FREE ENERGIES OF FORMATION AND HEATS OF FORMATION OF THALLIUM AMALGAMS

BY CHARLES EDWIN TEETER, JR.[1]

This paper is part of a general program for the study of the thermodynamics of amalgams. While the author was examining the suitability of different systems for study, he found that nearly complete data for thallium amalgams had already been obtained.[2,3,4,5] Among the quantities measured were the e. m. f.'s (with temperature coefficients) of concentration cells containing liquid thallium amalgams.[2] These data were used to calculate, among other things, the partial molal heat contents and activities of thallium and mercury.[3] Since Lewis and Randall's paper, e. m. f.'s have been measured for two-phase and solid thallium amalgams.[4,5]

The Free Energies of Formation.—From the data on concentration cells, the free energies of formation can be calculated as follows.

Consider an amalgam $Tl_{N_2}Hg_{N_1}$, where N_2, N_1 represent the mole fractions of thallium and mercury, respectively. The free energy of formation of a mole[6] of this amalgam is the value of ΔF, the change in free energy, defined by the equation

N_2 moles Tl (solid) + N_1 moles Hg (liquid) = $Tl_{N_2}Hg_{N_1}$ $i.e.$, Tl (amalgam, N_2), Hg (amalgam, N_1) + ΔF

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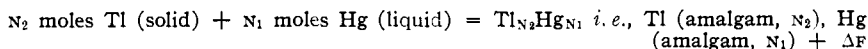
[1] These calculations were in part completed while the author was the incumbent of a National Research Fellowship.

[2] Richards and Daniels, THIS JOURNAL, 41, 1732 (1919).

[3] Lewis and Randall, ibid., 43, 233 (1921).

[4] Richards and Smyth, ibid., 44, 524 (1922).

[5] Richards and Smyth, ibid., 45, 1455 (1923).

[6] When we have an amount of solution such that the number of moles (N_1) of constituent 1 is equal to the mole fraction (N_1) of constituent 1, and similarly for the other constituents, we say we have one mole of solution. Cf. page 32, Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923. Since I shall use one mole of amalgam in all my calculations, I shall use N_1, N_2 throughout in place of n_1, n_2.

The free energy change may be found from the equation[7] $\Delta F = N_1 \Delta \bar{F}_1 + N_2 \Delta \bar{F}_2$, where $\Delta \bar{F}_1$, $\Delta \bar{F}_2$ are the partial molal free energies of transfer of mercury and thallium, respectively, from the pure state to amalgams of concentration N_1, N_2, *i. e.*

     1.   Hg (liquid) = Hg (amalgam, N_1) + $\Delta \bar{F}_1$
     2.   Tl (solid)   = Tl (amalgam, N_2) + $\Delta \bar{F}_2$

and $\Delta \bar{F}_1, \Delta \bar{F}_2$ must be multiplied by N_1, N_2, respectively, to take account of the transfer of N_1, N_2 moles instead of one. For each free energy of transfer, $\Delta \bar{F}_1 = -\mathbf{NFE} = RT \ln a_1$, where $\mathbf{E}$ is the e. m. f. of the cell whose cell reaction is given in equation 1 or 2 above. Because of this definition, values of $\Delta \bar{F}_2$ cannot be calculated from Lewis and Randall's values of a_2 because the standard state for thallium was defined in their treatment not as pure solid thallium, but as an infinitely dilute solution of thallium in

<div align="center">TABLE I</div>

<div align="center">MOLAL FREE ENERGIES OF FORMATION OF THALLIUM AMALGAMS AT 20°</div>

N_2, mole fraction of thallium	$-E$, volt	a_1	$-N_2 \Delta F_2$, joules	$-N_1 \Delta F_1$, joules	$-\Delta F$, joules
0	$-\infty$	1	?	0	?
0.0050	0.0112	0.9948	79.5	12.7	92.2
.0100	.0308	.9890	140.1	26.7	166.8
.0500	.0827	.9367	450.2	151.4	601.6
.1000	.1118	.8550	619.5	343.7	963.2
.2000	.1435	.6928	627.2	715.6	1342.8
.2850	.1588	.5720	473.0	973.5	1446.5
.3000	.1609	.5530	437.1	1010.7	1447.8
.3200	.1634	.5287	389.1	1056.3	1445.4
.4000	.1716	.4404	169.8	1199.3	1369.1
.4289	.17387	.4117	86.1	1235.4	1321.5
.5000	.17387	.4117	100.4	1081.6	1182.0
.6000	.17387	.4117	120.4	865.2	985.6
.7000	.17387	.4117	140.5	648.9	789.4
.8000	.17387	.4117	160.6	432.6	593.2
.853	.17387	.4117	171.2	318.0	489.2
.868	.17422	.3756	145.0	315.0	460.0
.885	.17462	.3359	113.6	305.8	420.4
.890	.17474	.3237	103.9	302.4	406.3
.904	.17508	.2868	75.9	292.2	368.1
.930	.17508	.2868	78.1	213.1	291.2
.945	.17508	.2868	79.3	167.4	246.7
.959	.17508	.2868	80.5	124.8	205.3
.970	.17525	.2390	65.5	104.7	170.2
.980	.17544	.1783	48.2	84.0	132.2
.990	.17567	.0939	26.8	57.7	84.5
1	.17595	0	0	?	?

[7] ΔF could also be found by integrating either of the partial molal free energies of transfer, as Professor George Scatchard has pointed out.

mercury. Hence it is simpler to use the e. m. f. values directly. Since these were referred to a dilute amalgam as reference electrode, the equation becomes $\Delta \bar{F}_2 = -NFE_2 = -NF[-E_{Tl} - (-E_{N_2})]$, where the e. m. f.'s are for concentration cells containing as one electrode solid thallium or thallium amalgam, mole fraction N_2, and as the other electrode the most dilute amalgam measured by Richards and Daniels. Values of $-E_{N_2}$ up to $N_2 = 0.5$ are taken from the data of Richards and Daniels[2] and for higher values of N_2 from those of Richards and Smyth.[4] The calculated values of $\Delta \bar{F}_2$ are given in Table I. The values of $\Delta \bar{F}_1$ can be calculated directly from the activity data of Lewis and Randall up to $N_2 = 0.4$ by the equation $\Delta \bar{F}_1 = RT \ln a_1$, since the standard state in this case is pure mercury.
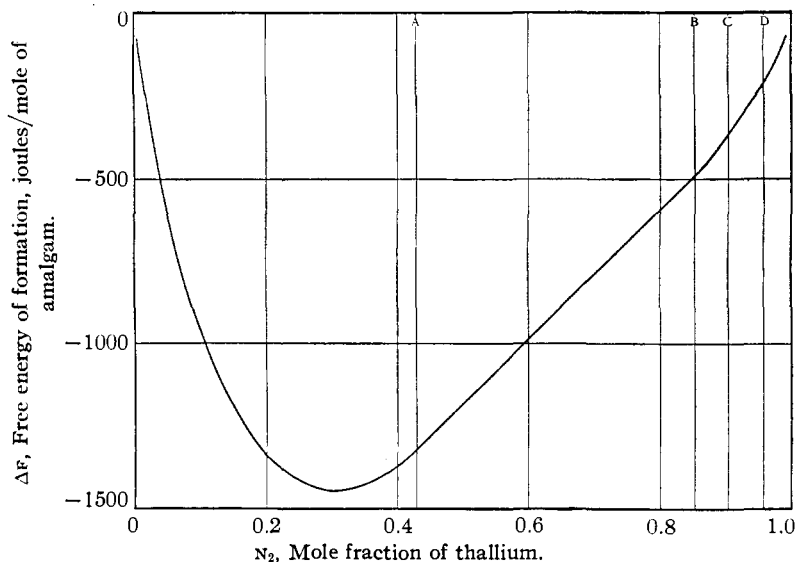

Fig. 1.—Free energy of formation of thallium amalgams at 20°. A indicates liquidus point ($N_2 = 0.4289$), and B, solidus point ($N_2 = 0.853$). C indicates transition point, solid solutions in α-thallium—two solid solutions ($N_2 = 0.904$), and D, transition point two solid solutions—solid solutions in β-thallium ($N_2 = 0.959$). For a discussion of the phase diagram see Richards and Smyth's papers.[4,5]

For the remainder of the curve it is first necessary to calculate a_2 from the e. m. f. data, plot N_2/N_1 against $\log a_2/N_2$, and find $-\log a_1/N_1$ by graphical integration as done by Lewis and Randall.[3] From the values of a_1, $\Delta \bar{F}_1$ may be obtained. These values are given in Table I, and a graph of the free energy–composition curve is given (Fig. 1).

The results obtained by preliminary calculation were presented in a Communication to the Editor.[8] Since this was submitted, the data have

[8] Teeter, THIS JOURNAL, **53**, 1180 (1931).

TABLE II
FREE ENERGIES OF FORMATION OF THALLIUM AMALGAMS AT 40°

N_2, mole fraction of thallium	$-E$, volt	a_1	$-N_2\Delta F_2$, joules	$-N_1\Delta F_1$, joules	$-\Delta F$, joules
0	$-\infty$	1	?	0	?
0.003259	0.00000	0.9967	58.5	8.8	67
.01675	.04833	.9804	222.2	50.7	273
.03723	.07603	.9524	394.4	122.3	517
.04856	.08620	.9353	467.2	165.7	633
.0986	.11667	.8523	658.3	375.1	1033
.1680	.14165	.7342	717.0	669.3	1386
.2074	.15148	.6714	688.0	822.2	1510
.2701	.16339	.5794	585.6	1037	1623
.3000	.16790	.5400	520.0	1123	1643
.3361	.17239	.4967	436.9	1210	1647
.4240	.18094	.4026	201.3	1364	1566
.4537	.18342	.3748	106.8	1396	1503
.5000	.18342	.3748	117.7	1277	1395
.6000	.18342	.3748	141.2	1022	1163
.7000	.18342	.3748	164.8	766.6	931
.8000	.18342	.3748	188.3	511.1	699
.8500	.18342	.3748	200.1	383.3	583
1.000	.18586[a]	0	0	?	?

[a] This value is obtained by extrapolation from the data of Richards and Smyth using temperature coefficients as given by Richards and Daniels. There is some uncertainty in this extrapolation, probably of the order of several hundredths of a millivolt. For this reason this calculation cannot be considered as accurate as the other, and the curve given separately (Fig. 2).

TABLE IIA
FREE ENERGIES OF FORMATION OF THALLIUM AMALGAMS AT 40°, MODIFIED TO TAKE ACCOUNT OF THE CHANGE IN FREE ENERGY OF THE COMPONENTS

N_2, mole fraction of thallium	$-\Delta F$, joules	ΔF_B, joules	$\Delta F'$, joules
0	0	+1400	+1400
0.00500	110	+1400	+1290
.02000	300	1402	1102
.04000	530	1405	975
.05000	640	1406	766
.1000	1050	1412	362
.1500	1300	1418	118
.2000	1485	1424	− 61
.2500	1600	1430	−170
.3000	1643	1436	−207
.3500	1645	1442	−203
.4000	1595	1448	−147
.4537	1503	1454	− 49
.5000	1395	1460	+ 65
.6000	1163	1472	+309
.7000	931	1484	+553
.8000	699	1496	+797
.8500	583	1502	+919

been entirely recalculated. The e. m. f. data of Richards and Daniels and Richards and Smyth have been replotted on a much larger scale, so that it was possible to carry the interpolation at round mole fractions to four and sometimes to five figures. Minor differences in these new values of the e. m. f., and a few other minor errors in the first calculations caused slight alterations in the position of individual points, and the curve has been redrawn.
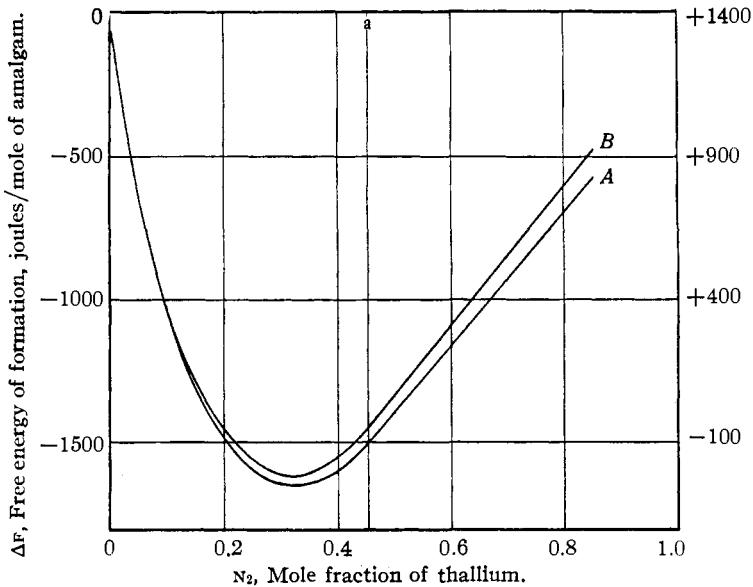

Fig. 2.—Free energy of formation of thallium amalgams at 40°. a indi- cates liquidus point (N_2 = 0.4537). Curve A is calculated as for Fig. 1. Curve B is modified to take account of the change of free energy of thallium and mercury on raising the temperature. Note different ordinates—scale at left for Curve A, at right for curve B.

In addition a calculation of ΔF has been made for part of the region at 40° (Table II and Fig. 2). In Fig. 2 Curve A has been brought down to the same zero as the curve of Fig. 1. Since the variation of free energy with temperature is known for thallium and mercury,[9] a second curve (B) has been plotted showing the effect of these changes. This curve was calcu- lated as follows: as pointed out below ΔF is equal to the difference between the partial molal free energies of the components in the mixture and in the pure state. Call the first F_A and the second $-F_B$. Then

$$\Delta F_{313.1} - \Delta F_{293.1} = \Delta F_A + \Delta F_B$$

where the last deltas refer to temperature. Also

$$\Delta F' = \Delta F_{313.1} - \Delta F_A = \Delta F_{293.1} + \Delta F_B$$

[9] See "International Critical Tables," 1929, Vol. V, pp. 88–89, calculated from data in the literature by W. H. and E. Rodebush.

Since

$$F_B = -N_2(F_1^\circ - F_2^\circ) - F_1^\circ$$

$$\Delta F_B = -N_2(\Delta F_1^\circ - \Delta F_2^\circ) - \Delta F_1^\circ$$

Substituting values interpolated and extrapolated from "International Critical Tables," $\Delta F_B = 120\, N_2 + 1400$. The results of the calculation are given in Table IIA. There is little change in the slope of the curve, since ΔF_1° and ΔF_2° are nearly equal, although the curve as a whole is shifted considerably upward.

Discussion of Results

As was pointed out in the preceding communication, Tammann has shown[10] how the different types of phase diagrams can be derived from purely thermodynamic considerations, using the "thermodynamic potential function, ζ," which is the same as our free energy, F. The free energy for a binary system is a function of the independent variables p, T and N_2, and for condensed systems p is constant. For each phase there is a surface in free energy–temperature–composition space. From the signs of the various partial derivatives it is possible to predict that the F-isobars will fall with falling temperature, and will be concave to the T-axis. The F-isotherms will be convex to the composition axis, except in special cases.

If the free energy–temperature curve were known for each of the pure substances, and the free energy surface for each phase, the phase diagram would be derived somewhat as follows. The intersections of successive isothermal planes with the F-surfaces would be constructed and values of F for the components laid off on the axes. Equilibrium points on an isothermal line across the phase diagram would then be defined. If the equilibrium point for pure A–liquid mixtures was desired, a tangent from the point F_A to the F-curve would be constructed. The abscissa (composition) corresponding to the point of tangency would be the point desired. If the tangent could not be drawn, no such equilibrium could exist at the given temperature. If the equilibrium points for two phases were to be determined (for example liquidus and solidus points for components forming both liquid and solid solutions), the common tangent to the free energy curves would be constructed. Other isothermal lines would be determined in the same way. This shows the method in its essentials. There is one more important point. The phase stable at any given value of the composition is the one that has the smallest free energy. Hence the free energy–composition curve for stable phases will be a broken curve made up of straight lines where the tangent from F_A to the F-curve, or the common tangent to the two F-curves, lies below the curve for homogeneous mixtures, and made up of curves where the curves are lowest.

[10] Tammann, "Lehrbuch der heterogenen Gleichgewichte," Vieweg und Sohn, Braunschweig, 1924.

What has been plotted is the difference between the partial molal free energies of the components in the mixture and the pure state

$$\Delta F = N_1 \Delta \bar{F}_1 + N_2 \Delta \bar{F}_2 = N_1(\bar{F}_1 - F_1^\circ) + N_2(\bar{F}_2 - F_2^\circ)$$

where F_1°, F_2° are molal free energies of liquid mercury and solid thallium. Hence

$$\Delta F = N_2\bar{F}_2 + N_1\bar{F}_1 - N_2 F_2^\circ - N_1 F_1^\circ = N_2\bar{F}_2 + N_1\bar{F}_1 - N_2 F_2^\circ - (1 - N_2)F_1^\circ$$

since $N_1 = 1 - N_2$. This may be regarded as the sum of two equations

$$F_A = N_2\bar{F}_2 + N_1\bar{F}_1, \text{ and}$$
$$F_B = -N_2 F_2^\circ - (1 - N_2)F_1^\circ$$

Since F_2° and F_1° are constants at any given temperature (though wholly unknown), the latter equation represents a straight line since it may be written $F_B = N_2(F_1^\circ - F_2^\circ) - F_1^\circ$. Hence the curve corresponding to ΔF is that corresponding to F_A subjected to a "shear," the transformation obtained by adding a linear equation to any given equation. While such a transformation changes the slope of the given curve, the curvature is not changed, as is easily seen by taking the first and second derivatives. Straight lines, therefore, remain straight lines after a shear.

The experimental curve should, therefore, have the characteristics of the theoretical curve as described above. On analyzing the former we see that it is made up of five sections, where the vertical lines **A,B,C,D** correspond to the singular points on the isothermal across the phase diagram. The curved portion between $N_2 = 0$ and the line **A** represents the free energy of liquid mixtures. The portion included between **A** and **B** is a straight line representing the common tangent to the free energy curves for liquid solutions and solid solutions of mercury in β-thallium. The fact that the common tangent is lower than either curve in this region shows that the heterogeneous mixture is more stable than either phase alone. The portion between **B** and **C** is again curved, representing the free energy of solid solutions in β-thallium; the portion between **C** and **D** is again a straight line, representing the common tangent to the curves for solid solutions in β- and in α-thallium; while the portion between **D** and $N_2 = 1$ is curved, representing the free energy for solid solutions in α-thallium.

The correspondence is hence complete. One further feature is of note. A minimum occurs in the liquid region near to but not coinciding with the composition of the known compound Tl_2Hg_5. The preliminary calculation seemed to show complete coincidence, but the recalculation showed that the composition corresponding to the minimum differed from that of the compound by an amount slightly greater than the experimental error. This lack of coincidence is not so surprising, for the slopes of the experimental and theoretical curves would coincide only if F_1° and F_2° are equal. (The slopes differ by $F_1^\circ - F_2^\circ$.) That the point is only slightly displaced would seem to indicate that the difference in F° is not large, and the slope

of the two curves not far different, if indeed a minimum is theoretically required at this point. Possibly the agreement is entirely fortuitous. The curve at 40° (Fig. 2) shows the minimum displaced to a slightly higher value of N_2.

Since Richards and Daniels have also given data for 30°, it would be possible to obtain a free energy curve for this temperature, and with the three curves a fair representation of a portion of the free energy surface could be constructed. It was not thought worth while to draw this 30° curve until more complete data were available. The curve at 40° shows well enough the change in shape of the F-isotherms with rising temperature.

The Heats of Formation.—The calculation of the heats of formation of amalgams can be carried out in three ways, provided the necessary data are available. One of these methods will be used for thallium amalgams, and the other two for cadmium amalgams in the paper that is to follow, but all will be described here for the sake of completeness.

Following Roozeboom[11] the integral heats of solution of the amalgamated and the unamalgamated constituents in the same solvent, in this case mercury, can be measured. The heat of formation can then be obtained as follows:

Let ΔH, the increase of heat content, be the heat of the reaction

$$N_2 \text{ moles Tl (solid)} + N_1 \text{ moles Hg (liquid)} = Tl_{N_2}Hg_{N_1} + \Delta H$$
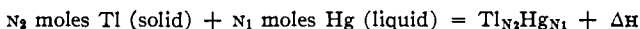
A positive value of ΔH then means heat *absorbed* in the formation of one mole of amalgam, and a negative value means heat *evolved*. Let L be the relative heat content defined as in the paper of Lewis and Randall.[3] L_1, the relative heat content of pure mercury, and L_2, the relative heat content of thallium in an infinitely dilute amalgam, are taken as zero. For an amalgam, therefore, the relative molal heat content is equal to the heat *liberated* on dissolving one mole in a large amount of mercury. (This is the convention of sign for ΔH and L used by Lewis and Randall.) For the unamalgamated constituents, the relative molal heat content is equal to the integral heat of solution of N_2 moles thallium in mercury plus the integral heat of solution of N_1 moles mercury in mercury (which is zero).

$$Tl_{N_2}Hg_{N_1} \ (i.\ e.,\ \text{one mole amalgam},\ N_2,N_1) = \text{Amalgam},\ N_2 = 0,\ + L_A \quad (1)$$
$$N_2 \text{ moles Tl(s)} + N_1 \text{ moles Hg(l)} = \text{Amalgam},\ N_2 = 0,\ + L_U \quad (2)$$

Subtracting (1) from (2)

$$N_2 \text{ moles Tl(s)} + N_1 \text{ moles Hg(l)} = Tl_{N_2}Hg_{N_1} + (L_U - L_A)$$

where the subscripts U and A refer to the unamalgamated and amalgamated constituents, respectively. Furthermore $L_U = N_2L_2(s) + N_1L_1$. From the convention of sign, it will be seen that $\Delta H = -(L_U - L_A)$.

The second method is essentially the same except that, in case the partial

[11] J. W. B. Roozeboom. "Die heterogene Gleichgewichte" (Binary Systems), **1904**, Vol. II, p. 1.

molal heat contents of thallium and mercury in the amalgam have been determined, L_A can be calculated instead of measured, using the equation $L_A = N_2\bar{L}_2 + N_1\bar{L}_1$. This is the method which has been used for thallium amalgams.

The third method may be used to calculate the heats of formation from e. m. f. data involving cells such as $Tl \mid Tl_2SO_4 \mid Tl_{N_2}Hg_{N_1}$. Using the Helmholtz equation, the molal heat of transfer of thallium from one electrode to the other can be calculated, assuming a cell so large that the concentration of thallium in the amalgam will not be altered by the transfer of one mole. The molal heat of transfer of thallium from an electrode of the pure metal to an imaginary electrode consisting of unamalgamated thallium and mercury of composition N_1,N_2 can also be calculated. This heat of transfer is equal to $N_1L_2(s)$, since the heat of solution of thallium in pure mercury is $L_2(s)$, while the heat of solution of thallium in thallium is zero. In calculating ΔH for one mole of amalgam each of these heats of transfer must be multiplied by N_2 to take account of the transfer of N_2 moles of thallium instead of one

$$Tl(s) = Tl_{N_2}Hg_{N_1} + N_2L_A' \qquad (3)$$

$$Tl(s) = N_2Tl + N_1Hg + N_2L_U', \quad L_U' = N_1L_2(s) \qquad (4)$$

Subtracting (4) from (3)

$$N_2Tl + N_1Hg = Tl_{N_2}Hg_{N_1} + N_2(L_A' - L_U'), \quad \Delta H = -N_2(L_A' - L_U')$$

From the data of Richards and Daniels,[2] using the partial molal heat contents of Lewis and Randall,[3] the heats of formation at 30° can be calculated for thallium amalgams up to $N_2 = 0.4$. Since there are also values of $\bar{c}_{p_1}$ and $\bar{c}_{p_2}$ for this range[2,3] the heats of formation at 20° can be calculated.

TABLE III

HEATS OF FORMATION OF THALLIUM AMALGAMS AT 20 AND 30°, IN JOULES PER MOLE OF AMALGAM

Mole fraction N_2	L_A at 30°	L_U at 30°	$\Delta H_{30°}$	L_A at 20°	L_U at 20°	$\Delta H_{20°}$
0	0	0	0	0	0	0
0.0500	46	148	−102	−241	+155	−396
.1000	174	295	−121	−121	310	−431
.1500	366	442	− 76	+67	465	−398
.2000	624	590	+33	+322	620	−298
.2500	933	738	195	628	775	−147
.3000	1259	885	374	950	930	+ 20
.3500	1598	1032	566	1288	1085	203
.4000	1962	1180	782	1648	1240	408
.4407	2262	1300	962			
.5000	2383	1475	908			
.6000	2585	1770	815			
.7000	2788	2065	723			
.8000	2991	2360	631			
.8500	3092	2502	584			

At 30°, solid begins to appear at 0.4407 mole fraction thallium, and the heats of formation can be calculated for the range 0.4407–0.8500 mole fraction, in which solid and liquid phases coexist and the e. m. f. is constant. The exact solidus point is not known. In the absence of heat capacity or further e. m. f. data in this latter range, it has been thought best not to attempt the calculation of the heats of formation at 20°. The partial molal heat contents were calculated as in Lewis and Randall's paper and the heats of formation then followed as detailed above.
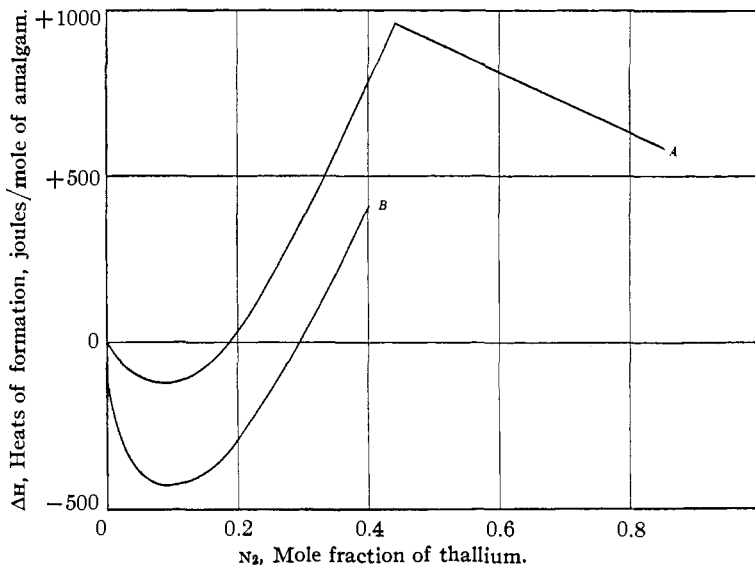

Fig. 3.—Heats of formation of thallium amalgams at 30°, Curve A, and at 20°, Curve **B**. The break in Curve A is at the liquidus point ($N_2 = 0.4407$).

The results of the calculation are presented in Table III and Fig. 3. The curves are to be particularly contrasted with the curves for cadmium amalgams, which will appear shortly. It is sufficient to say here that in the main the heats of formation of thallium amalgams are positive, and of cadmium amalgams negative, in line with the opposite heat effects caused by diluting amalgams of the two metals with mercury. It is hoped to extend the method to other types of amalgam systems in the near future.

Summary

1. The molal free energies of formation of thallium amalgams at 20° have been calculated from data on the e. m. f. of thallium amalgams. A portion of the curve at 40° has also been determined.

2. The free energy–composition curve is in accord with theoretical expectations.

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

BY CHARLES EDWIN TEETER, JR.[1]

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 shown[3] 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 contents[4] 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 air[5] 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-

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[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).