

3. The molal heats of formation of liquid and partly solid thallium amalgams have been calculated at 20 and 30°.

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HEATS OF SOLUTION, HEATS OF FORMATION AND FREE ENERGIES OF FORMATION OF CADMIUM AMALGAMS

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An account of the determination of the heats of solution of cadmium amalgams in mercury has already been given in the paper of Richards, Frevert and the writer.² Strictly speaking the effect measured was the heat of dilution of the amalgam to a final concentration of less than 0.5 wt. % of cadmium. However, Richards and Forbes have shown³ that the heat absorbed on diluting an amalgam from 3 to 1.5 wt. % of cadmium is less than one joule per gram atom of cadmium. Hence it may be assumed that within the experimental error the heats of dilution obtained are the same as the heats of solution in, or dilution with, an infinite amount of mercury. These heats of solution are also the total relative heat contents⁴ of the amalgam. Since the writer's previous experiments showed that Frevert's original values of the heat of solution were too high in the region mole fraction of cadmium $N_2 = 0.2 - 0.25$, and because of several added refinements of the new method, it was decided to repeat Frevert's experiments on cadmium rich amalgams.

Experimental

"Chemically pure" commercial cadmium and mercury twice distilled in a current of air⁵ after preliminary purification were used. Weighed amounts of the constituents were melted together under carbon dioxide in an electric furnace. The samples were stirred and kept liquid for a long time to ensure homogeneity, cast in Pyrex test-tubes, and later remelted, stirred to remove air bubbles, and quenched in liquid nitrogen. The quenching was obviously not as drastic as that employed before, when iron deflagrating spoons containing the sample were plunged directly into the liquid nitrogen. However, a much larger volume of the liquid was used, and the tube containing the molten metal immersed as far as possible beneath the surface. There was a com-

¹ This research was in part completed while the author was the incumbent of a National Research Fellowship.

² Richards, Frevert and Teeter, *THIS JOURNAL*, **50**, 1293 (1928).

³ Richards and Forbes, *Carnegie Inst. Publ.*, No. 56 (1906).

⁴ Lewis and Randall, *THIS JOURNAL*, **43**, 240 (1921).

⁵ Hulett, *Z. physik. Chem.*, **33**, 618 (1900).

pensating advantage in this method, as the entire sample was melted at once, instead of 4 g. at a time in the iron deflagrating spoons, and it was consequently less oxidized. To ensure favorable conditions for equilibration the samples were then annealed on an average forty-eight hours at a temperature a few degrees below the first melting point of each in a high temperature thermostat planned and made by Dr. Robert F. Mehl, who kindly put the apparatus at our service. After annealing, the amalgams were beaten into sheets and preserved in an atmosphere of carbon dioxide. Before use they were scraped bright and cut into small pieces. The mechanical work should not introduce much strain into metals as soft as these amalgams. The effect on the heat of solution, however, was tested in one case. Samples were respectively quenched and

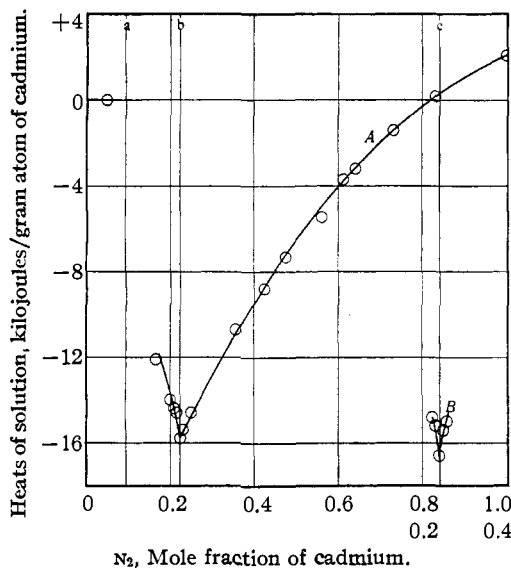


Fig. 1.—Curve A, heats of solution of cadmium amalgams in a large amount of mercury at 25°: a indicates the liquidus point ($N_2 = 0.0953$) and b, the solidus point ($N_2 = 0.2248$). No interpolation was attempted in the region $N_2 = 0.05-0.16$, since the curve is not linear. Curve B, heats of solution at 30° in the neighborhood of the solidus point, c ($N_2 = 0.234$). The line c has, of course, no significance for Curve A. Lower scale for Curve B.

of solid c. p. sodium carbonate were added through the long tube until the evolved carbon dioxide displaced most of the oxidizing gases. This procedure was found to be superior to boiling off the gases on an electric hot-plate, which was found to give low results, probably due to volatilization of mercuric chloride. The reduction to metallic mercury was carried out with stannous chloride according to the directions of Willard and Boldyreff, except that double the quantity of stannous chloride was taken to allow for any further oxidizing impurities in the solution. The results of the analyses showed that comparatively little cadmium was oxidized or mercury volatilized in the process of making the amalgams.

⁶ Willard and Boldyreff, *THIS JOURNAL*, **52**, 569 (1930).

cold worked; quenched, annealed and cold worked; and quenched, cold worked and then annealed. The heats of solution of the three samples were the same within the limit of error.

Two methods of analysis proved unsuccessful. The first involved an electrolytic separation of cadmium and mercury, and the second, a separation through the formation of $HgNH_2Cl$. Qualitative tests showed that neither separation was complete. The method finally adopted was that described by Willard and Boldyreff,⁶ modified slightly to adapt it to the analysis of a metallic alloy. In the procedure as finally employed, a Pyrex Erlenmeyer flask was fitted with an interchangeable Pyrex tube, 10 mm. in diameter \times 60 cm. long, and ground stopper. Samples of amalgam containing about one gram of mercury were weighed out in this flask and dissolved in 15 cc. of aqua regia, pouring the acid through the long tube to prevent loss by spattering. After several hours on the steam-bath to complete solution, portions

The heats of solution of the amalgams in mercury at 25° were measured in the calorimeter described in the first paper.² The cooling due to solution of the amalgam was balanced against the energy of an electric heating coil, the input to which was measured with a potentiometer and silver coulometer. The results are given in the table, and the curve is drawn (Table I and Fig. 1, Curve A).

TABLE I
HEATS OF SOLUTION OF CADMIUM AMALGAMS IN MERCURY IN KILOJOULES PER GRAM
ATOM OF CADMIUM AT 25°

Sample	Wt., % Cd	Ns. mole fraction Cd	Heat of solution
Richards and Forbes	3.0	0.050	- 0.001
Frevert		.167	-12.1
A'	12.27	.200	-14.0
G	12.88	.209	-14.4
C'	13.43	.216	-14.6
B'	13.96	.225	-15.8
J	14.38	.231	-15.4
D	15.75	.250	-14.6
V	23.8	.358	-10.7
P	29.3	.425	- 8.83
U'	33.8	.477	- 7.30
T	41.7	.561	- 5.44
L	47.2	.615	- 3.67
aQ cold worked	49.8	.642	- 3.18
bQ cold worked, annealed			- 3.18
cQ annealed, cold worked			- 3.17
S	60.8	.735	- 1.38
R	73.4	.831	+ 0.20
Cadmium	100	1.000	+ 2.11

TABLE II
HEATS OF SOLUTION OF CADMIUM AMALGAMS IN MERCURY IN KILOJOULES PER GRAM
ATOM OF CADMIUM AT 30°

Sample	Wt., % Cd	Ns. mole fraction Cd	Heat of solution
B'	13.96	0.225	14.8
J	14.38	.231	15.2
K	15.02	.240	16.6
D	15.75	.250	15.4
E	16.38	.259	15.0

The points previously obtained by the author (see the first paper²) are included, as well as that obtained by Richards and Forbes³ for a 5 at. % amalgam, and an average of three determinations by Richards and Lewis,⁷ Bijl,⁸ and Tammann⁹ for pure cadmium. This curve shows a cusp at 22.5 at. % Cd, agreeing with the solidus point determined by Bijl as 22.9 at. %.

⁷ Richards and Lewis, *Proc. Am. Acad. Sci.*, **34**, 83 (1898); *Z. physik. Chem.*, **28**, 1 (1899).

⁸ Bijl, *ibid.*, **41**, 641 (1902).

⁹ Tammann and Ohler, *Z. anorg. Chem.*, **135**, 118 (1924).

25°, and the data of Smith¹⁰ (22.48 at. %, 25°). As an added test that the cusp represented a physical transition point, and not the advent of a compound, a series of measurements made at 30° show that the minimum is shifted to higher cadmium concentrations by the rise in temperature—as will be seen from Table II and Fig. 1, Curve B. The figures are 30°, 24 at. % as compared with Bijl's 30°, 24.5 at. %, and Smith's 30°, 23.2 at. %.

Calculation of the Heats of Formation

Amalgam corresponding to a gram atom of cadmium absorbs at most 15.8 and 16.6 kj. of heat at 25 and 30°, respectively. Two factors enter into this heat absorption, namely, the latent heat of fusion of the amalgam and the work necessary to separate the atoms of cadmium and mercury. The sum of the heats of fusion of the cadmium and mercury making it up gives a first approximation to the heat of fusion of the amalgam. The heat of fusion of mercury at 25°, from data in the literature and Kirchoff's law, would be 586 cal._{15°}. For cadmium an approximate formula of Tamman⁹ gives 772 cal._{15°}. Thus for CdHg₃ (*i. e.*, the amount of an amalgam, N₂ = 0.25, containing one gram atom of cadmium and hence three gram atoms of mercury) the heat of fusion was 2530 cal. or 10,600 joules. The observed heat of solution was 14,400 joules. For CdHg_{3.33}, the heat of fusion was calculated to be 11,400 joules, while the measured heat of solution was 15,800 joules. Hence most of the heat absorption seems to be due to the latent heat of melting of the amalgam. This also means that the curve obtained by plotting the heats of dilution for quantities of amalgam containing one gram atom of cadmium will be somewhat distorted, since as the mole fraction of mercury decreases, the amount associated with one gram atom of cadmium increases, and a larger contribution to the heat effect may be ascribed to the latent heat of melting of the mercury. This can be avoided by calculating the heat of solution per mole of amalgam. This quantity is defined by Lewis and Randall.¹¹ The weight of one mole of amalgam in grams is given by the equation $M = N_2A_2 + N_1A_1$ where N₁, N₂ and A₁, A₂ are mole fractions and gram atomic weights of mercury and cadmium, respectively. Methods of calculating the heats of formation per mole of amalgam are given in the paper on thallium amalgams.^{11b} The results of the calculation from the data of Tables I and II are given in Tables III and IV, and Fig. 2.

It is possible to calculate heats of formation from the heats of solution of cadmium in amalgams which were calculated by Bijl⁸ from his own *e. m. f.* data. However, his experiments were made at 25, 50 and 75° and the

¹⁰ F. E. Smith, *Coll. Researches of Nat. Phys. Lab. (Teddington)*, **6**, 137 (1910); *Phil. Mag.*, [6] **19**, 250 (1910).

¹¹ (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923; see also (b) Teeter, *THIS JOURNAL*, **53**, 3917 (1931).

TABLE III
HEATS OF FORMATION PER MOLE OF AMALGAM, JOULES AT 25°

N ₂ , mole fraction Cd	Heat of solution, joules/g. amalgam	Weight/ mole, g.	Heat of solution of CdN ₂ HgN ₁ , L _A	Heat of solution of N ₂ Cd + N ₁ Hg, L _U	Heat of formation, -(L _U -L _A) = ΔH
0	0	200.6	0	0	0
0.050	0	106	-106
.200	-15.3	183.3	-2800	420	-3220
.209	-16.5	182.5	-3010	440	-3450
.216	-17.5	181.9	-3150	450	-3600
.225	-19.6	181.0	-3560	470	-4030
.231	-19.7	180.5	-3560	490	-4050
.250	-20.5	173.8	-3650	530	-4180
.358	-22.7	169.0	-3840	760	-4600
.425	-23.0	163.2	-3760	900	-4660
.477	-22.0	158.5	-3490	1010	-4500
.561	-20.2	151.2	-3050	1180	-4230
.615	-15.4	146.3	-2250	1300	-3530
.642	-14.1	144.0	-2030	1360	-3390
.735	-7.49	135.8	-1020	1550	-2570
.831	+1.31	127.3	+167	1750	-1580
1.000	...	112.4	+2110	2110	0

TABLE IV
HEATS OF FORMATION PER MOLE OF AMALGAM, JOULES AT 30°

N ₂ , mole fraction Cd	Heat of solution of CdN ₂ HgN ₁ , L _A	Heat of solution of N ₂ Cd + N ₁ Hg, L _U	Heat of formation, -(L _U -L _A) = ΔH
0.225	-3330	470	-3800
.231	-3510	480	-3990
.240	-3980	500	-4480
.250	-3850	520	-4370
.259	-3880	540	-4420

temperature coefficients leave much to be desired. Much better results should be obtained by using the data of Smith,¹⁰ who gives measurements at intervals of 5° for temperatures from 0 to 60°, and for mole fractions from N₂ = 0.035 to 0.373. It is rather difficult to use Smith's measurements directly, since the electrolyte differed from that in Bijl's cells, but it has been found possible, as will appear in the second part of this paper, to refer all the measurements on cadmium amalgams to a common standard independent of the electrolyte, and hence combine Bijl's measurements for pure cadmium with Smith's measurements for amalgams with no greater errors than those inherent in the separate measurements. It is thus possible to obtain values for the e. m. f. of cells Cd|CdSO₄|CdN₂HgN₁, *i. e.*, cadmium, solid|cadmium sulfate solution|cadmium amalgam of composition N₁,N₂. Taking these at 20, 25 and 30°, two series of values of the temperature coefficient can be obtained, which lead to values of the molal heat of transfer of cadmium from the pure metal to the amalgam. From

these the heats of formation can be calculated as detailed in the paper on thallium amalgams.^{11b} The results are presented in Table V, and Fig. 3.

The data are much more consistent and satisfactory than those of Bijl, but the agreement between thermal and electrical measurements is poor.

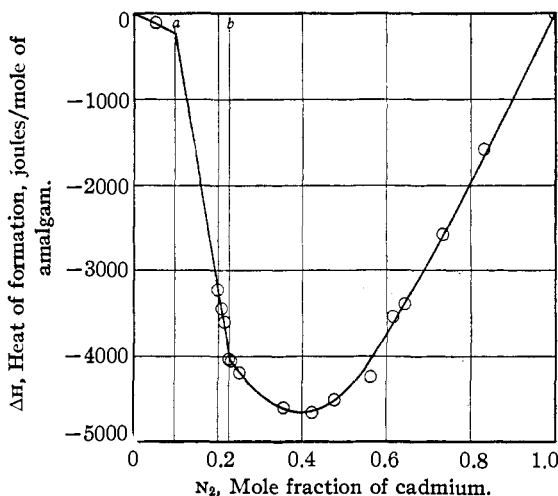


Fig. 2.—Heats of formation of cadmium amalgams at 25°, calculated from the heats of solution. Values are taken from the points, not from the smooth curve of Fig. 1. *a* indicates the liquidus point, and *b* the solidus point. More determinations should be made in the liquid and two-phase region, especially near the composition *a*. However, the agreement between the thermal and electrical measurements is fair in the liquid region (*cf.* Fig. 3). Also the points which were obtained in the two-phase region from the thermal measurements fall very nearly on a straight line, which is therefore produced to *a*. Another two-phase region (α , cadmium rich, + ω , mercury rich, solid solutions) exists in the range $N_2 = 0.65-0.80$ at 25° according to Bijl. In view of the uncertainty of their exact location, it was thought best not to draw these lines. The x-ray and microscopic evidence shows the approximate location of one boundary (see below). There is no evidence of a sharp break in the heat of formation curve, but it should be noted that a straight line (which would be expected in the heterogeneous region) could easily be fitted into the curve in the region 0.65–0.80.

Without further research it is not possible to decide between the results of the two methods, but it certainly seems that the discontinuities at the liquidus and solidus points in the curve from e. m. f. data are too abrupt, especially if we compare the curves with those for thallium amalgams.

TABLE V
HEATS OF SOLUTION AND HEATS OF FORMATION FROM SMITH'S E. M. F. DATA IN JOULES
AT 25°

N_2 , mole fraction Cd	E_{25}^a , milli- volts	Average temperature coefficient, $\Delta E / \Delta T$	Heat of solution of Cd in $Cd_{N_2}Hg_{N_1}$, L_A^b	Heat of solution of Cd in $N_2Cd + N_1Hg$, L_U^c	$L'_A - L'_U$	$-N_2(L'_A - L'_U)$ $= \Delta H$
0.0351	64.51	+0.1820	1980	2036	-56	+2
.0523	58.78	.1630	1967	2000	-33	+2
.0692	54.75	.1530	1764	1964	-200	+14
.0859	51.54	.1500	1316	1929	-613	+53
.09529	49.92	-.2320	22980	1909	+21070	-2008
.2248	49.88	-.2350	23160	1636	21520	4838
.2251	49.78	-.0480	12370	1635	10730	2415
.2395	47.92	+ .0300	7525	1605	5920	1418
.2537	45.85	+ .0400	6548	1575	4973	1262
.2677	44.26	+ .0380	6355	1545	4810	1288
.2815	42.05	+ .0380	5929	1516	4413	1242
.2951	40.44	+ .0380	5618	1487	4131	1222
.3085	38.92	+ .0400	5211	1459	3752	1161
.3730	31.81	+ .0400	3838	1323	2515	938

^a Of the cell $Cd | CdSO_4 | Cd_{N_2}Hg_{N_1}$.

^b $L'_A = 192,988 [E_{25} - 298.1(\Delta E / \Delta T)]$.

^c $L'_U = N_1L_2(s)$.

Possible reasons for the disagreement are: errors in Bijl's measurement of the cells containing pure cadmium, which would introduce a constant error, and lack of equilibration for the solid amalgams. Bijl's amalgams were certainly not thoroughly equilibrated, but some of Smith's were quenched to -50° before being used as electrodes. These amalgams of Smith give higher voltages than those of Bijl, but there is no certain proof that even these were fully equilibrated. A valuable check would be to measure the e. m. f. of the amalgams used for the thermal work, which have been kept for nearly five years after the original quenching and annealing treatment. At the same time, amalgams richer in cadmium as well as pure cadmium could be measured. This would also establish more exactly the limits of the region of existence of two solid solutions (see Bijl's paper).⁸ These boundaries were determined from his e. m. f. curves, which are probably somewhat in error.

It should be pointed out, also, that this method of calculating heats of formation has a large probable error, since the temperature coefficients are differences between e. m. f.'s which are themselves differences between much larger quantities, so that errors are magnified.

Electromotive Force Data and the Free Energies of Formation

Electromotive force data are available as follows: Bijl⁸ measured cells Cd amalgam $| CdSO_4 \text{ satd. at } 20^\circ || Hg_2SO_4 | Hg$ over the entire concentration range at 25, 50 and 75° . Richards and Forbes³ measured the e. m. f.

of concentration cells containing liquid cadmium amalgams at 23.03°. Hulett and DeLury¹² measured the e. m. f. of cells containing liquid amalgams to extreme dilutions at 25°, using a two-phase amalgam in each case as reference electrode. Smith¹⁰ measured the cells Cd amalgam | CdSO₄ satd. in presence of solid || Hg₂SO₄ | Hg over the range N₂ = 0.035 to 0.373 at temperatures from 0–60°.

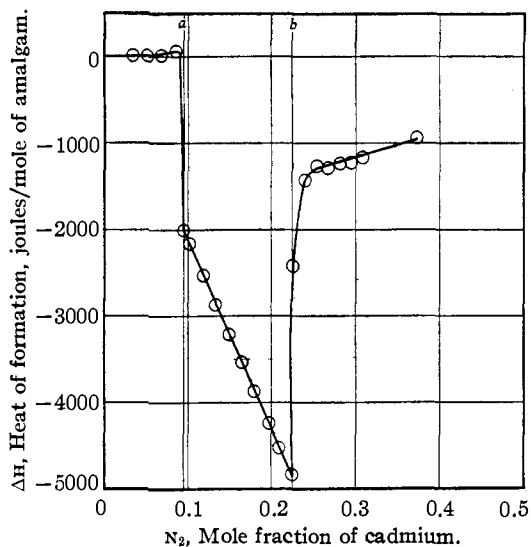


Fig. 3.—Heats of formation of cadmium amalgams at 25° calculated with the aid of the Helmholtz equation from the e. m. f. measurements of Smith. a indicates the liquidus and b the solidus point. The portion of the curve included between a and b is a straight line, agreeing with the thermally determined curve (Fig. 2), and also the corresponding curve for thallium amalgams. The slope of the line and its position, however, differ greatly from the thermal curve. The discontinuities at a and b arise from the changes in sign of the temperature coefficient, which make a large difference in the heat of formation. In the analogous case of thallium amalgams there is no change of sign. The portion of the curve representing solid amalgams (N₂ > 0.2248) is the most open to question. The e. m. f. values do not give points falling on the smooth curve for the free energy of formation (*cf.* Fig. 5).

e. m. f. for the cell Cd amalgam (satd.) | CdSO₄ | Cd amalgam*, which is independent of the concentration of the electrolyte, and therefore should be the same as the e. m. f. of the similar cell measured by Hulett and DeLury. We do not, of course, have measurements involving the very dilute amalgam

¹² Hulett and DeLury, THIS JOURNAL, 30, 1805 (1908).

The method of combining the data of all these investigators was as follows: Hulett and DeLury's data were taken as the standard, since they extended to greatest dilutions. The most dilute amalgam was rejected as giving less accurate values than the others, and the others were referred to the 0.00001 wt. % of amalgam as reference electrode.

These were plotted on as large a scale as possible on millimeter paper. Both Bijl and Smith have data for cells containing two-phase amalgams. By subtracting from the e. m. f. of these cells, the e. m. f. of the cell Cd amalgam* | CdSO₄ satd. at 20° || Hg₂SO₄ | Hg (where the star denotes the 0.00001 wt. % amalgam) in the case of Bijl's measurements, and that of the cell Cd amalgam* | CdSO₄ satd. in presence of solid || Hg₂SO₄ | Hg, in the case of Smith's measurements, we obtain the

against mercury in cadmium-mercurous sulfate, but if we arbitrarily assign the value $+0.173200$ volt to the two-phase amalgam against the reference amalgam, the e. m. f.'s of all the other amalgams are defined, and we can verify the correctness of this assumption by plotting all the points on the same diagram. This has been done in Fig. 4. The agreement is extremely good up to the solidus point. For the solid amalgams, as before noted, there is some question as to the equilibration of the amalgams. Smith's figures are taken as probably being more nearly correct, but this point should be verified.

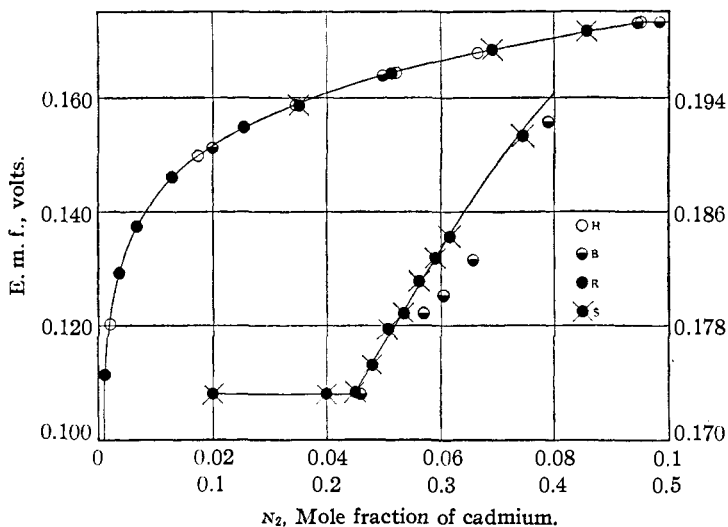


Fig. 4.—Electromotive force of concentration cells $\text{Cd}_{N_2}\text{Hg}_{N_1}|\text{CdSO}_4|\text{Cd}$ amalgam* at 25° , from the data of Hulett and DeLury (H), Bijl (B), Richards and Forbes (R), and Smith (S). Agreement is nearly perfect in the liquid and two-phase regions (upper curve). In the latter range the e. m. f. is constant. The greatest disagreement is for solid amalgams, $N_2 > 0.2248$ (lower curve). Left-hand and upper scales are for upper curve; right-hand and lower scales for lower curve.

Using these values of the e. m. f., the molal free energies of formation have been calculated exactly as done by the writer^{11b} for thallium amalgams. The results of the calculation are given in Table VI, and the curve is plotted (Fig. 5). The curve resembles the curve for thallium amalgams^{11b} as far as it goes, the parts of the curve representing liquid, two-phase, and solid amalgams being well defined. There is one more piece of information which may be gleaned from this curve. In the case of thallium amalgams, a glance at the curve shows that ΔF seems to be approaching zero at $N_2 = 0$ and at $N_2 = 1$. However, the expression for ΔF at these points involves the indeterminate form $0 \times \infty$, and the exact value of ΔF

cannot be found. In the case of cadmium amalgams we have measurements for extremely small values of N_2 , and from these a continuous series of decreasing values of $-\Delta F$ as N_2 decreases. Hence it is extremely probable that ΔF is actually 0 at $N_2 = 0$, and probably also at $N_2 = 1$. It may be pointed out that one of the objections to the use of the free energy, namely, that the partial molal free energy becomes infinite for zero mole fraction, disappears when using the quantities ΔF and $N_2\Delta\bar{F}_2$ or $N_1\Delta\bar{F}_1$ which approach zero instead of becoming infinite.

TABLE VI
MOLAL FREE ENERGIES OF FORMATION OF CADMIUM AMALGAMS AT 25°

N_2	$-E$, volts	$-N_2\Delta\bar{F}_2$, joules	$-N_1\Delta\bar{F}_1$, joules	$-\Delta F$, joules
0	$-\infty$?	0	?
0.061785	0	0.007686	0	0.008
.065000	0.0147	.02011	0	.02
.051000	.0240	.03842	0	.04
.055000	.0448	.1720	0	.17
.041000	.0537	.3269	0.05708	.38
.045000	.0745	1.434	.1142	1.55
.031000	.0834	2.696	.2283	2.92
.035000	.1041	11.48	1.255	12.74
.001000	.1130	21.25	2.451	23.70
.005000	.1337	86.27	12.38	98.65
.01000	.1426	155.4	24.75	180.2
.09529	.17320	899.5	242.0	1141.5
.1000	.17320	943.9	240.7	1184.6
.1500	.17320	1415.9	227.4	1643.3
.2000	.17320	1887.8	214.0	2101.8
.2248	.17320	2117.2	207.3	2324.5
.2500	.17662	2243.0	353.0	2596.0
.3000	.18322	2309.5	668.2	2977.7
.3500	.18904	2301.3	971.7	3273.0
.4000	.19428	2225.5	1261.2	3486.7

The Phase Diagram.—At the beginning of this investigation, freezing point determinations were made on a series of amalgams from 26–66 at. % of cadmium to see if any solidified at constant temperature. None were found, but the liquidus points checked very closely with those of Bijl. A previous check on the liquidus curve was reported by Schulze.¹³ Bijl was unable to determine the solidus points by means of cooling curves but succeeded by measuring volume changes on melting. He also determined solidus points by e. m. f. measurements. Schulze reported that he was unable to duplicate Bijl's dilatometric measurements, but presented a series of e. m. f. determinations of the solidus point. It is also possible to calculate solidus points from Smith's measurements on e. m. f.'s of cells containing slowly cooled and quenched amalgams. A summary of all these,

¹³ Schulze, *Z. physik. Chem.*, **105**, 177 (1923).

including the author's calorimetric measurements, is given in Table VII and the points are plotted (Fig. 6). Smith's measurements on quenched amalgams (a) and the author's (t) fall very nearly on the same straight line. The points from slowly cooled amalgams (b) are very much less consistent. The e. m. f. curves change in slope at the transition point much less abruptly than the curves for quenched amalgams. Further, the solidus points lie at

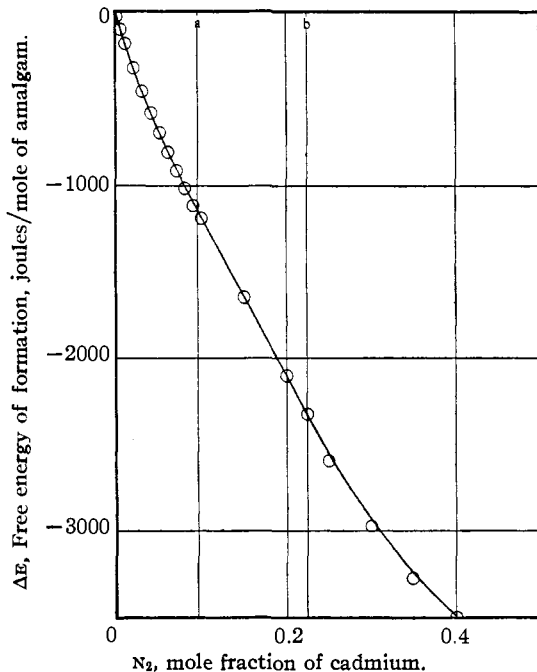


Fig. 5.—Free energies of formation of cadmium amalgams at 25°. a indicates liquidus point and b solidus point. Values in the liquid and two-phase region fall very well on the curve. In the solid region the agreement is not as good, and the curve is drawn so as to be tangent to the straight line included between a and b, as theoretically required.^{11b}

higher cadmium concentrations. Bijl's e. m. f. determinations (f) fall approximately on a straight line parallel to the line through the points a but displaced still further to the right. Schulze's values (r) also fall on a parallel straight line which lies between the two. Bijl's dilatometric measurements (e) fall along a curve which is considerably inclined to the other lines. Since the author and Smith alone used quenched (and hence presumably equilibrated) samples, it appears that the entire portions of Bijl's curve involving two-phase solid and solid-solid transitions should be repeated.

the last amalgam proved by Mehl¹⁵ by x-ray analysis to have the structure of the ω -solid solution was 64.2 at. %. The first to have the structure of the α -solid solution contained 73.5 at. % cadmium. No points were taken between these limits. The x-ray analysis (which was made with some of our quenched samples) is obviously more accurate than our photomicrographic evidence obtained with slowly cooled samples. However, the transition point is evidently somewhere in the neighborhood of 66 at. % cadmium, which is the figure given by Bijl at 25°. None of the data permit a check of the second solid-solid transition point.

General Conclusions

The work of Bijl⁸ and Smith¹⁰ is in the main, confirmed. The exact boundaries of certain portions of the phase diagram and the discrepancy between thermally and electrically determined heats of formation require further research. No extended theoretical treatment will be attempted until data for more systems have been obtained.

The present research reaffirms the conclusions made by Cohen¹⁶ and Bijl⁸ and by Smith,¹⁰ that the Weston standard cell containing a 12.5 wt. % cadmium amalgam is in a metastable condition below about 12° where the amalgam freezes. It may not actually become useless below 12°, as, due to enveloping or "Zonenbildung" (see the previous paper)², drops of liquid amalgam may still be left on the surface, so that the system is pseudo-two-phase. However, some cells will behave abnormally at low temperatures, and all cells would presumably behave abnormally (due to complete solidification) if kept for a sufficiently long time below the freezing point of the amalgam.

The results of this research are also in accord with the recent x-ray study by Mehl,¹⁵ who employed some of our solid amalgams for his work. The newer work of Mehl and Barrett¹⁷ on the phase diagram near the mercury end is supplementary to the field covered by the present paper. They found a second peritectic point and a third type of solid solution which they designated as ω' . This type, however, exists only below about -35°, and hence would not appear in any of our experiments. Our conclusions, therefore, which are substantially those made in 1927,¹⁸ are not altered by this work.

Summary

1. The heats of solution of solid cadmium amalgams have been measured at 25°.

¹⁵ R. F. Mehl, *THIS JOURNAL*, **50**, 381 (1928).

¹⁶ Cohen and Kruyt, *Z. physik. Chem.*, **65**, 359 (1909); Cohen and Moesveld, *ibid.*, **95**, 285 (1920).

¹⁷ Mehl and Barrett, Technical Publication No. 225, The American Institute of Mining and Metallurgical Engineers, issued with *Mining and Metallurgy*, August, 1929.

¹⁸ Charles E. Teeter, Jr., Thesis, Harvard University, 1927.

2. From these data and those obtained previously the molal heats of formation at 25° have been calculated.

3. The heats of formation for a portion of the range have been calculated from the data of Smith on the temperature coefficient of electromotive force for cells containing cadmium amalgams. These do not agree with the calorimetric data. Possible reasons are given for the disagreement.

4. The e. m. f. data of Hulett and DeLury, Richards and Forbes, Smith and Bijl have been combined.

5. From these data, the molal free energies of formation of cadmium amalgams at 25° have been calculated.

6. It is shown that the molal free energy of formation appears to approach zero instead of becoming infinite at $N_2 = 0$ and probably also at $N_2 = 1$.

7. The liquidus curve obtained by Bijl has again been confirmed. A revision of his solidus curve is indicated.

8. Conclusions made by Bijl, Smith, Cohen and Mehl concerning the system cadmium-mercury, are in the main substantiated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE PREPARATION OF LEAD DISULFIDE BY THE REACTION BETWEEN LEAD MERCAPTIDES AND SULFUR¹

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There is no evidence given in the literature proving the existence of any sulfides of lead other than normal lead sulfide, with the one exception of lead pentasulfide reported by Bodroux.² Berzelius³ observed that potassium pentasulfide when added to a solution of a lead salt gave a "beautiful blood red" precipitate which decomposed immediately into a mixture of the ordinary sulfide and sulfur. However, he did not determine the composition of this red precipitate which, judging from the results of the present investigation, was probably essentially the disulfide. The existence of the sesquisulfide, Pb_2S_3 , as the mineral jonstonite, reported by Playfair and Joule⁴ has not been confirmed. Some authorities⁵ believe it

¹ From the thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy by Wallace E. Duncan.

² M. F. Bodroux, *Bull. soc. chim.*, [3] **23**, 501 (1900); *Compt. rend.*, **130**, 1397 (1900).

³ J. Berzelius, *Ann. chim. phys.*, [2] **20**, 127 (1822).

⁴ L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **3**, 89 (1848).

⁵ J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 793 (1927).