present in appreciable amounts is contrary to the findings of Irving and Rosotti[9] who were the only other workers to observe the existence of the fourth complex. In all previous studies, any small error in the determination of the equilibrium concentration of indium and/or a graphically determined quantity might be amplified on successive graphical treatment with the result that the information on the highest complexes would be least accurate. The spectrophotometric method, however, is unique in that a direct measure of the fourth complex in aqueous solution is possible. The formation constants for the first three complexes obtained in this investigation agree reasonably well with those of previous authors.

The evidence was so clear-cut for the four monomeric species that it was not necessary to consider the possibility of dimerization. The dimeric species observed by Irving and Rossotti were found only for "macro" amounts of indium in high hydrobromic acid concentrations, conditions not strictly comparable to ours.

The fact that Woodward and Bill,[16] from a study of the Raman spectra of indium salts in the presence of a large excess of bromide, concluded no tetrahedral $InBr_4^-$ ion to be present in aqueous solution, does not necessarily contradict the present findings. Indium frequently shows hexacoördination, and one would expect to find $[In(H_2O)_2Br_4]^-$ ions in solutions such as ours. The case of iron is a pertinent analogy. It is extracted from hydrochloric acid solutions by ether and other solvents in the form of $HFeCl_4$, which is described as tetracoördination,[17] although some water is also extracted. The stoichiometric solubility of KCl in anhydrous ethyl acetate solutions of $FeCl_3$ to form the compound $KFeCl_4$ appears to be a clean-cut example of tetracoördination of iron[18]; yet in aqueous media, the octahedral character of ferric complexes is beyond question.[19]

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission.

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[CONTRIBUTION FROM THE DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Electrode Potential Studies of Liquid–Solid Equilibrium in Zn–Cd and Zn–In Alloys

BY R. W. BOHL[1] AND V. D. HILDEBRANDT

RECEIVED DECEMBER 14, 1956

Thermodynamic properties of liquid alloys were determined in binary Zn–Cd and Zn–In alloys by the measurement of electrode potentials of galvanic cells of the type: Zn(liq)/$ZnCl_2$(in KCl–LiCl liq)/Zn(in liq soln.). Measurements were carried out over a range of temperatures from 420 to 530°. Liquid–solid phase equilibrium was calculated by finding the temperature at which activities of zinc in the solid state and in liquid alloys were equal. The activity of zinc in the solid was calculated from heat of fusion and heat capacity data for pure zinc. The e.m.f. data were used in turn to calculate the heat of fusion of pure zinc, based on published values of liquidus point. Values thus determined showed much less scatter than published values based on calorimetric techniques. The properties of the liquid alloys were examined with regard to solution theory, and Zn–Cd alloys were shown to closely approach regular behavior, while Zn–In alloys showed some deviation from this behavior. Both systems showed positive deviations from Raoult's Law, and positive heats of solution over the entire composition range.

Introduction

Electrode potential studies have long been used to evaluate thermodynamic properties of solutions, but this technique has seldom been applied to the study of phase equilibrium in metal systems. Early applications of electrode potential studies to metal systems by Lindeck[2] and Richards[3] were limited to the study of thermodynamic properties of amalgams. Later, Taylor[4] and Hildebrand[5] used the principles of e.m.f. measurements in studying the thermodynamics of liquid metal solutions. Seltz and his co-workers[6] were among the first to apply the technique to the problem of phase equilibrium in binary metal systems. An excellent review of recent experimental results, techniques, and methods of calculation in this field is given by Dunkerley and Mills.[7]

In this investigation, accurate and precise e.m.f. measurements were made on galvanic cells of liquid alloys of the binary systems Zn–Cd and Zn–In, and the data used to calculate the thermodynamic properties of the liquid alloys and determine the liquid–solid equilibrium. The cells were of the type

$$Zn(liq)/Zn^{++}/Zn(in\ liq\ soln.) \qquad (1)$$

If the cell reaction, Zn(liq) → Zn(in liq soln.), is reversible and unique, and only Zn^{++} ions carry the current, the following relation applies to the reaction

$$\Delta \bar{F}_{Zn} = -2E\mathfrak{F} \qquad (2)$$

where $\mathfrak{F}$ is the Faraday constant and E is the e.m.f. in volts. If pure liquid zinc is taken as the standard state, the activity of Zn, the more electropositive component of the cell, can be calculated

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[1] Abstracted from a thesis submitted to the Graduate College of the University of Illinois, June, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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TABLE I

ELECTROMOTIVE FORCE DATA

T, °C.	N_{n}	E.m.f. (mv.)	N_{Zn}	E.m.f. (mv.)	N_{Zn}	E.m.f. (mv.)	N_{Zn}	E.m.f. (mv.)	N_{Zn}	E.m.f. (mv.)
Zinc–cadmium system										
422	0.970	0.797	0.939	1.57	0.906	2.31	0.873	2.89	0.837	3.69
435		.830		1.62		2.38		3.01		3.83
457		.863		1.69		2.49		3.16		4.03
468		.874		1.73		2.54		3.24		4.09
483		896		1.77		2.62		3.33		4.27
490		.914		1.79		2.63		3.39		4.29
513		.939		1.85		2.73		3.53		4.58
Curve	$E = 0.0016T + 0.14$		$E = 0.0032T + 0.22$		$E = 0.0049T + 0.26$		$E = 0.0069T - 0.01$		$E = 0.0084T + 0.21$	
dE/dT	1.6×10^{-3} mv./°		3.2×10^{-3}		4.9×10^{-3}		6.9×10^{-3}		8.4×10^{-3}	
424	0.760	5.06	0.679	6.12	0.584	7.37	0.482	9.37		
442		5.14		6.40		7.77		9.90		
462		5.43		6.68		8.22		10.51		
473		5.55		6.89		8.51		10.91		
486		5.63		7.02		8.70		11.18		
513		5.89		7.42		9.27		11.96		
Curve	$E = 0.0097T - 0.92$		$E = 0.0145T - 0.02$		$E = 0.0214T - 1.68$		$E = 0.0293T - 3.04$			
dE/dT	9.7×10^{-3}		14.5×10^{-3}		21.4×10^{-3}		29.3×10^{-3}			
421	0.365	12.70	0.301	15.13	0.233	19.02	0.161	25.75	0.084	39.98
432		13.15		15.68		19.68		26.59		41.19
450		13.83		16.54		20.78		28.00		43.15
464		14.45		17.24		21.60		29.04		44.58
477		15.01		17.91		22.43		30.09		45.96
498		15.83		18.93		23.69		31.70		48.15
515		16.56		19.82		24.81		33.13		50.07
529		17.20		20.61		25.78		34.38		51.69
Curve	$E = 0.0414T - 4.76$		$E = 0.0512T - 6.93$		$E = 0.0621T - 7.17$		$E = 0.0791T - 8.60$		$E = 0.1067T - 4.91$	
dE/dT	41.4×10^{-3}		52.1×10^{-3}		62.1×10^{-3}		79.1×10^{-3}		106.7×10^{-3}	
Zinc–indium system										
423	0.971	0.69	0.940	1.26	0.909	1.76	0.875	2.24	0.841	2.51
434		.70		1.30		1.80		2.30		2.61
448		.72		1.37		1.84		2.38		2.70
467		.75		1.41		1.90		2.49		2.85
478		.76		1.43		1.99		2.56		2.97
494		.79		1.47		2.02		2.65		3.09
508		.80		1.51		2.13		2.76		3.24
517		.82		1.51		2.11		2.78		3.32
Curve	$E = 0.0013T + 0.14$		$E = 0.0028T + 0.09$		$E = 0.0043T - 0.10$		$E = 0.0057T - 0.17$		$E = 0.0085T - 1.10$	
dE/dT	1.3×10^{-3} mv./°		2.8×10^{-3}		4.3×10^{-3}		5.7×10^{-3}		8.5×10^{-3}	
424	0.803	3.10	0.725	3.81	0.638	4.31	0.540	5.42	0.430	7.25
441		3.27		4.05		4.67		5.93		7.96
456		3.44		4.28		4.97		6.42		8.63
471		3.50		4.47		5.28		6.80		9.18
491		3.72		4.77		5.66		7.38		10.02
505		3.88		5.00		5.99		7.83		10.65
511		3.98		5.14		6.18		8.07		10.90
524		4.05		5.27		6.38		8.38		11.44
Curve	$E = 0.0096T - 0.98$		$E = 0.0151T - 2.62$		$E = 0.0211T - 4.65$		$E = 0.0299T - 7.25$		$E = 0.0420T - 10.56$	
dE/dT	9.6×10^{-3}		15.1×10^{-3}		21.1×10^{-3}		29.9×10^{-3}		42.0×10^{-3}	
424	0.370	8.96	0.304	11.47	0.238	15.33	0.165	22.30	0.086	36.75
434		9.47		12.08		16.06		23.21		38.52
446		10.07		12.79		16.92		24.24		39.83
458		10.56		13.36		17.62		25.25		41.25
474		11.46		14.41		18.90		26.76		43.29
493		12.37		15.51		20.30		28.50		45.58
513		13.39		16.79		21.72		30.23		47.84
526		14.13		17.65		22.76		31.53		49.50
Curve	$E = 0.0513T - 12.82$		$E = 0.0607T - 14.30$		$E = 0.0739T - 16.05$		$E = 0.0914T - 16.48$		$E = 0.1201T - 13.62$	
dE/dT	51.3×10^{-3}		60.7×10^{-3}		73.9×10^{-3}		91.4×10^{-3}		120.1×10^{-3}	

for the entire composition range from the relation

$$\ln a_{\text{Zn}} = \Delta\bar{F}_{\text{Zn}}/RT \qquad (3)$$

The activity of the second component of the system can then be determined by graphical integration of the Gibbs–Duhem equation

$$\log(a_2/N_2) = -\int_{N_{\text{Zn}}=0}^{N_{\text{Zn}}} (N_{\text{Zn}}/N_2)\log(a_{\text{Zn}}/N_{\text{Zn}}) \qquad (4)$$

If measurements are carried out over a sufficient temperature range, the slope of the e.m.f. *vs.* temperature curve can be established, and the enthalpy of the cell reaction can be calculated by the Gibbs–Helmholtz equation

$$T(\mathrm{d}E/\mathrm{d}T) = E - \Delta H/2\mathfrak{F} \qquad (5)$$

where $H = \bar{H}_{\text{Zn}} - H_{\text{Zn}}^{\circ}$, and is usually designated as $\bar{L}_{\text{Zn}}$.

Graphical integration again facilitates calculation of the partial molar enthalpy of the second component of the cell, $\bar{L}_2$

$$\bar{L}_2 = -\int_{N_{\text{Zn}}=0}^{N_{\text{Zn}}} (N_{\text{Zn}}/N_2)\mathrm{d}\bar{L}_{\text{Zn}} \qquad (6)$$

TABLE II

THERMODYNAMIC PROPERTIES AT 470°

Zinc–cadmium system

N_{Zn}	$\overline{\Delta F}_{Zn}$	$\overline{\Delta F}_{Cd}$	$\bar{L}_{Zn}$	$\bar{L}_{Cd}$	ΔH^M	$\overline{\Delta S}_{Zn}$	$\overline{\Delta S}_{Cd}$	$\bar{S}^{xs}_{Zn}$	$\bar{S}^{xs}_{Cd}$	$\bar{F}^{xs}_{Zn}$	$\bar{F}^{xs}_{Cd}$	F^{xs}
0.084	−2087	− 117	1578	10	141	4.93	0.17	0.01	0.00	1572	13	144
.161	−1364	− 213	1313	43	247	3.60	.34	− .03	− .01	1337	45	253
.233	−1016	− 297	1095	98	330	2.84	.53	− .05	.00	1136	95	337
.301	− 810	− 366	906	171	392	2.31	.72	− .08	.01	964	162	404
.365	− 678	− 435	741	257	433	1.91	.93	− .09	.03	812	234	445
.482	− 495	− 568	501	442	470	1.34	1.36	− .09	.05	583	403	490
.584	− 386	− 694	340	628	460	0.98	1.78	− .09	.04	408	601	488
.679	− 315	− 816	220	826	414	.72	2.21	− .05	− .05	257	862	451
.760	− 253	−1010	144	1005	351	.53	2.72	− .02	− .12	152	1131	387
.837	− 191	−1236	82	1210	271	.37	3.29	.02	− .31	72	1442	295
.873	− 149	−1473	61	1341	224	.28	3.79	.01	− .16	52	1572	245
.906	− 117	−1747	43	1518	182	.22	4.39	.02	− .31	29	1744	190
.939	− 80	−2212	27	1800	135	.14	5.40	.01	− .15	13	1917	129
.970	− 40	−3068	14	2165	79	.07	7.05	.01	.08	5	2109	68

Zinc–indium system

N_{Zn}	$\overline{\Delta F}_{Zn}$	$\overline{\Delta F}_{In}$	$\bar{L}_{Zn}$	$\bar{L}_{In}$	ΔH^M	$\overline{\Delta S}_{Zn}$	$\overline{\Delta S}_{In}$	$\bar{S}^{xs}_{Zn}$	$\bar{S}^{xs}_{In}$	$\bar{F}^{xs}_{Zn}$	$\bar{F}^{xs}_{In}$	F^{xs}
0.086	−1973	− 122	2142	11	193	5.54	0.18	0.67	0.00	1657	10	151
.165	−1221	− 225	1911	47	355	4.21	.37	.63	.01	1437	41	272
.238	− 862	− 317	1670	108	480	3.41	.57	.56	.03	1256	85	364
.304	− 656	− 390	1424	190	565	2.80	.78	.43	.06	1101	144	435
.370	− 521	− 460	1237	305	649	2.37	1.03	.39	.11	948	221	490
.430	− 423	− 525	1016	437	686	1.94	1.29	.26	.17	823	305	531
.540	− 314	− 629	711	723	722	1.38	1.82	.16	.28	596	518	560
.638	− 243	− 728	483	1047	688	0.98	2.39	.09	.37	422	773	549
.725	− 207	− 799	311	1426	618	.70	2.99	.06	.42	268	1109	499
.803	− 164	− 947	165	1892	505	.44	3.82	.00	.59	161	1449	415
.841	− 134	−1085	158	2116	471	.39	4.31	.05	.66	123	1626	362
.875	− 116	−1192	79	2338	360	.26	4.75	− .01	.62	80	1883	305
.909	− 89	−1417	58	2570	287	.20	5.37	.01	.61	52	2119	240
.940	− 65	−1718	31	2827	197	.13	6.12	.01	.53	25	2445	170
.971	− 35	−2382	10	3339	108	.06	7.70	.00	.67	9	2825	92

The partial molar entropies of the reactions can be calculated from the relationship

$$\Delta \bar{F}_i = \Delta \bar{H}_i - T\Delta S_i \qquad (7)$$

The integral molar quantities can be calculated from the partial molar functions by means of the general relation

$$G = N_1G_1 + N_2G_2 \qquad (8)$$

Experimental

The alloys studied were prepared from high purity metal obtained from commercial sources. The electrolyte, consisting of an eutectic mixture of potassium and lithium chlorides to which was added about 5% zinc chloride, was prepared from reagent grade chemicals.

The cell consisted of a water-cooled brass top sealed with black wax to an outer 64 mm. Pyrex tube. The top brass fitting was provided with openings through which seven electrodes could be placed in addition to a thermocouple well and an opening to a vacuum system. The alloy electrodes were contained in bulbs prepared from 13 mm. Pyrex tubing with tungsten wire leads sealed in 3 mm. tubing. The cell was assembled so that the electrode containers could be moved from the water-cooled section of the cell into the electrolyte without breaking the vacuum on the cell.

The cell was heated in a furnace consisting of a 5-in. i.d. Alundum core non-inductively wound with Kanthal, and surrounded by 3 inches of Sil-o-cel insulation.

A steel pot containing a low melting nitrate–nitrite salt bath was placed inside the Alundum core, and the cell was immersed in this bath to a depth near the water-cooled section. This arrangement provided very uniform heating of the cell, and the large thermal mass of the furnace protected against temperature fluctuations. The temperature of the furnace was controlled by a variable transformer. The water cooled top of the cell which projected out of the furnace was maintained at ambient temperatures. Thermocouples in the cell and at various positions in the furnace salt bath checked within 1°, ensuring against the presence of thermal gradients.

With seven electrodes, e.m.f. measurements between five alloys and a pure zinc electrode could be taken simultaneously; the seventh was a pure zinc electrode permitting measurement of the e.m.f. between two pure zinc electrodes. This measurement provided a check against spurious readings due to changes in electrolyte composition, thermal gradients, etc.

Tungsten leads from the electrodes were connected through a selector switch to a L and N Type K-2 potentiometer. The vacuum was provided by a mechanical pump operating through a pressure regulator. The system contained a three-way valve for admitting helium to the system.

The procedure followed in preparing the alloys consisted first of melting the as received metals under vacuum and casting them into sticks. The alloys were then weighed out, sealed under vacuum in Pyrex tubes, and again melted. The alloys thus prepared were cut into pieces for charging into the electrode containers described above. Weight checks made after alloying and after the experimental runs were completed showed a negligible change, and the analyses given are the as weighed analyses.

The electrolyte was melted in an open beaker to which a small pellet of zinc was added, and then cast into a 57 mm. Pyrex tube which fit inside the cell. The use of this inner cell was a precaution taken to avoid the danger of cracking the outer cell.

The cell was assembled with the electrode bulbs positioned in the water-cooled section of the cell. This assembly was placed in the salt pot furnace at a temperature just under the melting point of the electrolyte under a vacuum of 20 μ for a period of ten days prior to the actual experimental run in order to out-gas and desiccate the electrolyte and break up any complex chlorate ions which may have been present.

When the period of electrolyte desiccation was complete, the temperature of the furnace was raised to about 450° and the electrodes lowered from the cold zone into the molten electrolyte without breaking the vacuum on the system. The pressure regulator was set at about 8 mm. and retained for one hour after the alloys were melted to remove any dissolved gases. Helium was then flushed through the cell several times before the cell, containing about one-half atmosphere of helium, was sealed from the vacuum system. The cell was held overnight at constant temperature to attain equilibrium before readings were begun. Readings were repeated at each temperature at 10 minute intervals until a constant e.m.f. was obtained for each alloy. The temperature of the cell was then changed and the process repeated. Readings were made over a temperature range of 420 to 530°.

As a test of reversibility of the cell reaction, data were taken on both heating and cooling cycles. Readings on heating and cooling were as reproducible as were the readings at constant temperature; *i.e.*, within 0.02 mv. This reproducibility is taken as an excellent criterion of reversibility. The e.m.f. measured between the two pure zinc electrodes was 0.00 ± 0.03 mv. for all runs.

Discussion of Results

The e.m.f. measured between pure zinc and a series of Zn–Cd and Zn–In alloys as a function of temperature is given in Table I. These data lay on straight lines within the experimental accuracy of the readings. The equations of the lines were calculated by the method of least squares, and from the equations dE/dT and the e.m.f. at particular temperatures were determined. Subsequent calculations of thermodynamic properties were based on these values. Figures 1 and 2 show the activities of the components as a function of composition, while Table II gives the values of selected thermodynamic properties calculated at 470° about midway in the temperature range investigated. Both systems studied show positive deviation from Raoult's law, and positive heats of mixing.

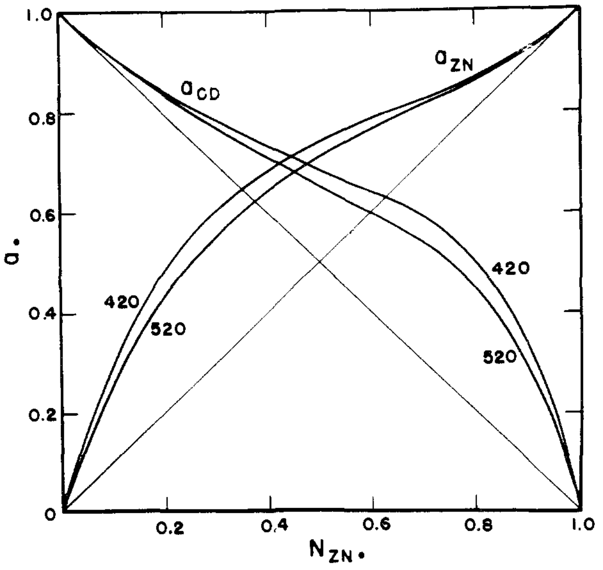

Fig. 1.—Activity *vs.* atom fraction for Zn–Cd alloys at 420 and 520°.

The liquid–solid equilibrium was determined by finding the temperature at which the activity of zinc in the liquid phase equalled that in the solid. A graphical solution was obtained by plotting

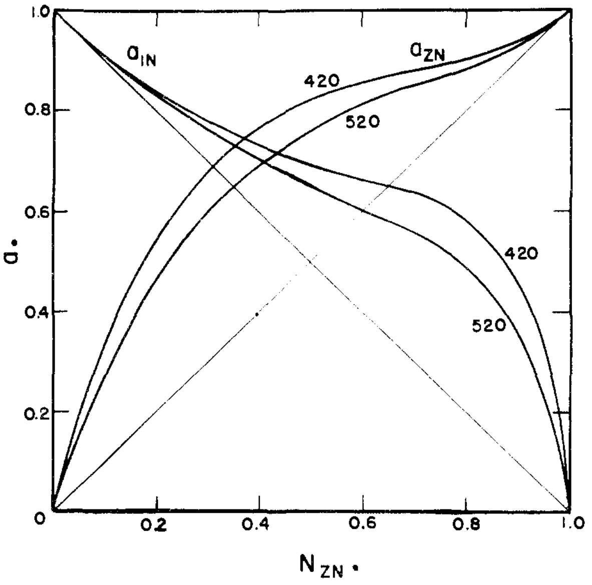

Fig. 2.—Activity *vs.* atom fraction for Zn–In alloys at 420 and 520°.

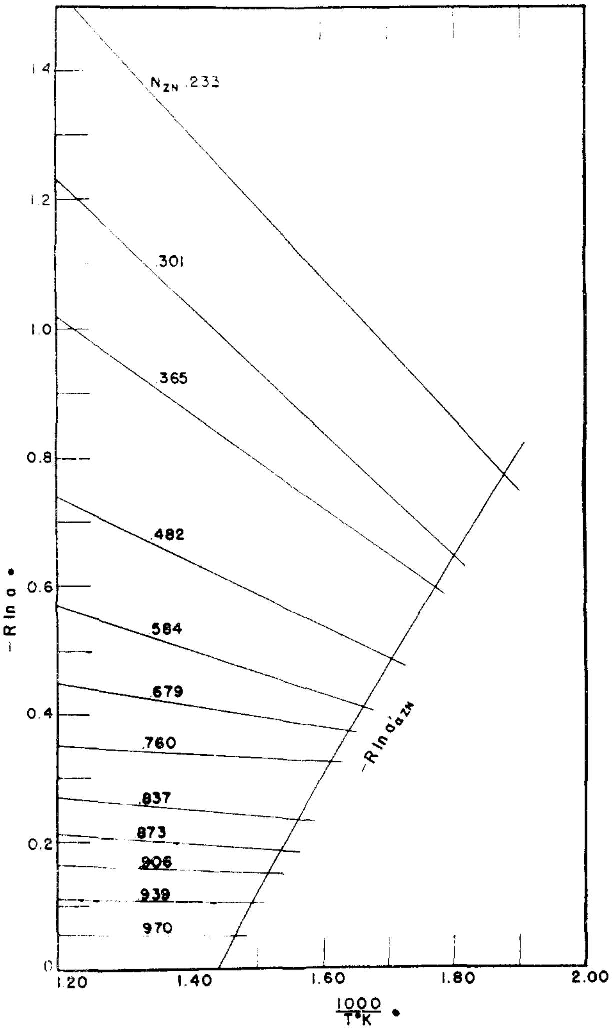

Fig. 3.—Plot of $-R \ln a$ *vs.* $1/T$ to determine Zn-rich liquidus points in Zn–Cd system.

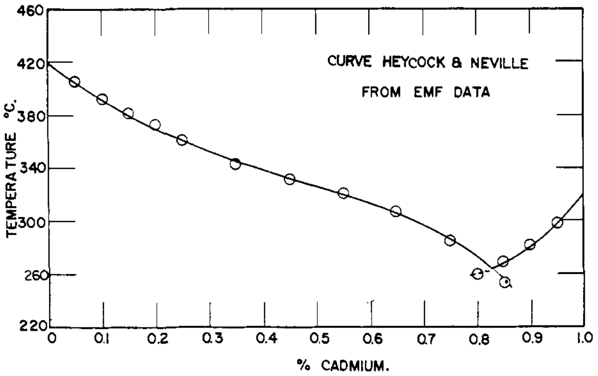

Fig. 4.—Comparison of calculated liquidus points in Zn–Cd system with data of Heycock and Neville.

$-R \ln a_{\mathrm{Zn}}$ against $1/T$. Since, according to the Gibbs–Helmholtz equation

$$\frac{\mathrm{d}(\Delta F/T)}{\mathrm{d}(1/T)} = -\Delta H \text{ and } \Delta F/T = -R \ln a_{\mathrm{Zn}} \quad (9)$$

such a plot should yield a straight line if ΔH is constant over the temperature range considered.

Values of $-R \ln a_{\mathrm{Zn}}$ for the liquid alloys are readily calculated from the e.m.f. data. The value of $-R \ln a'_{\mathrm{Zn}}$ (the prime indicates the solid phase) can be calculated from available thermodynamic data by application of another form of the Gibbs–Helmholtz equation to the reaction Zn(liq) → Zn(solid)

$$\mathrm{d}(\Delta F/T) = -(\Delta H/T^2)\,\mathrm{d}T \quad (10)$$

Using specific heat and heat of fusion data for pure zinc, this expression can be evaluated as

$$\Delta F/T = -7.6551 \log T + 0.2256 \times 10^{-2}\, T - 0.0023 \times 10^{-4} T^2 + 287.1/T + 19.8781 \quad (11)$$

The activity calculated by this expression must be multiplied by the composition of the α-solid–solution zinc phase to correct for the small amount of solubility which zinc has for the solute element. This correction assumes that Raoult's law is obeyed in the solid phase—a reasonable assumption in such a dilute solution. The solid solubility data for the Zn–Cd system were taken from the work of Stockdale,[8] and for the Zn–In system from Rhines and Grobe.[9]

The method is illustrated in Fig. 3 for the determination of the Zn-rich liquidus in the Zn–Cd system. Curves of $-R \ln a$ for the liquid alloys were extrapolated until they intersect the curve for the solid phase, the points of intersection giving the temperatures of the liquidus points.

Good agreement has been obtained with the generally accepted Zn–Cd liquidus of Heycock and Neville[10] as determined by thermal analysis. Figure 4 shows their curve, and the liquidus points calculated from the e.m.f. data are shown as experimental points. The comparative eutectic temperatures and compositions are 266° and 82.5% Zn by Heycock and Neville, and 265° and 82.5% calculated from these data as the intersection of the Zn-rich and Cd-rich liquidus curves.

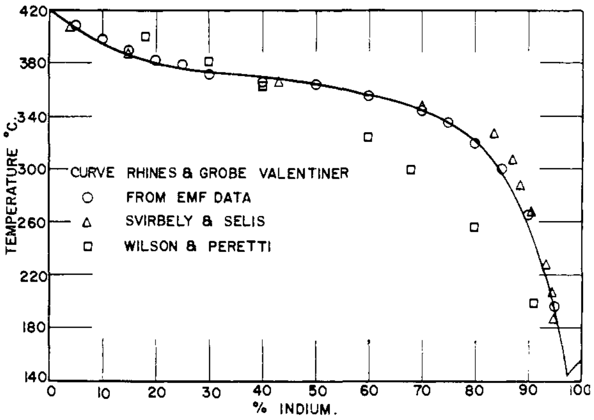

Fig. 5.—Comparison of calculated liquidus points in Zn–In system with data from other investigators.

The In–Zn phase diagram has been determined by Rhines and Grobe,[9] Valentiner,[11] Wilson and Peretti,[12] and Svirbely and Selis.[13] The curve shown in Fig. 5 is drawn from the data of the first two references, and represents the most widely accepted values. Values from the latter two investigations as well as from this study are shown as plotted points in the figure. Again the liquidus determined from these data agrees very well with the published values of the other investigators.

The results of Svirbely and Selis were also based on e.m.f. studies. In their work, e.m.f. data were taken below the melting point of Zn, with pure solid Zn as one electrode (Type II cells) as well as above the melting point (Type I cells) as in this study. The results of their work agree quite well with this study, although a different procedure requiring a more complicated graphical analysis was followed in the liquidus determinations. In their work the a_{Zn} in pure solid zinc and in liquid alloys was calculated with pure liquid Zn as the standard state. Phase equilibrium was then determined by simultaneous solution of plots of a_{Zn} *vs.* temperature for solid Zn and a_{Zn} *vs.* N_{Zn} at various temperatures for the liquid alloys.

Determination of liquidus points by either method depends on accurate values of specific heat and heat of fusion for pure Zn. Values of heat of fusion quoted in the literature, however, are widely scattered as might be expected in view of the experimental difficulties of high temperature calorimetry. The value chosen to calculate the activity of supercooled liquid Zn in this research is the result of a recent evaluation by the National Bureau of Standards.[14] Other sources quote values from 1504[15] to 1765[16] cal./mole. These discrepancies suggest the application of the e.m.f. data to evaluate the heat of fusion. The evaluation can be made by essentially the same method as the determination of the liquidus, but with ΔH_f of Zn as the unknown, and using reliable values of liquidus temperatures.

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[8] D. Stockdale, *J. Inst. Metals*, **44**, 75 (1930).

[9] F. Rhines and A. Grobe, *Trans. Am. Inst. Mining Met. Eng.*, **156**, 253 (1944).

[10] C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, **71**, 383 (1897).

[11] S. Valentiner, *Z. Metallkunde*, **35**, 250 (1943).

[12] C. Wilson and E. A. Peretti, *Ind. Eng. Chem.*, **28**, 204 (1936).

[13] W. J. Svirbely and S. M. Selis, THIS JOURNAL, **75**, 1532 (1953).

[14] D. D. Wagman, private communication.

[15] F. Wust, A. Meuthen and R. Durrer, *Forsch. Gebiete Ingenierw.*, No. 204 (1918).

[16] K. K. Kelley, U. S. Bur. Mines Bull. 476, 1949.

Such calculations were carried out for alloys in the Zn–Cd system with encouraging results. Accepting the specific heat data from the NBS (Zn(c): $C_p = 5.202 + 0.3238 \times 10^{-2}T - 0.01038 \times 10^{-4}T^2$: Zn(l): $C_p = 8.526 - 0.1274 \times 10^{-2}T$ cal./deg. g. atom), the expression for $\Delta F/T$ for the melting of Zn was derived

$$\Delta F/T = -7.6552 \log T + 0.2256 \times 10^{-2}T - 0.0023 \times 10^{-4}T^2 + \Delta H_f/T - 1362.9/T + 22.2601 - \Delta H_f/692.7 \quad (12)$$

The value of $\Delta F/T$ $(= -R \ln a)$ for each alloy was then determined from the e.m.f. data at the liquidus temperature given by the phase diagram and corrected for the solubility of Cd in solid Zn. With this value, ΔH_f was evaluated from the above equation. Such calculations made for four alloys in the Zn–Cd system are given in Table III. These results give a value of 1.64 ± 0.03 kcal./g. atom compared to the best evaluation from the literature of 1.66 ± 0.10 kcal./g. atom.

TABLE III

CALCULATION OF ΔH_f OF ZINC FROM E.M.F. DATA ON THE ZINC–CADMIUM SYSTEM

Alloy, wt. % Cd	ΔH_f, cal./g. atom
45	1672
55	1604
65	1616
75	1676

Values of the thermodynamic properties suggest that the behavior of these systems is regular, as defined by Hildebrand.[17] Since a regular solution has an ideal entropy of mixing, the temperature coefficient of the cell is an excellent criterion of regular behavior. If the entropy of mixing is indeed ideal, then the temperature coefficient can be expressed as

$$\frac{dE}{dT} = \frac{-2.303R}{n\mathfrak{F}} \log N_{Zn} \quad (13)$$

This curve is plotted in Fig. 6 along with experimental values measured for the cells studied. The data for the Zn–Cd system are seen to approach regular behavior closely, while the agreement is not as good for the Zn–In alloys.

A regular solution also can be shown to follow the relation

$$RT \ln \gamma_2 = BN_1^2 \quad (14)$$

Some departure from this relation is seen in Fig. 7. as the experimental points deviate from linearity. When the volume fraction rather than atom fraction is used, as Hildebrand has suggested, the agreement with the theoretical curve is much improved, as shown in Fig. 8. It is not unexpected that the volume fraction is of considerable importance in the properties of solutions, since the relative volumes greatly affect the degree of packing and the action of interatomic forces. Data for the molar volumes of the pure metals were taken from the density

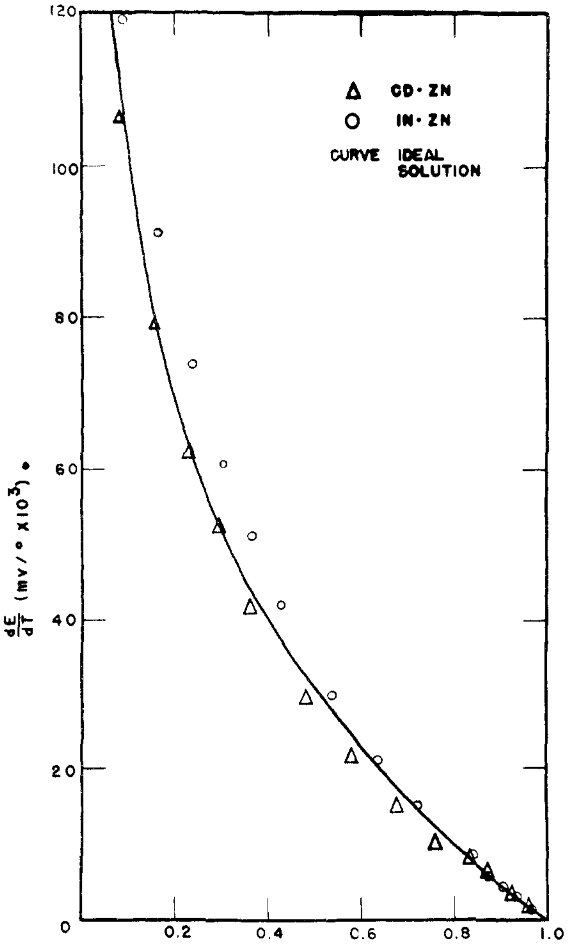

Fig. 6.—Curve shows dE/dT for cell whose components have ideal entropy of mixing. Experimental data shown as plotted points.

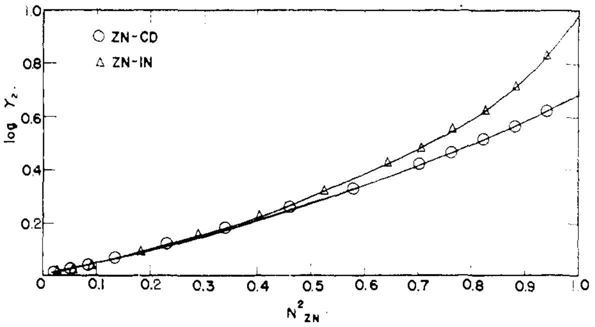

Fig. 7.—Variation of the log of the activity coefficient of the solute with the square of the atom fraction of Zn.

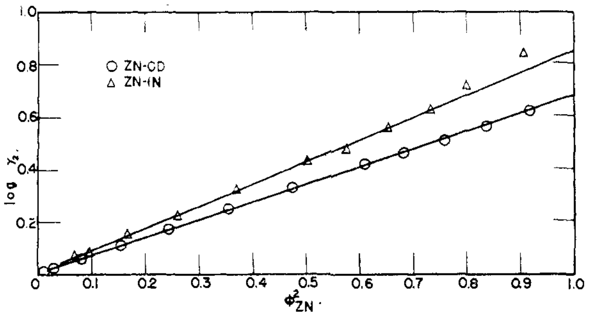

Fig. 8.—Variation of the log of the activity coefficient of the solute with the square of the volume fraction of Zn.

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[17] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," Am. Chem. Soc. Monograph #17, 1950.

data of Hogness[18] and Williams and Miller.[19] The value of the constant in the volume expression was evaluated at 470° as 2290 and 2810 cal./g. atom for the Zn–Cd and Zn–In systems, resp.

It might be argued that the regular solution concept is unrealistic (Lumsdem[20]), but an alternative approach to solution behavior based on a statistical model is so empirical at present that it is impossible to make any predictions of solution behavior from constituent properties. Until the state of statistical theory advances beyond the present empirical state, the concept of regular solutions appears justified.

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(18) T. R. Hogness, THIS JOURNAL, **43**, 1621 (1921).

(19) D. D. Williams and R. R. Miller, *ibid.*, **72**, 3821 (1950).

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Reaction of Mercury(II) with Halides in Glacial Acetic Acid

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The reaction between mercury(II) acetate and potassium halides in glacial acetic acid yields HgX_2 as the predominant species. The stoichiometry of the reaction was determined by potentiometric titrations with the glass and calomel electrodes, in which the glass electrode responds to changing acetate concentration. Potential difference measurements as a function of concentration of solution were made for reactants and products, and demonstrated the order of increasing acidity to be $Hg(OAc)_2 < KCl < KBr < KI$ for these weak acids in glacial acetic acid.

As a result of covalent bonding, mercury(II) chloride, bromide and iodide are soluble in a number of organic solvents, and form non-ionic aqueous solutions. In aqueous solutions containing excess halide, mercury(II) forms tetrahedral complexes of the type $HgX_4^{=}$, through (sp^3) hybridization. Analogous molecular and ionic species might be expected for glacial acetic acid solutions of mercury(II) halides, for it has been demonstrated that mercury(II) acetate reacts with amine hydrohalides, liberating the amine, quantitatively.[1] The present study confirms that the predominant species present in glacial acetic acid solutions of mercury(II) chloride, bromide and iodide is HgX_2, and that such solutions are essentially non-ionic.

The stoichiometry of the reaction between mercury(II) acetate and the potassium halides was established by potentiometric titrations. The covalent nature of the mercury–halide bond in glacial acetic acid solution was shown by potentiometric measurements, using the method of Higuchi, Danguilan and Cooper.[2] Curves representing the potential difference between the glass and calomel electrodes as a function of solution concentration were determined for the reactants and products, as well as for reference salts.

Experimental Details

All chemicals in these experiments were analytical reagent grade and were used without additional purification. Solution concentrations were restricted to the hundredth formal level by the limited solubility of alkali halide salts in glacial acetic acid.

Preparation of Standard Solutions.—Standard solutions of perchloric acid and hydrochloric acid were prepared by adding suitable amounts of the concentrated aqueous acids to glacial acetic acid and adding sufficient acetic anhydride to consume the water present from the concentrated acids. Each acid solution was allowed to stand for one week, then standardized potentiometrically against potassium acid phthalate (primary standard grade, dried two hours at 120°). The glacial acetic acid solution of hydrochloric acid was 0.00343 *F* and the perchloric acid was 0.0414 *F*, with an uncertainty of ±2 p.p.t.

The 0.0100 *F* solutions of potassium chloride, bromide, iodide, acetate and acid phthalate, and mercury(II) acetate and chloride, in glacial acetic acid were prepared from accurately weighed portions of finely ground and dried samples of the salts. All stock solutions and dilutions from these were carefully thermostated at 25.0 ± 0.1°. The somewhat rapid release of triiodide from glacial acetic acid solutions of potassium iodide necessitated immediate measurements on freshly prepared solutions for this salt.

Malachite green indicator solution was 0.001 *F* prepared by dissolving the solid (as the hydrochloride) in glacial acetic acid.

Volumetric Methods.—Indirect titrations of mercury(II) acetate were made by adding to aliquots of the mercury(II) solution known excesses of the potassium halide salt solution, and the equivalent potassium acetate released was titrated with standard perchloric acid. The end-points in these acid–base titrations were determined both potentiometrically with the glass–calomel electrode pair and with malachite green as a visual indicator, using 0.20 ml. of the latter solution per 30-ml. sample solution being titrated.

Direct titrations of 2.00-ml. aliquots of mercury(II) acetate solution with hydrochloric acid and the potassium halide solutions were made in a total solution volume of 15 ml., and the titration curves were determined from potentiometric measurements.

Potential Difference. Dilution Measurements.—The method employed for the determination of the potential difference as a function of concentration was that of Higuchi, Danguilan and Cooper.[2] In all potentiometric measurements a Beckman Model H-2 *p*H meter, equipped with the usual glass and calomel electrodes, was used. The reference solution was 0.100 *F* sodium salicylate in glacial acetic acid, and the reported values are differences in absolute magnitude between the e.m.f. for the sodium salicylate solution and that for the unknown solution. The e.m.f. for the reference solution was checked before and after each unknown solution. The experimental uncertainty in these potential measurements is ±1 millivolt.

Results

Titrations.—To establish the mole ratio in which the halide reacts with mercury(II) acetate, a number of direct and indirect titrations were performed. First, to a fixed amount of mercury(II) acetate, known amounts of potassium halide were added, and in accordance with equation 1 the released

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(1) C. Pifer and E. Wollish, *Anal. Chem.*, **24**, 300 (1952).

(2) T. Higuchi, M. Danguilan and A. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).