Pyro glass
G: Thermocouple

3. Experimental Procedure

The electrolyte was melted down in the cell at about 400°C and then weighed amount of pure cadmium was introduced into the both legs. The potential difference between the two pure cadmium reference electrodes, was measured and was found to be less than 0.05 mV. Then, weighed amount of pure tin were added to the one of two legs and an alloy electrode was obtained. A period of several hours was allowed to elapse for the cell to attain electrical and thermal equilibrium. In a period of 20 to 36 hours, some independent measurements of both temperature and electromotive force were carried out at 5~7 different temperatures.

The measurements were made over the temperature range 430~550°C. Chemical analyses of the pure cadmium electrode showed that there was less than 0.02 atomic per cent of the electronegative metal introduced during the operation of the cell. This amount was quite negligible compared with the amount of errors from other sources. No tin was found in the electrolyte.

Consequently the weighed compositions of these series were used in the computations.

4. Experimental Results

The experimental results were given in Table 1 and the electromotive forces for each alloy composition were plotted versus temperature in Fig. 2. The limits of error in the data in the table were estimated generally to be less than 0.07 mV. Those errors originate from the uncertainty of the observation, the temperature fluctuations during the experiments and impurities in the electrolyte.

TABLE 1. Experimental Results

$N_{Cd}=0.09957$			$N_{Cd}=0.2113$			$N_{Cd}=0.3042$		
T °C	E mV	$dE/dT\times10^3$ mV/°C	T °C	E mV	$dE/dT\times10^3$ mV/°C	T °C	E mV	$dE/dT\times10^3$ mV/°C
434	53.46	116.0	436	34.60	88.2	455	26.96	69.6
452	55.16		451	35.77		473	28.21	
458	56.05		473	37.65		495	29.69	
485	59.01		482	38.25		503	30.31	
495	60.16		508	40.66		511	30.82	
510	61.95					528	31.94	

$N_{Cd}=0.4291$			$N_{Cd}=0.4943$			$N_{Cd}=0.7341$		
T °C	E mV	$dE/dT\times10^3$ mV/°C	T °C	E mV	$dE/dT\times10^3$ mV/°C	T °C	E mV	$dE/dT\times10^3$ mV/°C
439	18.36	49.7	449	15.69	41.6	434	7.40	18.4
471	19.75		465	16.46		445	7.60	
496	20.80		501	17.82		464	7.95	
516	21.72		505	17.92		483	8.30	
546	23.13		549	19.84		513	8.82	
			554	20.00		537	9.28	

$N_{Cd}=0.8494$		
T °C	E mV	$dE/dT\times10^3$ mV/°C
456	4.46	9.41
478	4.60	
483	4.64	
488	4.69	
497	4.77	
522	5.03	

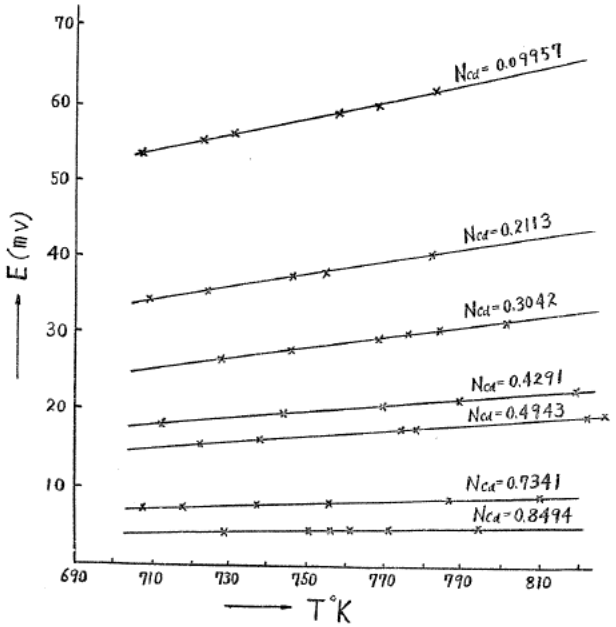

FIG. 2. Relation between temperature and electromotive force.

For the potential of the reversible cell for the transfer of cadmium from the anode to the cathode, we write $\Delta F_{Cd} = F_{Cd} - F^0_{Cd} = -2EF = RT \ln A_{Cd}$. ΔF_{Cd} is the free energy change per mole of cadmium transfered from the pure state into a very large quantity of alloy of the cathode composition.

F is faraday equivalent, a_{Cd} is the activity of cadmium in the cathode alloy referred to the pure cadmium as the standard state. Activity curves were plotted in Fig. 3 against the mole fraction of cadmium, together with the values obtained by Taylor, and by Chipman and Elliott.

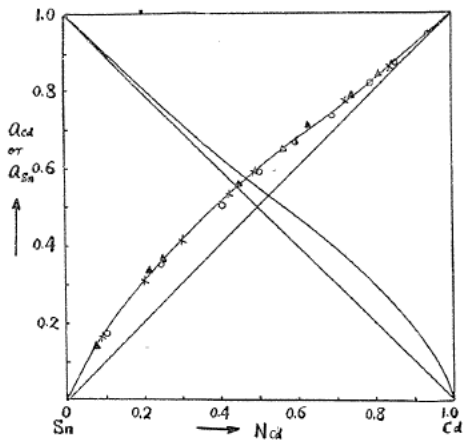

FIG. 3 (*left*). Activity curves of Cd-Sn solutions (500°C).
× Writers
▲ Taylor
○ Chipman and Elliott

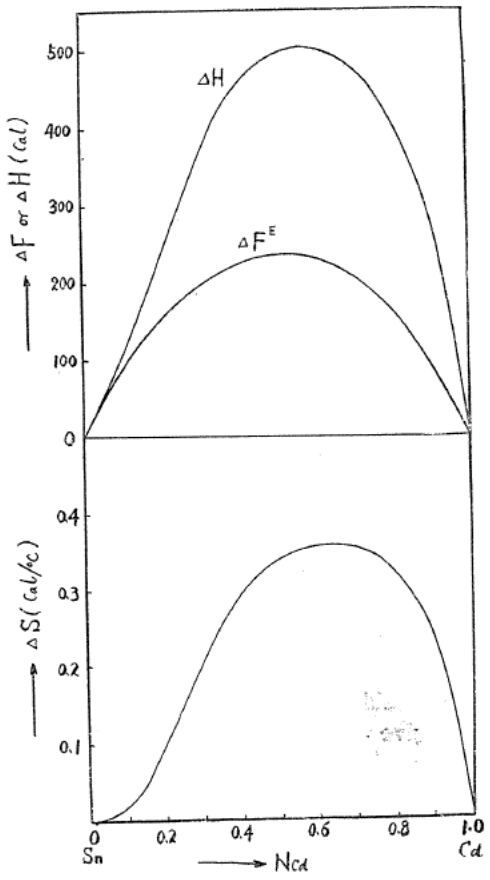

FIG. 4 (*right*). Thermodynamic functions of Cd-Sn solutions.

TABLE 2. Thermodynamic Functions

N_{Cd}	a_{Cd}	a_{Sn}	ΔS_{Cd} cal/°C	ΔS_{Sn} cal/°C	ΔF cal	ΔH cal	ΔS cal/°C
0.1	0.162	0.910	5.36	0.13	93	102	0.011
0.2	0.292	0.827	4.15	0.33	157	237	0.103
0.3	0.403	0.744	3.20	0.67	202	364	0.210
0.4	0.501	0 662	2.45	1.09	229	459	0.297
0.5	0.587	0.582	1.90	1.53	240	501	0.338
0.6	0.665	0.502	1.41	2.12	234	510	0.357
0.7	0.746	0.407	0.98	2.94	210	484	0.355
0.8	0.824	0.298	0.64	4.04	159	411	0.326
0.9	0.913	0.165	0.32	6.12	96	292	0.254

From the partial molar properties for one of the components over the whole concentration range, we can calculate the properties for the other component by graphical integration of the Gibbs-Duhem-Margules equation $X_1 d\bar{Y}_1 + X_2 d\bar{Y}_2 = 0$, where $\bar{Y}_1$ is any partial molar quantity for component 1, X_1 is the corresponding mole fraction. The values of the activities of tin have been deduced with the aid of the relations

$$\int_0^{\log a_{Sn}/N_{Sn}} d \log a_{Sn}/N_{Sn} = \int_0^{N_{Cd}/N_{Sn}} N_{Cd}/N_{Sn} d \log a_{Cd}/N_{Cd} .$$

The temperature coefficient of the electromotive force, dE/dT, will give the relative partial molar entropy $\Delta\bar{S}$ in the mixture through the relationship $\Delta\bar{S}_{Cd} = \bar{S}_{Cd} - S^0_{Cd} = 2F(\partial E/\partial T)$. The heat content change was obtained from the relationship $L_{Cd} = H_{Cd} = H^0_{Cd} = -2F[E - T(\partial E/\partial T)]$.

Also "excess" molar properties are defined by the following equations

$$\Delta F_i^E = RT \ln a_i/N_i = RT \ln \gamma_i$$
$$\Delta S_i^E = \Delta S_i + R \ln N_i$$
$$L_i^E = L_i = H_i - H_i^0$$
$$\Delta F^E = \Delta F - \sum_1^i N_i \Delta F_i \quad \text{(ideal)}$$
$$\Delta S^E = \Delta S - \sum_1^i N_i \Delta S_i \quad \text{(ideal)}$$
$$\Delta H^E = \Delta H = \sum_1^i N_i L_i .$$

Values of ΔF^E, ΔH and ΔS^E were listed in Table 2 and plotted in Fig. 4.

5. Discussion

Activity curves obtained was found to agree well with Taylor's, and Chipman and Elliott's data. They show relatively small positive deviations from ideality (see Fig. 3).

According to Raynor's discussion,[5] it is considered that the activity curves of the liquid system having no evidence of compound formation in the solid state will give rise to positive deviations from ideality. In the case of cadmium-tin system, this condition is satisfied. In recent paper, Mukherjee[6] described that the surface tension of liquid metals at the melting point is approximately proportional to their heat of fusion. The surface tension is believed to be due to the unbalanced force of the surface atoms. For each surface atom, these unbalanced forces are a fraction of the total forces.

Therefore, high heat of fusion will be required for the metal having strong interatomic forces. According to the statistical treatment using the quasi-crystal model, activity deviations from ideality are connected with the $(2W_{AB} - W_{AA} - W_{BB})$ values, where W_{AB}, W_{AA} and W_{BB} are the potential energies of the AB, AA and BB nearest neighbor interactions or bonds. Therefore, activity deviations from ideality are also remarkably related to the interatomic forces in solutions. We might thus expect an approximate correlation between the activity deviation and the relative difference in the heats of fusion between the two components consisting the solution. These were illustrated in tabular form in Table 3. In Table 3-*a* excepting for amalgams, the activities of the alloy systems of group *A* show large negative

TABLE 3-a. Correlation between the Activity Deviation and the Relative Difference in the Heats of Fusion of the Two Components Consisting the Solution

Group	Alloy	Difference in the heats of fusion[25] between the two components ΔL_m(kcal/mol)	Deviations of activity from Raoult's law Positive : + Negative : −	Degree of deviations from Raoult's law Large : L Medial : M Small : S	Evidence of compound formation in the solid state[26] Existent : ○ None : ×
A	Fe-Si[7]	5.91	−	L	○
	Cd-Sb[2]	3.31	−	L	○
	Zn-Sb[9]	3.17	−(some part)+	L	○
	Au-Tl[10]	2.27	−	M	○
	Pb-Mg[5]	2.23	−	L	○
	Au-Pb[11]	1.81	−	M	○
	Au-Cd[7](c)	1.57	−	L	○
	Cu-Zn[7](c)	1.51	−	L	○
	Tl-Bi[12]	1.48	−	L	○
	Au-Zn[7](c)	1.43	−	L	○
	Au-Sn[13]	1.31	−	L	○
	Bi-Pb[14]	1.29	−	S	×
	Ag-Cd[7](c)	1.24	−	M	○
	Ag-Zn[7](c)	1.10	−	L	○
B	Cd-Bi[2]	1.05	−(some part)+	S	×
	Tl-Sn[15]	0.96	+	M	×(?)
	Bi-Sn[12]	0.79	+	S	×
	Al-Zn[5]	0.78	+	M	×
	Fe-Ni[16]	0.64	−	S	○
	Au-Bi[10]	0.52	−	S	×
	Pb-Sn[18]	0.50	+	M	×
	Tl-Pb[15]	0.46	−(some part)+	S	○
C	Fe-Cu[7](c)	0.45	+	L	×
	Pb-Zn[5]	0.36	+	L	×
	Cd-Sn	0.26	+	S	×
	CdPb[1][2]	0.24	+	L	×
	Cd-Zn[1]	0.14	+	L	×
	Zn-Sn[1]	0.12	+	L	×

Pb-Sb,[5] Cd-Cu,[7](c) Pb-Na[17] and Au-Ag[12] system was excepted because above relations were not well fulfilled.

TABLE 3-b

Amalgam	Difference in the heats of fusion between the two components ΔL_m(kcal/mol)	Deviations of activity from Raoult's law Positive : + Negative : −	Degree of deviations from Raoult's law Large : L Middle : M Small : S	Evidence of compound formation in the solid state Have : ○ Have not : ×
Hg-Au[19]	2.45	+	L	○
Hg-Bi[19]	1.93	+	S	×(?)
Hg-Sn[20]	1.14	+	M	○
Hg-Zn[21]	1.02	+	S	×(?)
Hg-Cd[20]	0.88	−	M	○(?)
Hg-Pb[20]	0.64	+	M	×(?)
Hg-Li[24]	0.54	−	M	○
Hg-Tl[19]	0.18	−	S	○(?)
Hg-Cs[23]	0.08	−	L	○
Hg-Na[23]	0.05	−	L	○
Hg-K[22]	0.01	−	L	○

deviations from ideality, these of group B show small deviation and those of group C show large positive deviations. In the case of amalgams, these relations are reverse as seen in Table 3-b: when the differences in the heat of fusion, ΔL_m, are large, activities show tendency of positive deviations from ideality, but there will be, indeed, negative deviations as these differences decrease. The deviations illustrated in the table are suitable to experimental temperature respectively, but the above relation are comparatively well fulfilled.

The usual method of statistical treatment of solutions is based on the model of regular solutions assuming that there is no excess volume on mixing. A crude treatment of this model, assuming random mixing, gives $S^E=0$. But the refined treatment of strictly regular solutions by Guggenheim was a considerable improvement for non-randomness of mixing. This treatment gives a small negative excess entropy. But the experimental excess entropy is by no means negative. The situation in this whole field of the statistical theory of solutions appears unsatisfactory.

In recent years the cell method has been extended for the solutions by Prigogine and Mathot.[27] They have obtained important corrections on both the heat of mixing and the excess entropy to the classical regular solutions.

These corrections are related to the volume changes on mixing resulting from the changes of interactions between component atoms and a proportionate relation between excess entropy and excess volume can be found.

It seems possible that the contributions to the change of excess entropy arise from (a) volume change on mixing, (b) short range order, and (c) change in coordination number on mixing.

The effect of a volume change on an entropy change of mixing shall be expressed according to the formula

$$\left(\frac{\partial S_{Ir}}{\partial V}\right)_T = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_P}$$

$$\therefore \frac{\Delta S_{Ir}}{\Delta V} = \frac{\text{thermal coefficient of expansion } (\alpha)}{\text{isothermal compressibility } (\beta)}.$$

Only for a small number of systems are the density data for liquid metallic mixtures available through the work of Matuyama. Data for α and particularly for β are generally lacking, but approximate values can be obtained from those of the pure components. The order of magnitude of α/β can thus be established at $\cong 1$ cal/cc degree.[13]

Therefore, the volume contribution to excess entropy is approximately 0.29 at 0.5 mol fraction cadmium.

This value is not necessarily accurate, but it can be assumed that the volume contributes on the excess entropy to a remarkable degree.

6. Summary

1. The thermodynamic properties of the liquid systems cadmium-tin were investigated by the electromotive force method. From the result obtained, it was shown that the excess free energies, heat of mixing and excess entropies of this system have positive values.

2. The relation of differences in the heats of fusion of the two components and deviations of activity from Raoults' law was considered and furthermore the possible effect of volume change on the entropy of mixing was discussed.

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