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THE ACTIVITIES OF ZINC, CADMIUM, TIN, LEAD AND BISMUTH IN THEIR BINARY LIQUID MIXTURES¹

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Introduction

The experimental investigations of Tammann, Meyer, Ramsay, Richards and co-workers, Hulett and De Lury, Hildebrand and co-workers² on metallic solutions have been made with the object of discovering whether the simple laws of non-metallic solutions of low polarity were applicable or whether the existence of free electrons in the metals affected their thermodynamic properties. Although the deviations from the simple concentration laws have been found to be great in many cases, it appears that all systems investigated do approach this law asymptotically in dilute solutions. The dissolved molecules are believed to be monatomic and departures from the laws of the ideal solution are to be ascribed to causes other than polymerization or dissociation of the atoms into ions and free electrons. When definite compounds are known to exist in the solid state, it is easy to explain abnormally low fugacities of the components of the solution on the basis of compound formation; but there are a number of cases where the fugacities are much greater than the simple concentration law would require. This type, also very common to organic liquid mixtures, has been suggested by Hildebrand to be due to differences in the internal pressures of the components. This theory has been very well substantiated by a large amount of vapor pressure and solubility data, and by measurements on the critical mixing temperatures of two-phase liquid systems in cases where the relative internal pressures of the components are known. In the field of metallic solutions, however, experimental work has been entirely confined to amalgams and it is of interest to extend our knowledge to other liquid mixtures. In the present investigation, by working above 400°, it has been found possible to obtain accurate values for the activities of both components of the following liquid systems, zinc-cadmium, zinc-tin, cadmium-tin, cadmium-lead and cadmium-bismuth, over the complete concentration range.

¹ Submitted by the author in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of California, May, 1923.

² (a) Tammann, *Z. physik. Chem.*, **3**, 441 (1889). (b) Meyer, *Wied. Ann.*, **40**, 244 (1890). (c) Ramsay, *J. Chem. Soc.*, **55**, 521 (1889). (d) Hulett and De Lury, *THIS JOURNAL*, **30**, 1805 (1908). Richards and co-workers, (e) *Proc. Am. Acad. Arts Sci.*, **34**, 87 (1898); (f) *Carnegie Inst. Pub.*, **118** (1909); (g) *THIS JOURNAL*, **41**, 1732 (1919); (h) **44**, 60 (1922). (i) Hildebrand, *Trans. Am. Electrochem. Soc.*, **22**, 319 (1912); (j) **22**, 335 (1912); (k) *THIS JOURNAL*, **35**, 501 (1913). (l) Hildebrand and Eastman, *ibid.*, **36**, 2020 (1914); (m) **37**, 2452 (1915). (n) Hildebrand, Foster and Beebe, *ibid.*, **42**, 545 (1920).

There are two reliable methods available for investigating the activities of the individual components of liquid metal systems: first, measurements of vapor pressures at high temperatures, as exemplified by the work of Hildebrand and Eastman on silver, gold, bismuth and thallium amalgams; and second, measurements of the electromotive force of concentration cells, in which one electrode consists of a pure metal or an alloy in which this metal has a known activity. The second method has been applied by Richards and his co-workers to a large number of solutions of electropositive metals in mercury. Except in the case of thallium amalgams, the concentration range investigated never exceeded 10% in the electromotive-force measurements but was limited by the low solubility of most of the metals in mercury at room temperature. This method has the theoretical advantage that it measures the activity directly and does not involve the assumption that the vapor obeys the simple gas laws. It has the practical advantage that a number of alloys of different concentrations can be studied simultaneously, and considerable time may be saved. Further, it is possible to work with metals of low vapor pressure. For example, at 500° the vapor pressure of zinc is about 1 mm., which would make accurate measurements somewhat difficult for alloys of low zinc content. Such alloys offer no special difficulty when the electromotive-force method is applied. Finally, measurements may be readily made over a wide temperature range with none of the difficulties which usually attend vapor pressure work at very high or very low pressures.

In this research the electromotive-force method was used. The ordinary aqueous electrolyte used by Richards was replaced by a fused-salt mixture which contained the ion of the more electropositive component of the binary alloy under investigation. All alloys were measured against the pure electropositive metal. Thus in the system, zinc-tin, the cell may be represented as $\text{Zn}|\text{Zn}^{++}|\text{Zn-Sn alloy}$. The reaction taking place when the circuit is closed consists in a transfer of zinc from the pure state at unit activity, to the alloy where the activity of the zinc is a smaller value, a_1 . The electromotive force of such a cell is given by the equation, $E = RT/nF \ln 1/a_1$, where the symbols R , T , n and F have the usual significance. Throughout this article, the symbols a_1 and N_1 will be used to represent the activity and the mole fraction of the more electropositive component of the alloy. Thus from measurements of the electromotive force, the value of the activity may be readily calculated. It is obvious that the above reaction must be the only one taking place in the cell. The electrolyte must contain nothing which might react with either component of the alloy. It is, therefore, essential that the normal electrode potentials of the two components be sufficiently different that the more noble metal will have no effect on the ion of the other. This requirement limits our choice of metal pairs very considerably. The low-melting metals suitable

for this research have the following molal electrode potentials in aqueous solution at 25°. These values can give only a rough indication of the electrode potential of the metals against their fused salts.

Metal	Zinc	Cadmium	Thallium	Tin	Lead	Bismuth
M. p., °C.....	419	320	302	232	327	269
Elec. pot., volts..	0.76	0.40	0.34	0.14	0.12	-0.3

Excluding systems which form two liquid phases and those in which the difference between the electrode potentials is less than 0.20 volt, we are limited to the following cases: Zn-Cd, Zn-Sn, Cd-Sn, Cd-Pb, Cd-Bi, Tl-Sn, Tl-Pb, Tl-Bi. The first five of these systems have been investigated in the present research. It may be of interest to note that some preliminary experiments showed that at 500° in a fused-salt electrolyte the cadmium ion was largely reduced by thallium, which indicates that the thallium has very probably the higher electrode potential at this temperature.

When pure molten zinc chloride or cadmium chloride is used as the electrolyte, metallic fogs are formed.³ When these fogs occur in an alloy concentration cell there results a transfer of metal through the electrolyte until all the alloys have reached the same composition. Reproducible electromotive forces are therefore not obtainable. This difficulty was overcome by using as the electrolyte a eutectic mixture of 40% potassium chloride and 60% lithium chloride which contained a little zinc chloride (or cadmium chloride). This fused-salt mixture shows no tendency to fog formation with any of the alloys investigated. It should perhaps be mentioned that the concentration of zinc or cadmium ion has no effect on the electromotive force of the type of cell used in the present research.

Purity of Materials

The potassium and lithium chlorides used in this research were found to be entirely free from heavy metals. The cadmium and zinc chlorides and potassium hydroxide contained very slight traces of iron, just sufficient to give a faint pink color with potassium thiocyanate. This corresponds to about 0.005% of ferric ion, which is entirely too small to make any appreciable change in the composition of the alloys. These salts contained some water so that there was some hydrolysis on fusion, with the liberation of hydrogen chloride which was neutralized by addition of fused potassium hydroxide.

The cadmium and bismuth had been obtained from a foreign commercial source. Those metals were used without further purification. The presence of 0.5% of impurity would not affect the electromotive force of the cells more than 0.00015 volt, which was the accuracy obtained in the actual measurements. The zinc, tin and lead had been used in a previous investigation in this Laboratory, and were of known purity.⁴

Description of Apparatus

The cell used was a modification of the type used by Richards and Daniels in their study of the electromotive forces of thallium amalgams.^{2*} Since the work was all at high temperatures, Pyrex glass was used. The cell contained 6 cups, in 2 of which were

³ Lorentz, *Z. anorg. Chem.*, 91, 46 (1915).

⁴ Hogness, *THIS JOURNAL*, 43, 1621 (1921).

placed samples of the more electropositive metal while the other 4 cups contained alloys of known composition. These cups were approximately 12 mm. in internal diameter and 25 mm. in depth. Tungsten wires, sealed through the base of each cup, formed the electrodes. These were soldered with german silver to heavy copper wires which led out of the furnace and connected with the potentiometer. In the first experiments graphite electrodes were used, but this method was soon discontinued on account of the formation of metal carbides. During the course of the research there was no evidence of solution of tungsten in the molten alloys. The cell was supported in the furnace by the long glass tubes, *a*, Fig. 1. For suggestions in the design of all cells used in this research and for their construction the author is indebted to Mr. W. J. Cummings, glass blower of this Laboratory.

All measurements were made in a large, thick-walled electric furnace which was heated by 4 Nichrome units in parallel. The air inside was circulated by two large fans. By adjustments of current at half-hour intervals the temperature would remain at $580 \pm 1.5^\circ$ with a power input of 2.6 kilowatts. Four temperatures were used: 430° , 475° ,

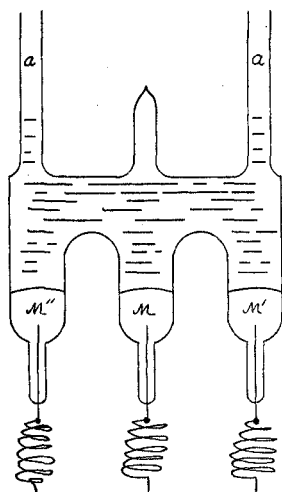


Fig. 1.—View of one-half of the 6-cup Pyrex cell. *M* is a pure metal, *M'* and *M''* are alloys

put into the proper cups in the cell, all but two inlet tubes were sealed off, and the cell was placed in the furnace and heated in a stream of pure hydrogen until the sticks of pure metal had melted and run together to form a more or less homogeneous alloy. In the meantime the electrolyte was prepared by fusion of the eutectic mixture of potassium and lithium chlorides with a small amount of zinc or cadmium chloride and potassium hydroxide. A stick of pure metallic zinc (or cadmium) was usually added to the electrolyte to ensure complete removal of hydrogen ion. When the metals in the cell were melted, the hydrogen flow was stopped and immediately the clear electrolyte was poured into the cell, and care was taken that the globule of zinc (or cadmium) was left behind. Sometimes the electrolyte contained small amounts of zinc oxide or cad-

540° and 580° . The temperatures were measured by means of 2 Chromel-alumel thermocouples which had been calibrated at the melting points of tin, zinc and antimony. The melting points of these metals had been previously determined by means of a platinum-resistance thermometer whose equation was accurately known. The values obtained in the calibration of the thermocouples were plotted on large cross-section paper and smooth curves drawn through them. From these curves all temperatures were obtained by interpolation. The accuracy was about 2° .

Experimental Procedure

Small sticks of the various pure metals were prepared by melting larger pieces in a vacuum and running the molten metal into glass tubes. When the glass was broken the stick came out with a clean surface. Alloys of known composition were prepared by weighing these sticks.

The average weight of the whole alloy was 7 or 8 g. These weighed sticks of pure metal were

mium oxide. This apparently did not affect the electromotive forces obtained.

The heavy copper wires from the cell connected through mercury cups to the potentiometer. This was a commercial instrument and was used in connection with a working battery of 2 Edison accumulators. A Weston cell, giving an electromotive force of 1.01862 volts at 22° was used as standard. This cell was frequently checked against other standard cells in this Laboratory, and was found to remain constant.

Using a 6-cup cell, in which 2 cups contain the same pure metal, it is possible to make duplicate measurements of the electromotive forces of the pure metals against each of the 4 alloys. These electromotive forces may be checked further by measurements of various combinations of the alloys themselves and by suitable additions and subtractions of the values obtained. The alloys at first were not homogeneous so that the electromotive forces changed more or less rapidly at first, but after 5 or 6 hours, they became constant to 0.1 mv. and remained so during the subsequent 3 days. Temperature readings and electromotive-force readings were taken every half hour until 10 or 12 readings had been obtained and it was evident that the electromotive forces were remaining constant.

The furnace temperatures were usually changed in the following order: 470°, 540°, 470°, 430°, 540°, 580° and 470°. The advantage of returning to a previous temperature after 8 or 10 hours is that the old electromotive forces may be thus checked to see whether they have remained constant over long periods of time. Any change which might take place in the composition of the alloys is thus readily detected. In some cases the electromotive forces were found to have risen 0.2 or 0.3 mv. over a 24-hour period. This was apparently due to a very slow diffusion of oxygen through the electrolyte to the alloy surfaces. In cases where the electromotive forces had changed in this way, all subsequent measurements were corrected by the amount of the change. All final electromotive force values are averages of 10 or more readings. The duration of a complete run was ordinarily 50 to 60 hours, but there were a number of cases where leaks developed and the run was not completed. The fused electrolyte has a devitrifying action on Pyrex glass so that the cell usually became quite fragile after 2 or 3 days' heating and it was necessary to build a new cell for every run.

To illustrate the constancy of the electromotive-force values over a long period of time, the following data are quoted from the system, cadmium-lead (Run 3). The time is measured from the beginning of the run.

The experimental results on the various alloy systems will now be recorded, together with the values of $\log (a/N)$ calculated from the actual data. The significance of the quantity $\log (a/N)$ may be made clearer by considering the following relationships. In general, when 1 mole of one

component is transferred from the pure state to an alloy in which its activity is a_1 the decrease of free energy is $\Delta F = RT \ln a_1$. If the liquid

TABLE I
SUMMARY OF TYPICAL RUN
Electromotive force of Cd concentration cells in Cd-Pb alloys, Run 3

Hours	Thermo-couple	Temperature °C.	Cell 12	Cell 13	Cell 14	Cell 15	Average of readings \times
0-12	0.01291	476	0.0060	0.0097	0.0181	0.0355	15
30-35	.01279	474	.0056	.0099	.0174	.0353	6
57-58	.01282	475	.0061	.00970347	2
	.01290	476	.0060	.0097	.0181	.0355	Weighted mean
12-15	.01137	427	.0054	.0080	.0154	.0307	4
24-29	.01140	428	.0054	.0082	.0154	.0306	10
	.01138	427	.0054	.0081	.0154	.0307	Weighted mean
35-38	.01515	544	.0074	.0122	.0225	.0424	6
48-50	.01518	545	.0073	.0122	.0226	.0422	4
	.01516	544	.0074	.0122	.0225	.0424	Weighted mean
51-56	.01610	572	.0078	.01315	.0244	.0450	10

alloy obeys Raoult's law the free energy decrease is $\Delta F = RT \ln N_1$. The excess free energy of one component of an actual alloy over the value which it would have if the solution were ideal, is $\Delta F = RT \ln (a_1/N_1)$. Furthermore, since a/N is equal to unity for an ideal solution, a curve of a_1/N_1 or $\log (a_1/N_1)$ plotted against N_1 makes a very satisfactory way of representing the deviation of any solution from the ideal. The horizontal line corresponding to $\log (a/N) = 0$ represents Raoult's law. By extrapolating the $\log (a_1/N_1)$ curve to the point where N_1 is equal to zero it is easy to obtain the limiting value of a_1/N_1 , which is the so-called Henry's-law constant for this component. As a matter of fact, the curves exhibited in this article show that a_1/N_1 is never constant over any finite range of concentration, and therefore the Henry's-law constant cannot really be considered a constant at all, although in a great deal of vapor-pressure data recorded in the literature this ratio has been found "constant" within fairly narrow limits of experimental error.

The activity of the second component of these alloys has been obtained from that of the first by means of the Duhem equation, which may be expressed as follows: $N_2 d \log (a_2/N_2) = -N_1 d \log (a_1/N_1)$. This may be written in the integrated form $\log (a_2/N_2) = - \int_0^{N_2} N_1/N_2 d \log (a_1/N_1)$. The value of the right-hand term of this expression may be determined by first deriving an empirical equation which will give the experimental values of $\log (a_1/N_1)$ as a function of N_1 , and then carrying out the above integration. In the present research it was found simpler, however, to plot the smoothed-out values of $\log (a_1/N_1)$ at even mole fractions as abscissas against the corresponding values of N_1/N_2 as ordinates, and to determine

the area under the curve up to any desired value of N_2 . This process, although somewhat tedious, may be carried out with a fairly high degree of accuracy and rapidity. There are two choices of a standard state for the second component of the alloy. The standard state of the first component has been fixed by defining $a_1 = 1$ when $N_1 = 1$. The same choice is made in this article for the second component, namely $a_2 = 1$ when $N_2 = 1$. The other possibility is to define a_2/N_2 as equal to unity when $N_2 = 0$. The two standard states are related by a constant factor. For example, in cadmium-tin solutions at 483° , the value of $a_2/N_2 = 2.15$ when $N_2 = 0$. If the value of a_2/N_2 when $N_2 = 0$ had been defined as equal to unity, all the other values for a_2/N_2 in the other concentrations would be obtained by dividing the present values by 2.15.

The System: Cadmium-Tin

Four runs were made, two of which were successful. The following values are the actual electromotive forces obtained. Each value is the average of about 10 readings taken at half-hour periods. In this and in

TABLE II
THE SYSTEM: CADMIUM-TIN

RUN 2					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.816	0.569	0.258	0.0835
Electromotive force in volts					
Temp. °C.	Cell 12	13	14	15	
430	0.0051	0.0129	0.0292	0.0578	
483	.0053	.0141	.0324	.0632	
545	.0061	.0161	.0368	.0707	
585	.0064	.0173	.0395	.0749	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
430	0.015	0.060	0.170	0.250	
483	.018	.057	.157	.236	
545	.013	.047	.135	.207	
585	.013	.042	.124	.198	
RUN 4					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.749	0.630	0.451	0.222
Electromotive force in volts					
Temp.	Cell 12	13	14	15	
432	0.0071	0.0099	0.0166	0.0315	
482	.0077	.0111	.0185	.0355	
543	.0085	.0126	.0213	.0406	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
432	0.024	0.059	0.108	0.203	
482	.023	.053	.099	.180	
543	.021	.045	.083	.152	

subsequent tables, the term, "Cell 12," is used to represent a cell of which one electrode was pure cadmium and the other electrode was alloy No. 2.

TABLE III
THE SYSTEM: CADMIUM-TIN

A 431°					B 483°				
N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	0.305	0.000	0.000	1.00	0.279	0.00	0.000	1.00	1.0
.1	.253	.179	.003	0.91	.229	.17	.0027	.91	0.9
.2	.206	.32	.011	.82	.184	.31	.0105	.82	.8
.3	.161	.435	.026	.74	.144	.42	.024	.74	.7
.4	.122	.53	.047	.67	.109	.51	.043	.66	.6
.5	.087	.61	.076	.60	.079	.60	.067	.58	.5
.6	.058	.68	.109	.52	.054	.68	.098	.50	.4
.7	.034	.76	.154	.43	.033	.76	.137	.41	.3
.8	.017	.83	.207	.32	.017	.83	.184	.31	.2
.9	.006	.92	.273	.19	.006	.91	.250	.18	.1
1.0	.000	1.00	.35	.00	.000	1.00	.333	.00	.0
C 544°					D 585°				
N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	0.246	0.00	0.0000	1.00	0.232	0.00	0.0000	1.00	1.0
.1	.200	.16	.0025	0.91	.188	.15	.0023	0.91	0.9
.2	.160	.29	.0095	.82	.148	.28	.0093	.82	.8
.3	.123	.40	.022	.74	.112	.39	.021	.74	.7
.4	.093	.50	.038	.66	.083	.48	.037	.65	.6
.5	.067	.58	.059	.57	.059	.57	.057	.57	.5
.6	.045	.67	.086	.49	.039	.66	.082	.48	.4
.7	.027	.75	.117	.39	.024	.74	.110	.39	.3
.8	.014	.83	.158	.29	.012	.82	.147	.28	.2
.9	.005	.91	.210	.16	.0045	.91	.193	.16	.1
1.0	.000	1.00	.275	.00	.0000	1.00	.25	.00	.0

The calculated values of $\log(a_1/N_1)$ obtained from these two runs have been plotted against N_1 . The average deviation of the individual values from the smooth curves is 0.006 at 433°, 0.004 at 484° and 0.002 at 546°. In determining the curve, equal weight has been given to all the experimental points, but it is possible that the values for Run 2 are somewhat low and that all the values on the curve should be slightly higher. The smoothed-out values of $\log(a_1/N_1)$ and the corresponding calculated values of $\log(a_2/N_2)$ at various mole fractions are recorded in Table III (A-D). The values of a_1 and of a_2 are also given.

Part of the data is summarized further in Fig. 2, and in Fig. 3. The results at all the temperatures are not shown in these curves but are used later in calculating heats of dilution.

The System: Cadmium-Lead

Three complete runs were made on cadmium-lead alloys. The electromotive-force values recorded are each averages of 10 or more individual readings.

The average deviation of the individual points from the smooth $\log(a_1/N_1)$ curve is as follows: 0.004 at 432° ; 0.002 at 480° ; and 0.002 at

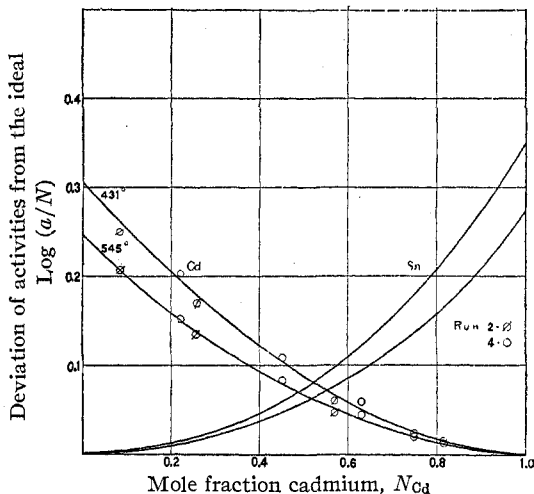


Fig. 2.—System, cadmium-tin. Deviation from the laws of the perfect solution. The horizontal line $\log(a/N) = 0$ corresponds to Raoult's law

544°; and 0.001 at 572° . The smoothed-out values of $\log(a_1/N_1)$ and the corresponding values for $\log(a_2/N_2)$ are recorded in Table V (A-D). Part

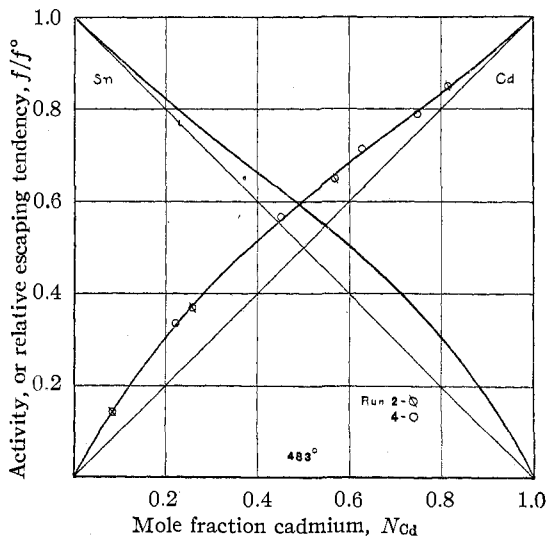


Fig. 3.—Activity curves for the system, cadmium-tin, at 483°

of the data is summarized further in Figs. 4 and 5. Comparison of these with the corresponding curves for cadmium-tin alloys shows about

TABLE IV
THE SYSTEM: CADMIUM-LEAD

Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.786	0.584	0.401	0.155
RUN 1					
Electromotive force in volts					
Temp. °C.	Cell 12	13	14	15	
436	0.0043	0.0073	0.0108	0.0274	
484	.0047	.0081	.0131	...	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
436	0.0441	0.130	0.243	0.421	
484	.042	.126	.223	...	
RUN 2					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.696	0.509	0.569	0.123
Electromotive force in volts					
Temp.	Cell 12	13	14	15	
427	0.0054	0.0081	0.0154	0.0307	
476	.0060	.0097	.0181	.0355	
544	.0074	.0122	.0225	.0424	
572	.0078	.0132	.0244	.0450	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
427	0.080	0.176	0.349	0.469	
476	.077	.163	.327	.434	
544	.066	.143	.293	.389	
572	.064	.136	.280	.375	
RUN 3					
Composition of alloy		No. 2			
Mole fraction Cd (N_1)		0.293			
Electromotive force in volts:		544°	0.0215	466°	0.0170
Calculated values of $\log(a_1/N_1)$		544°	0.268	466°	0.301

twice as great departure from Raoult's law as in the case of the system, cadmium-lead. This important fact will be discussed later.

TABLE V
THE SYSTEM: CADMIUM-LEAD

A 432°					B 480°				
N_1	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	N_2
0.0	0.57	0.000	0.0000	1.000	0.55	0.000	0.0000	1.000	1.0
.1	.484	.305	.0047	0.910	.455	.285	.0052	0.910	0.9
.2	.398	.500	.0197	.835	.369	.470	.021	.840	.8
.3	.316	.620	.047	.780	.292	.590	.046	.780	.7
.4	.244	.700	.086	.730	.226	.675	.082	.725	.6
.5	.180	.755	.138	.685	.169	.740	.129	.675	.5
.6	.125	.800	.204	.640	.119	.790	.190	.620	.4
.7	.078	.840	.292	.585	.075	.830	.272	.560	.3
.8	.040	.875	.406	.510	.038	.875	.383	.485	.2
.9	.013	.925	.560	.365	.012	.925	.539	.345	.1
1.0	.000	1.000	.80	.000	.000	1.000	.74	.000	.0

C 544°					D 572°				
0.0	0.480	0.000	0.0000	1.000	0.463	0.000	0.0000	1.000	1.0
.1	.404	2.55	.0042	0.910	.391	.245	.0039	0.910	0.9
.2	.334	.430	.017	.830	.322	.420	.016	.830	.8
.3	.266	.555	.039	.765	.257	.540	.038	.765	.7
.4	.202	.635	.074	.710	.196	.630	.071	.710	.6
.5	.148	.705	.118	.655	.140	.690	.117	.655	.5
.6	.103	.760	.173	.595	.097	.750	.170	.590	.4
.7	.065	.815	.244	.525	.063	.810	.233	.515	.3
.8	.034	.865	.336	.435	.035	.865	.316	.415	.2
.9	.011	.920	.476	.300	.0105	.920	.464	.290	.1
1.0	.000	1.000	.67	.000	.0000	1.000	.63	.000	.0

The System: Cadmium-Bismuth

Satisfactory measurements were obtained in four different runs. The recorded electromotive-force values are again averages of 10 or more individual readings.

During this run (No. 4) the wire connecting with the pure cadmium electrode broke, and it was impossible to measure Cells 12, 13, etc., directly. Cells 32, 34 and 35 were, therefore, measured and the electro-

TABLE VI
THE SYSTEM: CADMIUM-BISMUTH

RUN 3				
Composition of alloy	No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)	0.727	0.639	0.456	0.230
Electromotive force in volts				
Temp. °C.	Cell 12	13	14	15
433	0.0090	0.0139	0.0269	0.0477
475	.0098	.0154	.0289	.0513
534	.0106	.0170	.0311	.0562
Calculated values of $\log(a_1/N_1)$ from these measurements				
Temp.	Alloy No. 2	No. 3	No. 4	No. 5
433	0.0100	-0.0051	-0.0425	-0.0423
475	.0063	-.0129	-.0479	-.0526
534	.0061	-.0176	-.0470	-.0632
RUN 5				
Composition of alloy	No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)	0.864	0.472	0.282	0.1134
Electromotive force in volts				
Temp.	Cell 12	13	14	15
422	0.0039	0.0257	0.0416	0.0673
471	.0040	.0279	.0446	.0726
528	.0043	.0305	.0509	.0789
Calculated values of $\log(a_1/N_1)$ from these measurements				
Temp.	Alloy No. 2	No. 3	No. 4	No. 5
422	0.0070	-0.0465	-0.0540	-0.0305
471	.0095	-.0521	-.0548	-.0379
528	.0096	-.0579	-.0911	-.0474

TABLE VI (Continued)

		RUN 6			
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.857	0.605	0.372	0.164
Electromotive force in volts					
Temp.	Cell 12	13	14	15	
431	0.0041	0.0161	0.0034	0.0570	
479	.0045	.0175	.0361	.0620	
533	.0051	.0193	.0393	.0673	
577	.0056	.0207	.0420	.0717	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
431	0.0086	-0.0119	-0.0483	-0.0298	
479	.0070	-.0159	-.0540	-.0445	
533	.0035	-.0227	-.0620	-.0550	
577	.0009	-.0270	-.0680	-.0640	
		RUN 4			
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Cd (N_1)		0.859	0.478	0.316	0.127

motive-force values are recorded here. The electromotive force for Cell 13 has been obtained by assuming that the $\log(a_1/N_1)$ value for Alloy 3 is correctly given by interpolation from the smooth plot of the other $\log(a_1/N_1)$ values obtained from the other runs. Thus for Cell 13, $E = RT/nF [\log(a_1/N_1) + \log N_1]$. The measured values are as follows.

Temp. °C.	Cell 32	34	35	Log(a_1/N_1) for Alloy No. 3
473	-0.0222	0.0146	0.0423	-0.0470
532	-.0241	.0157	.0457	-.0540

Each electromotive-force value at the lower temperature represents the average of 16 actual readings. They are, therefore, quite reliable. Each of the values at 532° is an average of 7 readings. From these results the following electromotive forces are obtained by the method just described.

Temp. °C.	Cell 12	13	14	15
473	0.0042	0.0264	0.0410	0.0685
532	.0050	.0291	.0448	.0748

The corresponding calculated values for $\log(a_1/N_1)$ are

Temp. °C.	Alloy No. 2	No. 3	No. 4	No. 5
473	0.0095	-0.047	-0.053	-0.027
532	.0034	-.054	-.061	-.039

The point corresponding to Alloy No. 5 is entirely off the $\log(a_1/N_1)$ curve, but the other points from this run fall very close to this curve with an average deviation of 0.0005 at 473° and of 0.004 at 532°. When all the points from the 4 runs are examined the average deviation of these points from the accepted smooth curve is found to be 0.002 at 431°, 0.001 at 477° and 0.002

at 533°. This is about the magnitude of the effect produced by an uncertainty of 0.1 mv. The activities of the components of the system cadmium-bismuth are, therefore, known with considerable accuracy.

Table VII (A-C) records the interpolated values of $\log (a_1/N_1)$ and of $\log (a_2/N_2)$ at various mole fractions of cadmium. The results are of great interest, in that they show the remarkable behavior of the system, cadmium-bismuth, in deviating to a greater extent from the ideal solution [where $\log (a_1/N_1) = 0$] at high temperatures than at low. Cases of this kind are very rare. The system, cadmium-bismuth, is evidently very complex. It is possible that some tendency exists to form a weak compound, Cd_3Bi_2 , in the liquid state. Such a factor would reduce the activities of both components and would tend to annul the effect of any factor which produces abnormally large activities. When this system was investigated no compound between cadmium and bismuth had been reported in the literature from a study of freezing-point data. At the suggestion of the author, Mr. H. C. Betts of this Laboratory made a series of cooling curves on cadmium-bismuth alloys of about the composition corresponding to Cd_3Bi_2 . He discovered at 161° a slight break in the freezing-point curve, which indicates the existence of a weak compound. The existence of this compound is not surprising, since freezing-point diagrams show evidence of compounds corresponding to Zn_3Sb_2 and Cd_3Sb_2 .

The results are further summarized in Figs. 6 and 7. The initially high activity of each component when present in large excess is evidence that at such concentrations the internal pressure difference is the predominating factor. As the mole fractions of the two components become more nearly

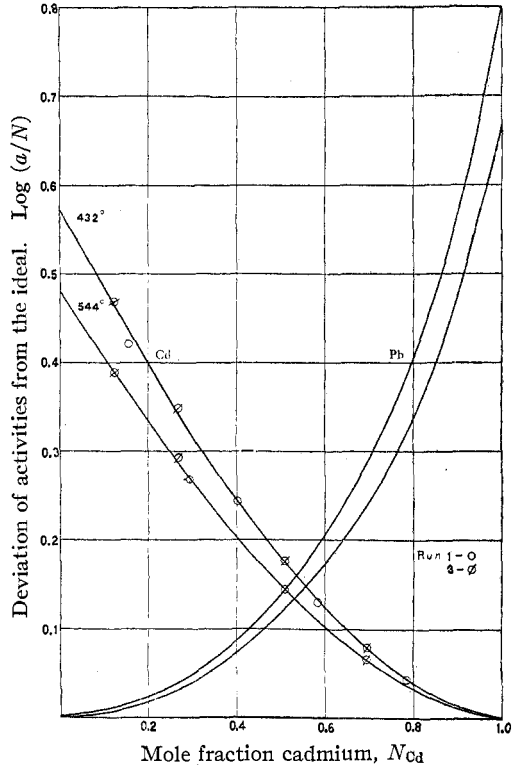


Fig. 4.—System, cadmium-lead. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

The results are further summarized in Figs. 6 and 7. The initially high activity of each component when present in large excess is evidence that at such concentrations the internal pressure difference is the predominating factor. As the mole fractions of the two components become more nearly

equal, their activities are abnormally reduced by formation of compounds in solution. The Duhem relation requires that when the $\log (a_1/N_1)$

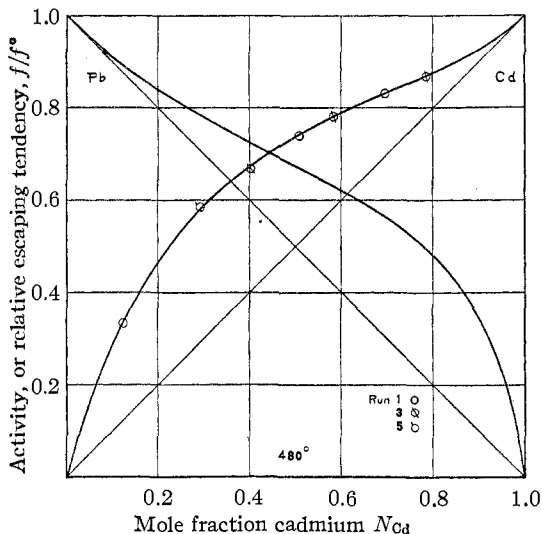


Fig. 5.—Activity curves for the system, cadmium-lead at 480°

curve shows a minimum there will be a corresponding maximum for the $\log (a_2/N_2)$ curve at the same composition. This is well brought out in Fig. 6. Similarly, when one curve shows a point of inflection the other must

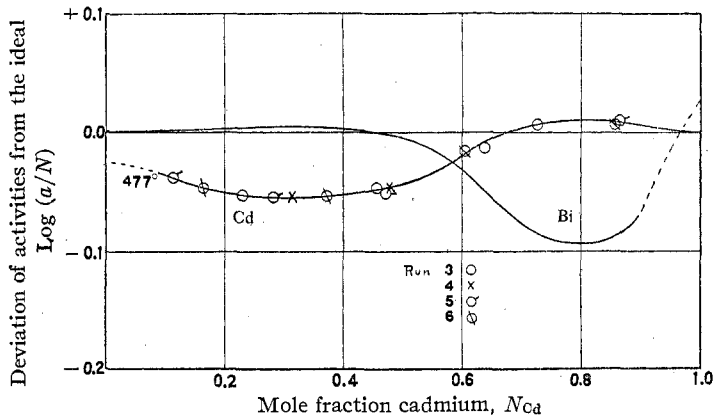


Fig. 6.—System, cadmium-bismuth. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

also change its curvature. In Fig. 6 the $\log (a_2/N_2)$ curve (for bismuth) inflects at about $N_{Cd} = 0.15$. Hence, the $\log (a_1/N_1)$ curve (for cadmium) has been drawn with an inflection at the same point, although unfortu-

TABLE VII
THE SYSTEM: CADMIUM-BISMUTH

A 431°					B 477°				
N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	-0.010	0.000	0.0000	1.000	-0.024	0.000	0.0000	1.000	1.0
.1	-.025	.095	.0008	0.902	-.036	.092	.0006	0.902	0.9
.2	-.039	.183	.0033	.806	-.050	.178	.0031	.806	.8
.3	-.048	.269	.0063	.710	-.055	.264	.0046	.708	.7
.4	-.048	.358	.0062	.609	-.053	.354	.0034	.605	.6
.5	-.039	.457	-.0013	.498	-.044	.452	-.0043	.495	.5
.6	-.014	.581	-.0300	.373	-.021	.572	-.033	.371	.4
.7	+.008	.714	-.0690	.256	+.004	.707	-.078	.251	.3
.8	+.0106	.82	-.0760	.168	+.010	.818	-.095	.161	.2
.9	+.006	.913	-.046	.090	+.006	.912	-.070	.085	.1
1.0	+.000	1.000	+.12	.000	+.000	1.000	+.024	.000	.0

C 533°					
N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	-0.030	0.000	0.0000	1.000	1.0
.1	-.046	.090	.0008	0.902	0.9
.2	-.060	.174	.0033	.806	.8
.3	-.064	.259	.0044	.707	.7
.4	-.061	.348	.0028	.604	.6
.5	-.052	.444	-.0050	.495	.5
.6	-.028	.563	-.035	.369	.4
.7	+.002	.704	-.091	.243	.3
.8	+.0085	.816	-.110	.155	.2
.9	+.0055	.912	-.091	.081	.1
1.0	+.000	1.000	+.010	.000	.0

nately no experimental point was obtained at concentrations of cadmium less than $N_{Cd} = 0.1$.

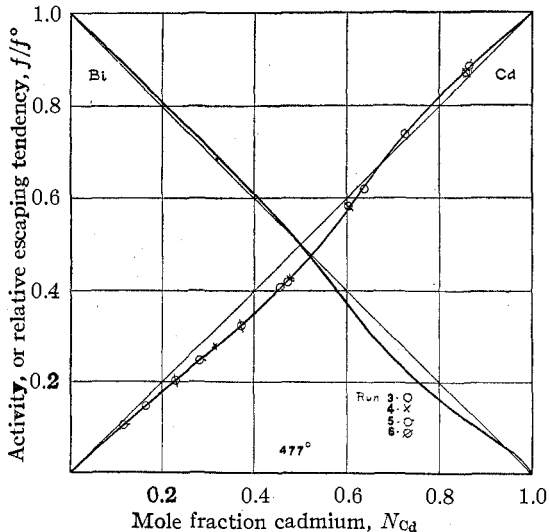


Fig. 7.—Activity curves for the system, cadmium-bismuth at 477°

The System: Zinc-Cadmium

Three independent runs were made on zinc-cadmium alloys and reliable electromotive-force measurements were obtained at 435°, 466° and 540°. The data follow. Each electromotive-force value is the average of 10 or more readings.

TABLE VIII
THE SYSTEM: ZINC-CADMIUM

RUN 1					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)		0.786	0.602	0.373	0.244
Electromotive force in volts					
Temp. °C.	Cell 12	13	14	15	
469	0.0037	0.0069	0.0125	0.0237	
539	.0042	.0080	.0153	.0291	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
469	0.054	0.127	0.259	0.291	
539	.052	.121	.238	.251	
RUN 2					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)		0.150	0.344	0.536	0.690
Electromotive force in volts					
Temp.	Cell 12	13	14	15	
436	0.0275	0.0136	0.0083	0.0058	
464	.0294	.0147	.0084	.0063	
541	.0367	.0182	.0105	.0068	
572	.0396	.0200	.0126	.0080	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
436	0.432	0.271	0.153	0.0786	
464	.421	.263	.156	.0750	
541	.368	.239	.141	.0769	
572	.351	.225	.121	.0657	
RUN 3					
Composition of alloy		No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)		0.848	0.687	0.456	0.251
Electromotive force in volts					
Temp.	Cell 12	13	14	15	
434	0.0021	0.0047	0.0170	
464	.0024	.0052	0.0129	.0186	
541	.0031	.00670235	
Calculated values of $\log(a_1/N_1)$ from these measurements					
Temp.	Alloy No. 2	No. 3	No. 4	No. 5	
434	0.0422	0.0958	0.359	
464	.0385	.0910	0.164	.347	
541	.0333	.0798310	

These $\log(a_1/N_1)$ values have been plotted against N_1 and smooth curves obtained. The average deviation of the experimental points

from the accepted curves is 0.004 at 435°, 0.003 at 466° and 0.003 at 540°. These correspond to an average accuracy of 0.2 mv.

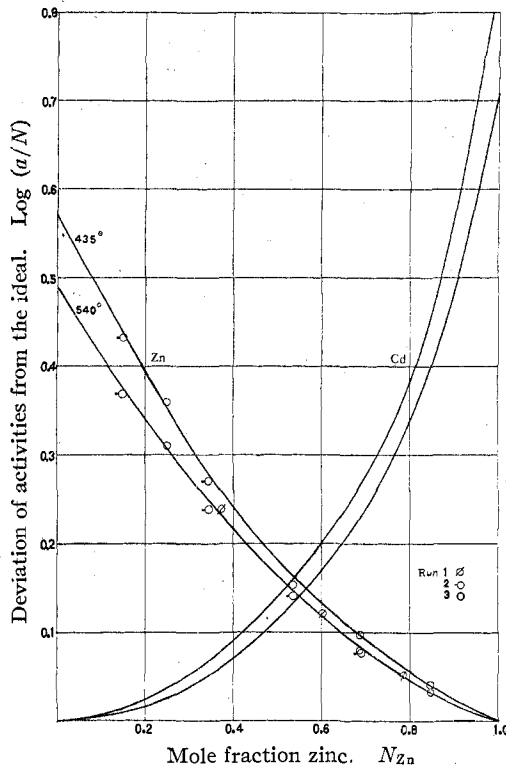


Fig. 8.—System, zinc-cadmium. Deviation from the laws of the perfect solution. The horizontal line $\log(a/N) = 0$ corresponds to Raoult's law

The smoothed-out values at even mole fractions are recorded in Table IX (A-C). The $\log a/N$ data for 540° and for 435° are further summarized in

TABLE IX
THE SYSTEM: ZINC-CADMIUM

A 435°					B 466°				
N_1	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	N_2
0.0	0.57	0.000	0.0000	1.000	0.55	0.000	0.000	1.000	1.0
.1	.482	.303	.0040	0.909	.46	.288	.005	0.910	0.9
.2	.395	.497	.0205	.838	.383	.483	.019	.835	.8
.3	.311	.615	.050	.784	.302	.600	.046	.780	.7
.4	.240	.695	.089	.740	.233	.684	.083	.725	.6
.5	.181	.758	.138	.685	.176	.750	.130	.675	.5
.6	.131	.811	.199	.635	.127	.805	.190	.620	.4
.7	.092	.865	.272	.560	.087	.855	.265	.550	.3
.8	.056	.910	.382	.48	.052	.900	.370	.470	.2
.9	.025	.950	.561	.365	.020	.945	.54	.35	.1
1.0	.000	1.000	.84	.000	.000	1.000	.80	.000	.0

TABLE IX (Continued)

C 540°					
N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	0.490	0.000	0.000	1.000	1.0
.1	.413	.260	.004	0.910	0.9
.2	.340	.440	.017	.830	.8
.3	.274	.565	.039	.765	.7
.4	.216	.660	.070	.705	.6
.5	.163	.730	.113	.650	.5
.6	.117	.785	.169	.590	.4
.7	.079	.840	.242	.525	.3
.8	.046	.890	.341	.440	.2
.9	.018	.940	.50	.32	.1
1.0	.000	1.000	.71	.00	.0

Fig. 8, while the activities of each component at 466° are plotted against the mole fraction of zinc in Fig. 9.

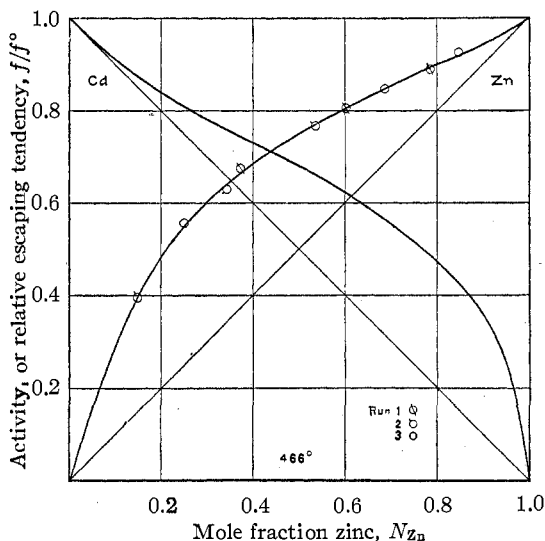


Fig. 9.—Activity curves for the system, zinc-cadmium at 466°

The System: Zinc-Tin

Three independent runs have been made on alloys of zinc with tin, and reliable results have been obtained at 431°, 466°, 539° and 570°. The data follow. Each electromotive-force value is the average of 10 or more readings.

When these $\text{log}(a_1/N_1)$ values are plotted against N_1 the points from Run 2 are found to fall uniformly lower than the points from the other two runs. This was to be expected, since in preparing the electrolyte for Run 2 no potassium hydroxide was added to neutralize the hydrogen chloride

liberated by hydrolysis of the fused chlorides. When the electrolyte was poured into the cell a small evolution of hydrogen took place. Since the zinc in these alloys would be preferentially oxidized by the hydrogen ion in the electrolyte, its mole fraction in the alloys would be reduced, the elec-

TABLE X
THE SYSTEM: ZINC-TIN

RUN 1				
Composition of alloy	No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)	0.845	0.583	0.384	0.221
Electromotive force in volts				
Temp. °C.	Cell 12	13	14	15
431	0.0024	0.0065	0.0138	0.0267
466	.0026	.0078	.0161	.0303
537	.0035	.0104	.0205	.0369
570	.0038	.0106	.0226	.0401
Calculated values of $\log(a_1/N_1)$ from these measurements				
Temp.	Alloy No. 2	No. 3	No. 4	No. 5
431	0.0389	0.1409	0.2183	0.2734
466	.0385	.1280	.1965	.2430
537	.0298	.1045	.1605	.1960
570	.0280	.0955	.1455	.1765
RUN 2				
Composition of alloy	No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)	0.142	0.310	0.473	0.721
Electromotive force in volts				
Temp.	Cell 12	13	14	15
467	0.0436	0.0220	0.0123	0.0050
537	.0523	.0276	.0161	.0068
Calculated values of $\log(a_1/N_1)$ from these measurements				
Temp.	Alloy No. 2	No. 3	No. 4	No. 5
467	0.253	0.209	0.157	0.074
537	.197	.165	.125	.058
RUN 3				
Composition of alloy	No. 2	No. 3	No. 4	No. 5
Mole fraction Zn (N_1)	0.173	0.497	0.644	0.780
Electromotive force in volts				
Temp.	Cell 12	13	14	15
432	0.0327	0.0088	0.0050	0.0029
467	.0364	.0102	.0061	.0035
541	.0443	.0135	.0078	.0045
Calculated values of $\log(a_1/N_1)$ from these measurements				
Temp.	Alloy No. 2	No. 3	No. 4	No. 5
432	0.294	0.178	0.120	0.067
467	.266	.165	.108	.060
541	.213	.137	.095	.052

tromotive forces obtained would be too high and the calculated values of $\log(a_1/N_1)$ would be too low. When these $\log(a_1/N_1)$ values from Run 2 are corrected by adding a constant factor of 0.010 at 466° and of 0.012

at 539° they fall very closely upon the smooth curve obtained from the data of the other two runs. The average deviation of all the experimental points from the accepted curve then becomes 0.001 at 431°, 0.001 at 466°, 0.003 at 539° and 0.000 at 570°.

The smoothed-out values of $\log(a_1/N_1)$ and the corresponding values of $\log(a_2/N_2)$ calculated by the Duhem relation are recorded in Table XI (A-D). Figs. 10 and 11 also summarize part of these data. The values from Run 2 are not shown in the plots.

TABLE XI
THE SYSTEM: ZINC-TIN

A 431°					B 466°				
N_1	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	N_2
0.0	0.339	0.000	0.0000	1.000	0.302	0.000	0.0000	1.000	1.0
.1	.310	.204	.0016	0.904	.276	.189	.0014	0.903	0.9
.2	.280	.380	.007	.815	.249	.355	.0062	.810	.8
.3	.248	.530	.018	.730	.220	.500	.015	.725	.7
.4	.213	.655	.037	.655	.192	.620	.032	.645	.6
.5	.176	.750	.068	.585	.160	.725	.058	.570	.5
.6	.136	.821	.117	.524	.124	.800	.102	.505	.4
.7	.097	.875	.191	.465	.088	.860	.170	.445	.3
.8	.058	.914	.308	.405	.053	.905	.274	.375	.2
.9	.024	.950	.506	.320	.022	.945	.459	.290	.1
1.0	.000	1.000	.76	.000	.000	1.000	.72	.000	.0
C 539°					D 570°				
N_1	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	$\log(a_1/N_1)$	a_1	$\log(a_2/N_2)$	a_2	N_2
0.0	0.240	0.000	0.0000	1.000	0.212	0.000	0.0000	1.000	1.0
.1	.221	.165	.0010	0.902	0.196	.157	.0008	0.902	0.9
.2	.202	.318	.0044	.808	.180	.303	.0037	.806	.8
.3	.181	.455	.011	.720	.162	.435	.010	.720	.7
.4	.158	.575	.024	.635	.142	.555	.021	.630	.6
.5	.132	.680	.045	.555	.117	.655	.041	.550	.5
.6	.103	.760	.080	.480	.090	.740	.074	.475	.4
.7	.073	.830	.136	.410	.062	.810	.127	.402	.3
.8	.0445	.885	.222	.333	.038	.875	.198	.315	.2
.9	.0185	.940	.379	.240	.016	.935	.325	.210	.1
1.0	.000	1.000	.60	.000	.000	1.000	.54	.000	.0

The form of the $\log(a_1/N_1)$ -curve for zinc in these alloys differs somewhat from that shown by the components of cadmium-tin, cadmium-lead, cadmium-zinc alloys. For these the $\log(a/N)$ curves are approximately though not exactly represented by a half-parabola, whereas for zinc in zinc-tin alloys the $\log(a_1/N_1)$ curve flattens out considerably in all alloys containing less than about 60% zinc. The limiting value of $\log(a_1/N_1)$ where $N_1 = 0$, is about one-half what it would be if the curve had remained parabolic over the whole range. The activity coefficient of tin, $\log(a_2/N_2)$, is also reduced in the same region, but the effect is not so apparent because the $\log(a_2/N_2)$ values are normally rather small for all alloys rich in tin. This reduction of the activities of zinc and tin in alloys rich in

tin may possibly be due to the formation of a weak compound in the liquid alloy. The freezing-point diagram shows no solid compound, but it might be mentioned that the electromotive-force method is a much more delicate means for determining activities than the average alloy freezing-point diagram now in existence.

Comparison of the Activity Curves for Various Alloys

Of the five liquid metal systems investigated, three exhibit simple type $\log(a/N)$ curves for which the activities of each component are greater than demanded by Raoult's law. These are cadmium-tin, cadmium-lead, and cadmium-zinc. The system zinc-tin also shows too high activities, but the curve is not quite so simple as in the three cases just mentioned. The system cadmium-bismuth is still more complicated. Certain amalgams also show abnormally high activities for each component. Thus the vapor pressure of mercury at 320° from amalgams of zinc, bismuth, gold, tin and lead, is abnormally high.^{2i,2j,2k}

If the internal pressure difference between the two components of an alloy is responsible for their abnormal increase in activity, there should be some parallelism between the values of these two quantities in various alloys.

The internal-pressures of liquid zinc, cadmium, tin, lead and bismuth can be estimated⁵ from existing surface-tension and density data⁴ on these metals. The values at 450° of the quantity $E_\sigma/V^{1/3}$ where E_σ represents the surface energy and V the molal volume, are as follows: zinc, 380; cadmium, 274; tin, 222; lead, 182; bismuth, 150. In Table XII values of $\Delta(E_\sigma/V^{1/3})$ for certain alloys are

⁵ Harkins, *Proc. Nat. Acad. Sci.*, 5, 566 (1919).

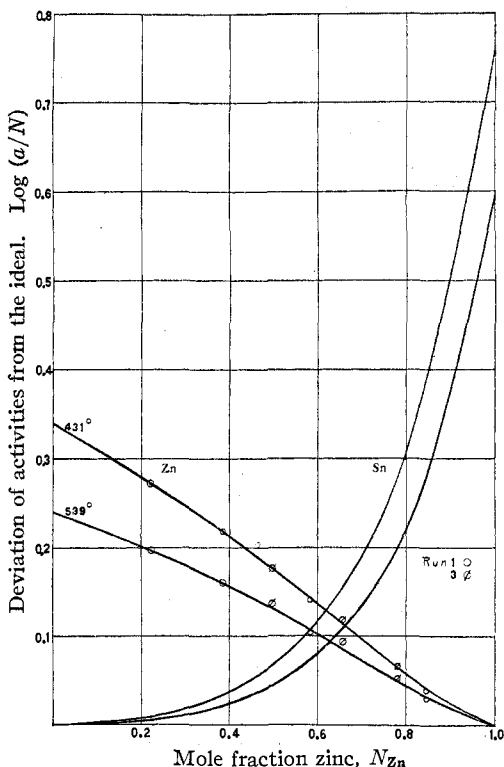


Fig. 10.—System, zinc-tin. Deviation from the laws of the perfect solution. The horizontal line $\log(a/N) = 0$ corresponds to Raoult's law

compared with the corresponding activity coefficients of cadmium and tin from these alloys.

TABLE XII
ACTIVITY COEFFICIENTS IN VARIOUS ALLOYS

Alloy	t °C.	Log(a/N) for Cd			Int. press. diff. $\Delta(E_\sigma/V^{1/3})$
		$N_{Cd}=0.0$	$N_{Cd}=0.1$	$N_{Cd}=0.2$	
Cd-Sn	483	0.28	0.228	0.185	52
Cd-Pb	480	.55	.455	.369	92
Cd-Zn	466	.80	.540	.373	106
		Log(a/N) for Sn			
		$N_{Sn}=0.0$	$N_{Sn}=0.1$	$N_{Sn}=0.2$	
Sn-Zn	466	0.72	0.459	0.274	158
Sn-Cd	483	.33	.250	.184	52

It will be observed that in the case of both the cadmium and the tin alloys there is a parallelism between the log (a/N) and the $\Delta(E_\sigma/V^{1/3})$ values. The two series are not strictly proportional, but there is enough evidence to show that a difference of internal pressure is a large factor in determining activities in liquid metal systems.

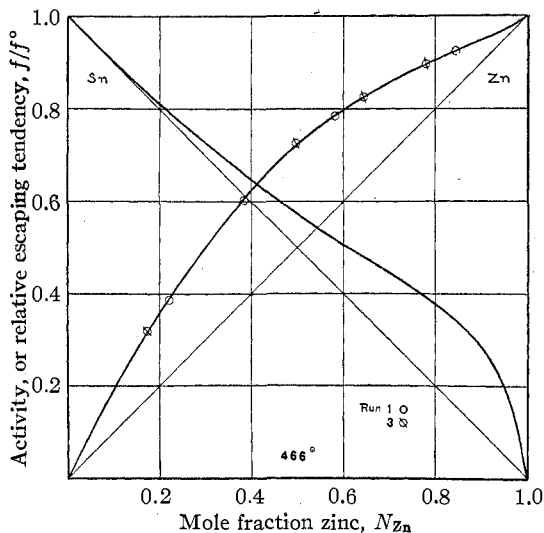


Fig. 11.—Activity curves for the system, zinc-tin at 466°

A similar comparison might be made of the escaping tendencies of zinc from zinc-cadmium and zinc-tin alloys, but the results would mean very little, since in the latter case the log (a/N) curve is quite irregular and is probably complicated by compound formation. The internal-pressure theory requires that solutions of zinc with lead, and zinc with bismuth show still greater positive deviations from ideal behavior than have been found in the case of cadmium-lead or zinc-cadmium solutions. The theory is

corroborated by the fact that both zinc-lead and zinc-bismuth alloys form two liquid phases. The critical mixing temperature, for these two systems are given in Landolt-Börnstein "Tabellen" as about 850° for zinc-bismuth and about 950° for zinc-lead. This temperature should be higher for zinc-bismuth if internal pressures were the only factor, but it is possible that the activities of both components are considerably reduced by compound formation just as has been found in cadmium-bismuth alloys. The fact that 2 phases are formed, however, is strong evidence in favor of the internal-pressure theory.

The Heat of Mixing

The heat of the reaction taking place in a galvanic cell may be readily calculated from measurements of the electromotive force of the cell at different temperatures. Calculations made using the electromotive-force data obtained in the present research, give the heat absorbed during the transfer of 1 mole of pure liquid metal from the pure state to an alloy of known composition. If, for example, H_1 is the molal heat content of pure zinc, and \bar{H}_1 is the partial molal heat content of zinc in a given zinc alloy, then according to the so-called Kirchhoff equation $\bar{H}_1 - H_1 = 2.303 RT^2 \frac{d \log (a_1/N_1)}{dT}$, where the values of $\log (a_1/N_1)$ are those given earlier in this article. This equation is applicable also to the second component of the alloy; thus $\bar{H}_2 - H_2 = 2.303 RT^2 \frac{d \log (a_2/N_2)}{dT}$. The Helmholtz equation may also be used to calculate the partial molal heat of dilution of that component with respect to which the cell is reversible. Thus, $\bar{H}_1 - H_1 = nF[T \cdot (dE/dT) - E]$, where n is the valence of the reacting ion, and F is the Faraday constant, namely 23074 calories per volt-equivalent. The quantity $\bar{H} - H$ has been defined as the relative heat content, \bar{L} , of one component of an alloy of some definite composition.⁶ The absolute values of H and of \bar{H} have no interest in the present connection; it is only the heat effect accompanying the reaction which is important.

The partial molal heats of dilution of the more electropositive component of each alloy system have been obtained in the two ways—by applying the Helmholtz equation to the individual electromotive values, and then plotting these heats and interpolating at even mole fractions, and also by using the Kirchhoff relation with the $\log (a/N)$ values at these even mole fractions. The heat values obtained by these two methods have been averaged and the results are recorded below. In general the agreement between the two sets of values was just about proportional to the average deviation of the experimental $\log (a/N)$ values from the accepted smooth curves. If these points had exactly fitted the $\log (a/N)$ curves there would

⁶ Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920).

of course have been no discrepancy between the 2 sets of heat values. The Kirchhoff equation is the only one applicable to the less electropositive component of the alloy.

The accuracy of the heat values depends upon the size of the temperature interval. For example, in the neighborhood of 500°, an error of 0.0001 volt in one of the electromotive-force values produces an uncertainty of 25 calories in the heat effect when the temperature interval is 140°, about 50 cal. when the temperature interval is 70°, and about 100 cal. when this interval is only 35°. Calculations of the partial molal heats of dilution for each component of the systems cadmium-tin, cadmium-lead, cadmium-zinc and zinc-tin have been made for two or three temperature intervals in the attempt to determine (1) the relation between the heat of mixing and the deviation from the laws of the perfect solution, and (2) how the heat of dilution changes with the temperature.

The heat values are recorded in Table XIII. In the first line it will be seen that when 1 mole of pure liquid cadmium is added to a very large amount of pure liquid tin at the same temperature, the heat absorbed amounts to 1360 calories. Similarly, if 1 mole of pure liquid cadmium is added to a very large amount of a cadmium-tin alloy in which the mole fraction of cadmium (N_{Cd}) is 0.3, only 830 calories will be absorbed. It will be noticed that certain values in the third column of Table XIII are in parentheses. These values are somewhat uncertain. All the values in this column are extrapolated from the data in the remaining columns.

TABLE XIII
SUMMARY OF PARTIAL MOLAL HEATS OF DILUTION, $\bar{H}-H$
IN CALORIES

Solute	In alloy	Temp. interval °C.	Mole fraction of the solute named										
			0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Cd	Cd-Sn	431-585	1360	1170	1000	830	650	480	320	190	100	40	0
		431-544	1400	1210	1030	840	650	460	300	180	80	30	0
		483-544	1470	1280	1100	920	740	560	410	270	140	40	0
Sn	Cd-Sn	431-585	1800	1450	1090	790	530	340	190	90	30	10	0
		431-544	1800	1480	1170	870	600	370	210	95	35	10	0
		483-544	(2500)	(1800)	1280	900	590	370	220	110	40	10	0
Cd	Cd-Pb	432-572	2150	1820	1510	1220	950	720	510	300	140	50	0
		480-544	2300	1960	1620	1280	1040	800	600	410	240	70	0
		432-572	3500	2580	1770	1160	720	440	270	150	70	15	0
Pb	Cd-Pb	480-544	3600	2660	1860	1250	820	550	350	220	120	45	0
		435-540	(2000)	1580	1260	1000	780	580	420	280	140	60	0
		466-540	(1900)	1490	1180	940	740	560	400	260	140	60	0
Zn	Zn-Cd	435-540	2500	1900	1380	980	650	460	320	220	140	70	0
		466-540	2500	1900	1400	1050	720	500	350	240	150	70	0
		431-570	2490	2220	1940	1650	1370	1110	840	600	350	140	0
Zn	Zn-Sn	466-539	2380	2120	1850	1580	1310	1060	800	560	340	140	0
		431-466	2560	2290	2020	1720	1420	1140	850	600	370	150	0
		431-570	4500	3340	2170	1340	850	530	310	160	70	20	0
Sn	Zn-Sn	466-539	4600	3060	1990	1300	840	510	300	150	70	20	0
		431-466	(4100)	3200	2340	1560	1000	620	370	190	70	20	0

Inspection of this table shows that in general the various sets of heat values, calculated from different temperature intervals, are concordant.

As a rule the discrepancies are not larger than the error of measurement. It must, therefore, be concluded that the change in the heat of dilution with temperature is fairly small.

The heat values given in the fourth column of Table XIII, under the heading "0.0," correspond to the heat absorbed when 1 mole of pure liquid A is added to a very large amount of pure liquid B. These particular heats of dilution bear a simple relation to the differences between the internal pressures of the two components, A and B. In order to show this relationship the values of Col. 4 are averaged and recorded in Table XIV together with the corresponding internal-pressure differences.

TABLE XIV

INTERNAL PRESSURE DIFFERENCE AND HEAT OF MIXING WHEN 1 MOLE OF LIQUID A IS ADDED TO A VERY LARGE AMOUNT OF LIQUID B

A	B	Heat absorbed $\bar{H}-H$ Cal.	Internal press. diff.		Ratio	
			$\Delta(E\sigma/V^{1/3})$	$\Delta(\gamma/V^{1/3})$	$(\bar{H}-H)/\Delta(E\sigma/V^{1/3})$	$(\bar{H}-H)/\Delta(\gamma/V^{1/3})$
Cd	Sn	1400± 60	52	58	27.0±1.2	24.1±1.0
Cd	Pb	2200± 50	92	93	24.0±0.6	23.6±0.6
Cd	Zn	1950±200	106	94	18.4±1.9	20.8±2.1
Sn	Cd	1800± 50	52	58	34.6±1.0	31.0±0.9
Sn	Zn	4550±150	158	152	29.0±1.0	30.0±1.0

In this table two criteria have been used for estimating internal pressure. The ratios given in the last two columns are approximately constant, being especially so in the last column. The discrepancies in these ratios are no greater than the uncertainty of the internal-pressure values themselves. It may be concluded, therefore, that in liquid alloys which are not complicated by compound formation between the components, the heat of mixing is directly proportional to the internal-pressure difference. A comparison similar to that in Table XIV might be made in the case where zinc is the solute, that is, in zinc-tin and zinc-cadmium alloys. The results, however, would mean very little, since the activity curves of zinc in zinc-tin alloys are not of the simple type, and very probably the internal-pressure difference is in this case not the only factor which operates to produce departures from Raoult's law.

It has been shown that where an alloy solution is free from compounds between the components, both the deviations from Raoult's law and the partial molal heats of mixing are proportional to differences of internal pressure. It follows, therefore, that these first two quantities are closely related. For a given solute in different liquid alloy systems the partial molal heat of dilution is very nearly directly proportional to the deviation of this solute from Raoult's law.

This research was undertaken at the suggestion of Professor Joel H. Hildebrand. I wish in conclusion to express my sincere appreciation of his personal kindness and stimulating counsel throughout the investigation.

Summary

Accurate determinations of the activities of liquid zinc, cadmium, tin, lead and bismuth in five binary-alloy systems have been made at temperatures ranging from 400° to 600°.

With the single exception of the system, cadmium-bismuth, which gave a very complicated type of activity curve, all the alloy systems investigated showed escaping tendencies or activities greater than required by Raoult's law. In regard to departures from this ideal solution law, and also in regard to the heats of mixing, the results of this research furnish strong evidence for the validity of the internal-pressure theory as applied to liquid metal systems.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE EFFECT OF PRESSURE ON OVERVOLTAGE

BY S. J. BIRCHER AND WILLIAM D. HARKINS

RECEIVED SEPTEMBER 6, 1923

In 1919 MacInnes and Adler¹ published a theory of overvoltage based in part upon the theory of Möller² and in part upon the then unpublished work of Goodwin and Wilson. Since then the latter have published their data,³ which indicate that overvoltage increases as the pressure is reduced, and with extreme rapidity at low pressure.

In 1914, Harkins and Adams⁴ determined the effect of pressure on the hydrogen overvoltage of mercury. They state, "Keeping the current constant, the pressure in the hydrogen cell may be raised from one atmosphere to three and reduced to twenty millimeters, without producing any significant change in the potential between the cathode and the hydrogen electrode. In such a system the potential values are never absolutely constant. They may undergo a progressive gradual change or be subject to slight eccentric variations, but such changes can in no way be correlated with changes in pressure." Newbery found that oxygen overvoltage is practically constant in the range between 1 and 100 atmospheres.⁵

It will be noted that the conclusions reached by Goodwin and Wilson, and by Harkins and Adams are quite contradictory, but it is thought that the data and discussion herein contained, which are much more closely in agreement with the latter, indicate how both conclusions have been reached.

¹ MacInnes and Adler, *THIS JOURNAL*, **41**, 194 (1919).

² Möller, *Z. physik. Chem.*, **65**, 226 (1909).

³ Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **11**, 172 (1921).

⁴ Harkins and Adams, *Thesis*, Library of the University of Chicago, 1914.

⁵ Newbery, *J. Chem. Soc.*, **105**, 2419 (1914).