Table IV. A Comparison of Reported High Temperature Heat Capacities for ZrB_2

T, °K.	Krestovnikov (*7*)	SRI (*8*)	Barnes (*1*)	AVCO (*2*)	Prophet (*10*)	Westrum (*11*)	This Work
	C_p in cal. deg.$^{-1}$ mole^{-1}						
298.15	(14.41)^a	...	(13.0)	...	(10.55)	11.53	(11.53)
500	15.77	11.52	16.50	...	(14.06)	...	14.70
1000	17.74	19.36	19.66	...	(20.22)	...	17.07
1500	17.70	21.50	...	...	21.37	...	(18.7 ± 0.8)
2000	(15.64)	23.50	...	38.37^b	22.99	...	(19.4 ± 1.5)
2500	...	25.20	...	41.76^b	...	...	...

[a] Parentheses indicate extrapolated values, often beyond reliable limits of equations used.
[b] These excessively high results probably arise because no correction for sublimation of the sample was made.

presents thermodynamic functions based on experimental data up to 1200° K. and on the average extrapolations of the computer-selected fits up to 2000° K.

For comparison, high temperature heat capacities based on all the available measurements on ZrB_2 samples are tabulated in Table IV. The discrepancies clearly show the need for further studies, especially at temperatures over 1200° K., on well-characterized samples of ZrB_2.

ACKNOWLEDGMENT

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Thermodynamic Activities of Cadmium and Zinc in Binary Mercury-Rich Amalgams

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Thermodynamic activities, as determined from e.m.f. data, are presented for solute cadmium and zinc in their respective mercury-rich amalgams. The calculated activities are relative to a standard state of the saturated amalgam at the temperature of measurement. Concentration cell potentials were measured at 50.0, 70.2, and 93.2° C. for various amalgam concentrations up to the equilibrium solubility. Values of the equilibrium solubilities for these amalgam systems were determined at the same temperatures.

MANY OF THE theoretical correlations for diffusion phenomena in binary solutions require the use of thermodynamic activity data to correct for the departure from ideal solution behavior. Thus, the thermodynamic activities presented in this paper were determined in the course of studying diffusional behavior in cadmium and zinc amalgam systems.

MATERIALS AND APPARATUS

All materials used in this research were ACS Reagent Grade or better. Amalgams were prepared by dissolving solute zinc or cadmium directly in mercury. Compositions were established by gravimetric preparation with an estimated relative accuracy of better than 0.0001 per cent (*7*); absolute accuracy was limited only by the residual

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impurities in the Reagent Grade materials and was estimated as better than 0.001 per cent.

Modified *H*-type cells were employed in the potential measurements. The amalgam wells were equipped with either tungsten or platinum electrodes. The modified cell embodied an offset connecting bridge which prevented any amalgam mixing during filling of the wells.

The electromotive force measurements were made in a constant temperature bath. A sufficient number of calibrated thermocouples were placed in the bath to determine that temperature variations did not exceed 0.01° C. during the duration of the measurement.

Rubicon precision potentiometers were employed in all e.m.f. measurements. Galvanometer sensitivity was better than 0.002 mv., readability and accuracy were ± 0.001 and ± 0.01 from 0 to 16.1 mv. and ± 0.005 and ± 0.05 from 16.1 to 80.5 mv.

EXPERIMENTAL PROCEDURES

All e.m.f. measurements were made between a reference amalgam comprising a saturated solution of zinc or cadmium in mercury and an unsaturated amalgam of known composition. The reference amalgam, corresponding to the solute standard state for this study, was produced by saturating an amalgam at a temperature slightly above the desired temperature of measurement and then cooling slowly so as to cause an equilibrium precipitate of excess solute.

A 0.1*m* solution of zinc sulfate or a 0.5*m* solution of cadmium sulfate was used as cell electrolyte for the measurement of zinc and cadmium amalgam potentials. These electrolyte solutions were heated to about their boiling points and then cooled while bubbling argon through the solutions to preclude dissolved oxygen.

The reference amalgams and dilute amalgams of interest were preheated to insure complete single phase solution and were charged into the legs of the e.m.f. cell. Heating and handling was done under an argon blanket. The electrolyte solutions were added, and the cell and its contents were preheated in an auxiliary bath to a temperature five to ten degrees higher than that desired for the determination. The cell was then transferred to the constant temperature bath for e.m.f. measurements. This superheating procedure hastened the attainment of equilibrium conditions in the two-phase reference amalgam.

After sufficient time for thermal equilibration of the cell and contents at the temperature of measurement, the potential developed by the cell was measured. These procedures gave highly reproducible measurements among several different lots of gravimetrically-prepared constant-composition amalgams. The measurements were checked also by taking repetitive readings on a single amalgam over a period of days. No change in e.m.f. was observed.

RESULTS

The results of the concentration-cell potential measurements are summarized in Figure 1, which shows the logarithm of the weight per cent solute versus the e.m.f. developed by the cell. Measurements were made at 50.0, 70.2, and 93.2° C. These data are consistent with the zinc amalgam e.m.f. data of Crenshaw (*2*) at 25° C. and of Schadler (*6*) at 30° C. and with the cadmium amalgam e.m.f. data of Hulett and De Lury (*4*) at 25° C.

During the determination of the amalgam e.m.f. values, the equilibrium solubilities of cadmium in mercury and of zinc in mercury at these temperatures were evaluated to check various data available in the literature. Solubility limits were established by extrapolation of the concentration-electromotive force curves of Figure 1 to a zero potential. Amalgams were prepared having compositions corresponding to the extrapolated concentration values and their null cell potentials were checked against the saturated amalgams to confirm the solubility limit values thus determined. The results of this research, given in Figure 2 and

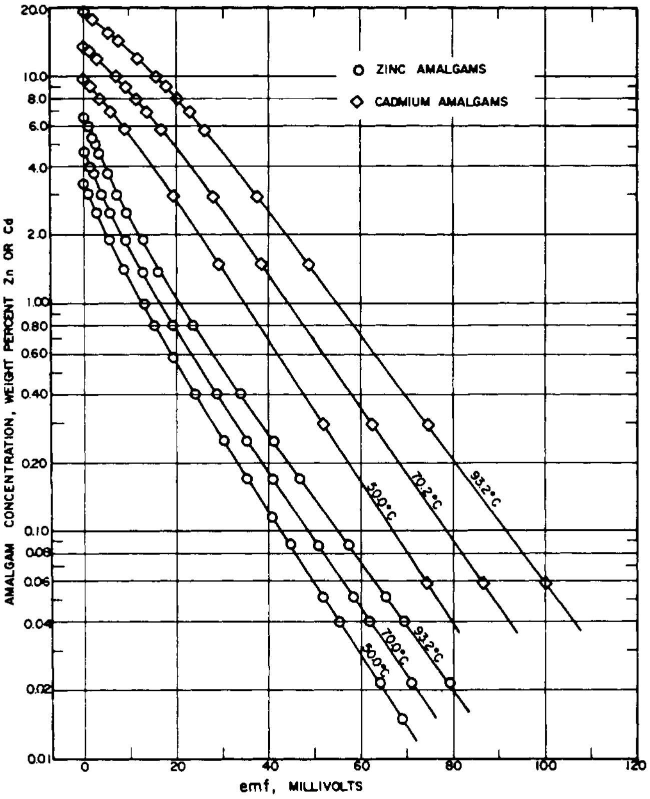

Figure 1. Concentration cell potential for various amalgams

Cells: (1) Cd-Hg (sat) 0.5M Cd^{++} Cd-Hg (dilute)

(2) Zn-Hg (sat) 0.1M Zn^{++} Zn-Hg (dilute)

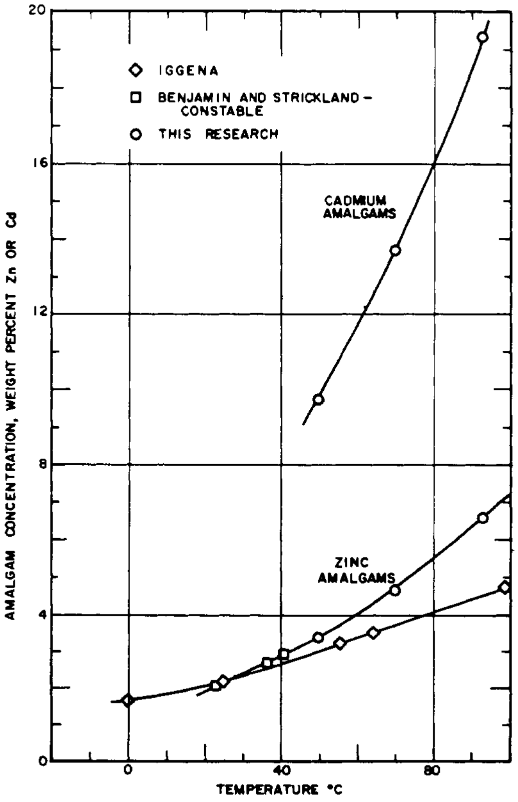

Figure 2. Equilibrium solubilities of various amalgams

Table I, are in close agreement with the values presented by Hansen (*3*). The equilibrium solubilities for zinc amalgams deviate from Iggena's data as referred to by Mellor (*5*), and the use of these latter data in lieu of the values from Hansen does not appear to be justified (*6*). The zinc amalgam data of Benjamin and Strickland-Constable (*1*), measured at lower temperatures, are consistent with an extrapolation of the data from the present research.

Table I. Equilibrium Solubilities of Zinc or Cadmium in Mercury, this Research

Temp., °C.	Wt. % Zinc	Wt. % Cadmium
50.0	3.348	9.710
70.2	4.645	13.758
93.2	6.540	19.310

The thermodynamic activity, *a*, of the solute zinc or cadmium in the amalgams may be determined from the e.m.f. and temperature data by the expression:

$$\ln \frac{a}{a_{ss}} = -\frac{nFE}{RT} \qquad (1)$$

where:

a_{ss} = thermodynamic activity of zinc or cadmium in the standard state and assigned a value of unity; in this research, the standard state was the saturated amalgam at the given temperature of measurement

n = number of equivalents per mole, 2 in this case

F = 23.074 cal./mv.-eq.

R = gas constant, 1.987 cal./mole-° K.

T = temperature in ° K.

E = e.m.f. expressed in mv.

Substitution of the numerical values for constants and changing the logarithm base gives:

$$\log_{10} a = -10.085(E/T) \qquad (2)$$

Equation 2 was used to calculate the thermodynamic activities of zinc or cadmium in their respective amalgams. These values are presented in Tables II and III. The activity coefficients given in these same tables were calculated from the defining equation:

$$\gamma = (a/N) \qquad (3)$$

where:

γ = activity coefficient of zinc or cadmium in the amalgam

a = activity of zinc or cadmium in the amalgam

N = atomic fraction of zinc or cadmium in the amalgam

The maximum uncertainty in the activity data presented is estimated to be 4 in the fourth significant figure. This estimate is based on the temperature error and the error limits of the potentiometer used for the measurement of the concentration cell potentials.

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Table II. Thermodynamic Activities and Activity Coefficients of Zinc and Zinc Amalgams, Calculated from Concentration Cell Potentials at Various Temperatures

Wt. % Zinc	Atomic % Zinc	e.m.f. mv.	Activity of Zinc	Activity Coefficient of Zinc
		50.0° C.		
3.348[a]	9.608	0.000	1.0000	10.408
3.300	9.479	0.130	0.9907	10.452
3.198	9.204	0.412	0.9708	10.548
3.000	8.667	1.000	0.9308	10.740
2.980	8.613	1.050	0.9273	10.766
2.949	8.528	1.132	0.9219	10.810
2.898	8.389	1.296	0.9111	10.861
2.496	7.283	2.652	0.8265	11.348
1.900	5.609	5.702	0.6639	11.836
1.500	4.464	8.020	0.5620	12.590
1.150	3.447	11.060	0.4518	13.107
0.970	2.918	13.111	0.3894	13.345
0.799	2.412	15.245	0.3345	13.868
0.577	1.750	19.420	0.2488	14.217
0.400	1.217	24.120	0.1768	14.528
0.250	0.763	30.290	0.1135	14.875
0.170	0.520	35.520	0.07793	14.987
0.114	0.349	41.400	0.05109	14.639
0.0864	0.265	44.890	0.03976	15.004
0.0510	0.156	52.130	0.02363	15.147
0.0400	0.123	55.530	0.01851	15.049
0.0214	0.0656	64.280	0.009873	15.050
0.0150	0.0460	69.320	0.006874	14.943
		70.2° C.		
4.645[a]	13.003	0.000	1.0000	7.691
4.630	12.965	0.030	0.9980	7.698
4.501	12.634	0.247	0.9834	7.784
4.252	11.992	0.797	0.9475	7.901
3.996	11.325	1.321	0.9145	8.075
3.720	10.599	2.097	0.8678	8.188
2.992	8.646	3.904	0.7680	8.883
2.898	8.389	4.217	0.7519	8.963
2.496	7.283	5.718	0.6793	9.327
1.900	5.609	9.021	0.5436	9.692
1.378	4.111	12.890	0.4182	10.173
0.799	2.412	19.250	0.2720	11.277
0.400	1.217	28.675	0.1438	11.816
0.250	0.763	35.280	0.09201	12.059
0.170	0.520	40.860	0.06309	12.133
0.0864	0.265	50.860	0.03208	12.106
0.0510	0.156	58.470	0.01918	12.295
0.0400	0.123	62.100	0.01500	12.195
0.0214	0.0656	71.570	0.007907	12.053
		93.2° C.		
6.540[a]	17.676	0.000	1.0000	5.657
6.495	17.569	0.065	0.9959	5.669
6.201	16.864	0.496	0.9691	5.747
5.995	16.366	0.802	0.9504	5.807
5.300	14.656	1.899	0.8866	6.049
5.000	13.904	2.366	0.8608	6.191
4.530	12.709	3.315	0.8105	6.377
3.720	10.599	5.192	0.7197	6.790
3.000	8.667	7.170	0.6349	7.325
2.496	7.283	9.203	0.5581	7.663
1.900	5.609	12.734	0.4462	7.955
1.378	4.111	16.610	0.3490	8.489
0.799	2.412	23.810	0.2212	9.171
0.400	1.217	33.910	0.1166	9.581
0.250	0.763	40.960	0.07461	9.779
0.170	0.520	46.940	0.05108	9.823
0.0864	0.265	57.700	0.02583	9.747
0.0510	0.156	65.760	0.01550	9.936
0.0400	0.123	69.550	0.01219	9.911
0.0214	0.0656	79.590	0.006452	9.835

[a] Equilibrium solubility at temperature.

Table III. Thermodynamic Activities and Activity Coefficients of Cadmium in Cadmium Amalgams, Calculated from Concentration Cell Potentials at Various Temperatures

Wt. % Cadmium	Atomic % Cadmium	e.m.f. mv.	Activity of Cadmium	Activity Coefficient of Cadmium
		50.0° C.		
9.710[a]	16.102	0.000	1.0000	6.210
9.435	15.677	0.502	0.9646	6.153
9.009	15.016	1.304	0.9106	6.064
8.005	13.442	3.419	0.7822	5.819
6.975	11.802	5.780	0.6602	5.594
5.860	9.998	8.745	0.5335	5.336
2.964	5.169	19.340	0.2492	4.821
1.488	2.665	28.935	0.1251	4.766
0.295	0.525	51.635	0.02449	4.760
0.0587	0.105	74.060	0.004890	4.657
		70.2° C.		
13.758[a]	22.161	0.000	1.0000	4.512
13.476	21.750	0.390	0.9740	4.478
12.990	21.038	1.082	0.9294	4.418
12.000	19.573	2.682	0.8341	4.261
9.999	16.546	6.934	0.6257	3.782
9.009	15.016	8.974	0.5450	3.629
8.005	13.442	11.258	0.4670	3.474
6.975	11.802	13.613	0.3983	3.375
5.860	9.998	16.655	0.3242	3.243
2.964	5.169	27.535	0.1553	3.004
1.488	2.625	38.000	0.07655	2.916
0.295	0.525	62.130	0.01497	2.851
0.0587	0.105	86.420	0.002896	2.758
		93.2° C.		
19.310[a]	29.927	0.000	1.0000	3.341
19.299	29.912	0.015	0.9990	3.340
18.500	28.831	1.161	0.9291	3.223
18.042	28.205	1.845	0.8897	3.154
18.000	28.148	1.851	0.8893	3.159
17.286	27.165	2.775	0.8387	3.087
15.739	25.001	5.411	0.7097	2.839
14.437	23.143	7.457	0.6234	2.694
12.000	19.573	11.821	0.4728	2.416
9.999	16.546	15.815	0.3671	2.219
9.009	15.016	17.950	0.3206	2.135
8.005	13.442	20.395	0.2746	2.043
6.975	11.802	22.900	0.2343	1.985
5.860	9.998	26.080	0.1915	1.915
2.964	5.169	37.750	0.09144	1.769
1.488	2.625	48.905	0.04510	1.718
0.295	0.525	74.630	0.008834	1.683
0.0587	0.105	100.030	0.001767	1.683

[a] Equilibrium solubility at temperature.

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Aqueous Systems at High Temperature. XIV.

Solubility and Thermodynamic Relationships for $CaSO_4$ in NaCl–H_2O Solutions from 40° to 200° C., 0 to 4 Molal NaCl

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A SYSTEMATIC INVESTIGATION of the solubilities of $CaSO_4$ and its hydrates in NaCl-H_2O solutions at temperatures between 25° and 200° C. is of considerable interest in developing distillation processes for desalinating water. Calcium sulfate is a major constituent of scales which form on heat exchanger surfaces when sea water or other saline waters are distilled. Furthermore, a study of the solubility of a 2-2 salt in an electrolytic medium as a function of ionic strength provides a means for testing Debye-Hückel theory at high temperature. The purpose of this investigation was to obtain solubilities for application to desalination programs and to obtain data for testing solubility theory at temperatures above 25° C. Upon agreement with theory, the solubilities of $CaSO_4$ and its hydrates could then be estimated in electrolytic media other than in NaCl-H_2O solutions.

Solubilities of $CaSO_4 \cdot 2H_2O$ in NaCl-H_2O at 25° C. have been obtained by Shternina and Frolova (*15*), at 26° C. by several investigators (*4*), and recently of both $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ at 26°, 30°, 40°, and 50° C. by Bock (*2*). Solubilities of $CaSO_4 \cdot \frac{1}{2}H_2O$ and $CaSO_4$ in sea water concentrates at 100° C. have been determined by Langelier, Caldwell and Lawrence (*11*). Some solubilities of anhydrous $CaSO_4$ in NaCl-H_2O solutions at concentrations from 1 to 7.7 molal NaCl and at temperatures between 100° and 200° C., obtained by V.P. Il'inski, A.F. Sagaidachnyi, and others, have been compiled in graphical form by Zdanovskii (*17*). There have been extensive investigations of the solubilities of $CaSO_4$ and its various hydrates in H_2O beginning with the work of van't Hoff (*16*) and continuing until the present time (*3*, *5*). A comprehensive review of studies prior to 1938, with presentation of some additional solubility data, is given by Posnjak (*13*), together with his conclusions on the nature of the solid phases. A very extensive evaluation of thermodynamic properties of the solids which further defines and correlates the distinct solid phases is given by Kelley, Southard, and Anderson (*10*).

This paper presents solubilities of metastable $CaSO_4 \cdot 2H_2O$ at 40° and 60° C., of metastable $CaSO_4 \cdot \frac{1}{2}H_2O$ [designated $\alpha CaSO_4 \cdot \frac{1}{2}H_2O$ by Kelley and coworkers (*10*)] at 125° C. and of $CaSO_4$ [designated anhydrite or "insoluble" anhydrite (*10*) or $\beta CaSO_4$ (*13*)] at 125° to 200° C. in NaCl-H_2O solutions, compares them with literature values, and interprets the results in terms of the Debye-