the cell may, nevertheless, not be satisfactory unless the standard solutions cover the correct range of resistance. In the cells H1 and H3, the average of the ratio of the resistance of the 0.01 *N* to that of the 0.02 *N* potassium chloride solution is 1.9580. In the "Arrhenius" cell the ratio is 1.9566, which differs from the one obtained in the other cells by only 0.07%. In other words, the cell constant of the "Arrhenius" cell calculated from the resistance of the 0.01 *N* solution would differ hardly at all from that calculated from the resistance of the 0.02 *N* solution and the unreliability of the cell would have been overlooked had only these two solutions been used.[1]

Summary.

It has been pointed out that even though the minima obtained in the measurement of the resistance of solutions by the usual method may be perfectly sharp, the results may nevertheless be incorrect and criteria for determining the reliability of the measurements and methods for overcoming some of the difficulties encountered have been suggested.

CHICAGO, ILL.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

CONCENTRATED THALLIUM AMALGAMS: THEIR ELECTROCHEMICAL AND THERMOCHEMICAL BEHAVIOR, DENSITIES AND FREEZING POINTS.

BY THEODORE W. RICHARDS AND FARRINGTON DANIELS.

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More than twenty years ago a series of investigations on the thermodynamics of amalgams was begun in Harvard University.[2] Recently, similar investigations have been conducted by G. A. Hulett.[3] The further interesting contributions of Joel H. Hildebrand concerning the vapor pressure of amalgams have added important auxiliary information.[4]

Nevertheless, the complete understanding of the electrochemical, thermochemical, and osmotic performance of these interesting metallic solutions has not been attained. This is unfortunate, since the nature of amalgams renders them more susceptible to varied investigation than that of many other types of solutions. It might reasonably be hoped that knowledge gained from these might be transferred by analogy to

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[1] Errors of the kind found in the case of the "Arrhenius" cells are doubtless due to polarization.

[2] T. W. Richards and G. N. Lewis, *Proc. Am. Acad.*, **34,** 87 (1898); T. W. Richards and G. S. Forbes, *Carnegie Inst. Publications*, **56,** 1 (1906); T. W. Richards and J. H. Wilson and R. N. Garrod-Thomas, *Ibid.*, 118, 1 to 72 (1908); T. W. Richards and F. Daniels, *Trans. Am. Electrochem. Soc.*, **22,** 343 (1912).

[3] G. A. Hulett and DeLury, THIS JOURNAL, 30, 1805 (1908).

[4] J. H. Hildebrand and E. D. Eastman, *Ibid.*, **36,** 2020 (1914); **37,** 2452 (1915).

other solutions, even to aqueous ones, as regards those aspects of solution not involving electrolytic dissociation.

Therefore it seemed to be worth while to follow further possible lines of investigation suggested by earlier researches in the hope of attaining a satisfactory solution of the points not yet completely understood. For this purpose thallium lends itself more advantageously than any common metal possessing a moderate solution tension, because thallium is extraordinarily soluble in mercury. Even at 20° the liquid amalgam may contain as much as 43.3% of thallium. Such amalgams give sharp and constant values for their single potentials in aqueous solutions of thallous salts. Hence the free energy of transfer of thallium from one to another of these amalgams can be determined with great accuracy.

Bearing these facts in mind, about 8 years ago we began an extended research upon both concentrated liquid and solid thallium amalgams, using both electrochemical and thermochemical methods. The experimental part of the research, which was to supplement the earlier work of one of us with J. H. Wilson on dilute thallium amalgams, was completed in the spring of 1914, but its publication has been delayed partly by the desire to correlate more fully the varied results, and partly by other pressing duties, occasioned by the great war. The work involved the determination of electromotive forces at several temperatures, densities, heat capacities, heats of solution of thallium in mercury, heats of dilution of the amalgams, melting points of solid amalgams, and allied problems. The several details are recorded below, together with some of the conclusions which may be drawn from the facts. The discussion of the theory is best postponed until the facts have been presented, since the method of attack was inductive rather than deductive. A more complete interpretation, which attempts to present a consistent theory of the constitution of the amalgams, and indicates the general tendencies at work in all such systems, will be the subject of a later communication.

The Purification of Materials.

The thallium material came from different sources, some from pure metallic thallium of commerce, some from earlier pure amalgams, and some from older residues purified by precipitating as iodide, converting into the nitrate, and precipitating impurities with hydrogen sulfide. A slight residue left after the solution of metallic thallium in strong sulfuric acid was filtered off and discarded, and the excess of acid was driven off by heating. The fused cake of thallium sulfate from all sources dissolved completely in water. The salt was once crystallized, and its solution then allowed to stand in porcelain for a week or more with occasional stirring, in contact with pure electrolytic metallic thallium. After filtration of this solution, the salt was 3 times crystallized, being drained each time with a small efficient centrifuge.

Pure thallium was prepared by electrolysis of a solution of this sulfate and pure ammonium oxalate, using platinum electrodes. Thallium peroxide persistently formed on the anode, although conditions were varied over a wide range. An electrolyte made by mixing equal parts of saturated solutions of each salt, with a moderate current density, was the most satisfactory. A piece of chemically clean cotton cloth tied around the anode of platinum foil kept the peroxide from gaining access to the cathode. From time to time the thallium collecting on the cathode was removed, washed, and preserved in pure water in contact with another platinum cathode (3 volts), and thus preserved from oxidation. The electrolysis was continued until a portion of the solution showed only a slight turbidity with potassium iodide. The thallium was then thoroughly washed, although it was found impossible to remove the last trace of salt, as shown with either barium acetate or potassium iodide. After being pressed into small porcelain boats, the metal was fused in a current of hydrogen in a porcelain tube, and kept in dry glass bottles. Of course it oxidized slightly on the surface, but before weighing it was carefully scraped clean and bright. Because of its manner of preparation it may have contained a trace of sulfide, but this was probably removed and accounted for during amalgamation.

Crude mercury, after long contact with conc. sulfuric acid, was dropped in a fine stream several times through a solution of mercurous nitrate and dil. nitric acid, and then distilled in a current of air under reduced pressure, as recommended by Hulett.[1] Mercury thus prepared can hardly contain any impurity except dissolved oxygen. In order to eliminate this possibility, the metal was redistilled in a current of purified hydrogen, and sealed under hydrogen in a glass bulb, provided with a stopcock. Subsequently the mercury was kept and used wholly out of contact with air. Oxygen, which is fatal to accurate measurement of this kind, must have been excluded.

Ammonium oxalate used for the electrolysis of thallium was made from oxalic acid and ammonium hydroxide. A strong solution of oxalic acid (58%) was brought to boiling, filtered and strongly acidified with redistilled hydrochloric acid. After cooling and recrystallizing 3 times, the chloride was found to have been removed. The oxalic acid was neutralized with concentrated, freshly distilled ammonia, and the resulting ammonium oxalate was 3 times recrystallized. More ammonia was added as needed to replace that driven off by heating.

Distilled water was redistilled from alkaline permanganate solution and again from a few drops of sulfuric acid, using block tin condensers.

All the hydrogen used was generated from pure zinc and hydrochloric

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[1] *Z. physik. Chem.*, 33, 611 (1900); *Phys. Rev.*, 21, 388 (1905).

acid,[1] and was purified and dried by passing over a strong solution of caustic potash on glass pearls, and through two towers containing fused potassium hydroxide. Rubber tubes were avoided, and in this apparatus sealed glass connections everywhere effectually excluded air from the hydrogen.

The Preparation of the Amalgams.

The method of making amalgams used by Richards and Wilson[2] was first employed. Thallium was electrolytically deposited in pure mercury, the concentration being calculated from the weight of silver deposited in a coulometer in the same circuit.

By a method of analysis to be described presently it was found that although dilute amalgams may be made fairly accurately in this fashion, concentrated amalgams always contained less thallium than the quantity corresponding to the current and time. This is doubtless due to the diffusion of dissolved oxygen or thallic sulfate from the anode to the neighborhood of the cathode after the current has been running a few minutes. No matter how carefully the electrolyte is at first freed from oxidizing material, it must very soon be impregnated with it. Accordingly the electrolytic method was later abandoned, and the amalgams were made separately, by mixing actually weighed amounts of mercury and thallium. The amalgamation of each piece of the metal was effected with the help of a few cc. of dilute standard acid, which dissolved the superficial trace of oxide on the thallium.[3] The amalgamation was conducted in a closed test tube, into which projected a very finely pointed, small pipet arranged essentially in the fashion adopted in the electrolytic method. The mixing was completed by bubbling hydrogen through the amalgam. Precautions against the presence of air are not very important at this stage, since allowance would be made for oxidation by means of the acid titration which immediately followed. The remaining acid was immediately titrated with standard alkali (using methyl orange), and the weight of thallium present in the aqueous solution was calculated and subtracted from the weight of thallium taken. The end-point was accurately determined and the correction (which never amounted to more than a few milligrams) for the dissolved thallium must have been accurate to within 0.1 or 0.2 mg. The only uncertainty lay in a doubt as to the exact composition of the trace of oxidized film on the surface of the metal at the time of weighing, but when large quantities are taken this uncertainty is negligible, especially since thallium has so large an equivalent.

When the amalgamation and mixing were complete (and before the

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[1] The generator used is described in *Carnegie Inst. Publications*, 56, 19 (1906).

[2] *Carnegie Inst. Publications*, 118, 9, 10, 11 (1909).

[3] Richards and Forbes, *Carnegie Inst. Publications*, 56, 18 (1906). The trace of sulfide, if present, was probably also dissolved.

titration of the supernatant acid), the homogeneous liquid amalgam was almost all drawn into the small pipet which had previously delivered the gas. When the amalgam has been almost wholly withdrawn from the test tube, the suction was stopped, hydrogen was admitted above, and the pipet was removed for immediate discharge into the electrolytic cell in which it was to be measured.

The advantages of this procedure over the former method of Richards and Wilson are several. Large bulbs and stopcocks need not be put on the balance, and weighings may be made accurately to tenths of a milligram. Each amalgam was made up separately and a possible error in one concentration would not be repeated in the others. Hence the absolute average values are safer. The mixing by bubbling hydrogen gas was more efficient than could be caused by the gentle rocking of the cell. The manipulation was simpler and more rapid; and with pure materials ready, the amalgams could be made, the cell filled, and measurements taken at different temperatures, all in one day—a distinct advantage when the amalgams may change in composition on standing a long time under the electrolyte, as in this case. On the other hand, the new method lacks the consistency as regards relative measurements which is attained by making all of the amalgams from a single "parent" amalgam. This last circumstance was that which determined the procedure in the work of Richards and Wilson.

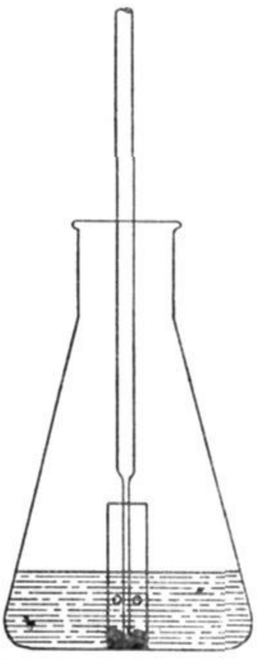

Fig. 1.—Apparatus for preparing thallium amalgams for volumetric analysis.

In order to test the concentration of these and other thallium amalgams, a convenient method of volumetric analysis was devised which proved to be accurate, simple, and rapid, and may find application in other work. The sample of amalgam, which should contain about 0.2 g. of thallium, is accurately weighed, placed in a 100 cc. Erlenmeyer flask, and covered with 50 cc. of standardized 0.02 *N* sulfuric acid. A short piece of wide, glass tubing is fitted snugly over the globule of amalgam to hold it in place, and a long capillary tube is inserted under the metal so that pure air may be bubbled through it and cause rapid oxidation. Two small holes blown near the bottom of the larger tube aid in the circulation of the acid (Fig. 1). The thallium is oxidized and the oxide at once dissolves in the sulfuric acid, which is too dilute to attack the mercury as long as any thallium remains. The end-point of the oxidation may be estimated readily from the behavior of the mercury, since, when the thallium has been removed, the agitation due to the air causes the formation of a great number of small globules which will not unite again, probably because of a very thin, unweighable film of mercurous sulfate. Subsequent bubbling fails to diminish the concentration of the supernatant acid. When the small globules thus no longer unite to form larger ones, the flask is removed and the excess of acid titrated with exactly standardized alkali. To make sure that all the thallium has been oxidized, one cc. of acid is added and air bubbled through for an hour more. If the alkali then required is not equivalent to the added acid, the removal of thallium has not at first been complete, and the process must be repeated until there is no loss. Another trial is rarely necessary. The time required varies with the rate of bubbling and the adjustment of the tube from perhaps 2 to 10 hours, but the procedure requires no attention. Methyl orange or methyl red may be used as an indicator. The best results are of course obtained if the end-point is judged by comparison with indicator in thallium sulfate solution or in a properly prepared buffer solution. The accuracy of the method may be gathered from the results shown in Table I. The first 3 results were obtained in 1912 and the rest in 1913, using a new standard solution.

TABLE I.

Comparison of Methods of Determining Composition.

Amalgam.	By titration. %.	By direct weighing. %.	Error. %.
A	21.70	21.722	0.10
B	13.07		
	13.09	13.128	0.37[1]
C	4.936	4.930	0.12
D	10.02		
	10.01	10.019	0.04
E	42.93	42.858	0.13

The Thermostats.—Two thermostats were used, one at 30°. The other, containing two regulators, could be set either at 20° or at 40°. They were electrically heated, constant within 0.01°, and thoroughly stirred.

The Cell.—The amalgams were contained during the electrical measurements in the 4-cupped glass vessel used previously in this laboratory[2] and shown in the diagram (Fig. 2). It has an advantage over the later modification of Hulett's,[3] in that larger amounts of amalgam may be used without danger of accidental mixing, and therefore slight losses due to possible oxidation are robbed of much of their injurious effect.

In a cell composed of dilute and concentrated amalgam, both lose

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[1] With the exception of the doubtful case B, the volumetric results were accurate within 0.1 or 0.2 mg. of thallium with the weights taken. This degree of accuracy is not of the same order as the high accuracy of the potential measurements, but it affords nevertheless a useful check on the results.

[2] Richards and Forbes, *Carnegie Inst. Publications*, **56**, 22 (1906).

[3] Hulett and De Lury, THIS JOURNAL, **30**, 1814 (1908).

thallium by oxidation, but the dilute amalgam loses a larger percentage of its contents than the concentrated one, in a given time, since the oxidation is more rapid than the diffusion of dissolved oxygen. Hence the electromotive force of the cell rises. On this account not only was air scrupulously excluded, but all the measurements were made as quickly as possible. Although in early measurements trouble was experienced from oxidation, in the later ones it was adequately excluded, as is shown by the following two series of measurements, the first made immediately after the preparation of the amalgams, and the second after 9 days:

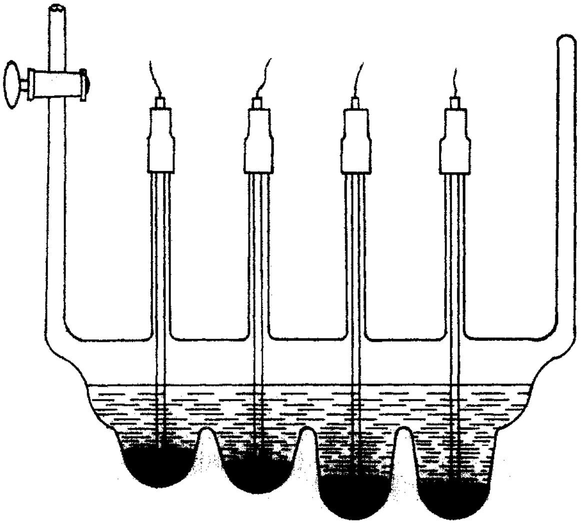

Fig. 2.—Cell with amalgams.

TABLE II.

Constancy of Measurements.

	20°.	1-2.	2-3.	3-4.
I..........	April 15	0.011572	0.008681	0.008174
II..........	April 24	0.011574	0.008681	0.008175

Concentrations, %:

1 = 20.970, 2 = 27.362, 3 = 34.029, 4 = 42.858.

The precautions needful to attain such a result are so important that they follow in detail.

The multiple cell was fused to the hydrogen generator, and after having been evacuated and filled with hydrogen several times it was almost filled with the electrolyte—a solution (about 2%) of the purest thallium sulfate in freshly distilled water. The solution had been boiled, cooled in pure hydrogen, subjected to a continuously bubbling stream of this gas (in order to remove dissolved air), then drawn into a hydrogen-filled finely pointed pipet, provided with a stopcock, and finally sealed off in hydrogen. From this pipet the filling of the cell was conducted through one of the projecting tubes of the latter in the presence of a counter current of hydrogen, the other tubes being closed. As a further precaution, the cell was subsequently evacuated and the solution was allowed to boil under reduced pressure, all of the 4 projecting tubes being closed by short lengths of cleaned pressure tubing and glass rods.

When all was ready, the several amalgams were introduced into their respective cups as rapidly as possible. The capillary jet of a pipet was inserted into one of the rubber tubes of the glass cell until the point extended below the surface of the electrolyte, in such a position as to be free from the danger of introducing any amalgam into the wrong cup. On the withdrawal of the pipet, the platinum wire (protected by glass) for making electrical connection was immediately substituted, the hydrogen stream continuing. Thus in rapid succession the 4 cups were filled, and the cell was ready for electrical measurement. The copper wires making connection with the potentiometer joined the platinum in mercury contacts beneath the level of the thermostat; hence thermoelectric effects were excluded.

The Potentiometer.—The potentiometer was that used in the earlier investigation by Wilson and Garrod-Thomas, already mentioned, but for the final readings it was adjusted anew and several improvements were made tending toward the elimination of parasitic electromotive forces. This instrument and all the rest of the measuring apparatus was shielded by a grounded equipotential shield[1] of copper, the various parts of the potentiometer being mounted on separate glass plates held firmly in place on the shield with paraffin. The heavily insulated copper wires forming the connections were enclosed in glass tubes. The binding posts as well as connectors were of solid copper, and contacts between unlike metals were reduced to a minimum. The potentiometer was covered by a large glass case in which a small fan (rotated by a distant electric motor) kept all parts at uniform temperature. The rocker switches and bridge rider were operated by cotton strings from a considerable distance.

The thermostat was found sometimes to be the seat of parasitic effects. When it was insulated, these effects were greatly magnified. Accordingly the water in the thermostat, and the relay, were grounded, whereupon this trouble disappeared. Too much emphasis cannot be put upon this precaution with regard to electrically heated thermostats.

The arrangement thus mounted permitted reading to one one-millionth of a volt. Sundry experiments were made in order to determine if its accuracy corresponded with this high degree of sensitivity. The agreement found by measuring separately several cells and comparing the sum of the separately measured electromotive forces with the actually measured total value of all in series was as good as could be expected. Such comparison is easily made in the 4-cupped cell employed. For example (in Series III at 30.00°), the cell I–L equalled 0.028945, whereas this value calculated as the algebraic sum of other combinations yielded, respectively, 7, 8 and 9 instead of 5 as the last figure, the other figures

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[1] W. P. White, *Phys. Rev.*, **25**, 341 (1907); THIS JOURNAL, **36**, 2011 (1914).

being the same. Thus the greatest deviation was 0.000004 volt, and the average could hardly be in error 0.000002 volt.

TABLE III.
Final Results (1913).
(Series III.)
E. in Millivolts.

	Concentration.	20°.	30°.	40°.
A...............	0.3315			
		45.550	46.937	48.326
B...............	1.704			
		26.395	27.050	27.704
C...............	3.788			
		9.763	9.968	10.168
D...............	4.935			
E...............	4.930			
		29.480	29.971	30.467
F...............	10.019			
		24.342	24.660	24.981
G...............	17.049			
		9.581	9.703	9.833
H...............	21.025			
I...............	20.970			
		11.572	11.741	11.915
J...............	27.362			
		8.681	8.844	9.001
K...............	34.029			
		8.174	8.360	8.547
L...............	42.858			
F...............	10.019			
		33.769	34.208	34.656
M...............	20.780			
		20.341	20.678	21.011
N...............	34.029			
		8.518	9.761	11.034
P...............	(49.418) Solid			
Q...............	10.30			
		32.360	32.791	..
R...............	20.78			
		28.892	30.477	..
S...............	(49.48) Partly solid			
		2.5[1]	2.7[1]	2.8[1]
Tl...............	Pure Tl			
U...............	(49.418) Partly solid Amalgam			
		—0.001	0.000	..
V...............	Amalgamated Tl			

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[1] These figures are only approximate. The potential of pure thallium is being investigated further.

Search was made for other possible disturbing conditions, however remote, which might be a source of error, but none was found. The room was usually very dry, and the introduction of a desiccating agent in the potentiometer case made no appreciable difference. The apparatus was never used in very humid weather, when, of course, electrical measurements are always difficult.

The Measurement of Amalgam Cells.—With amalgams and potentiometer prepared as described above, and with gradually increasing trustworthiness as the work proceeded, measurements were made during many months. As a rule, the readings were very definite and constant, although in a few cases shaking of the cell caused slight fluctuations in the electromotive force, dispelled by a few seconds' repose. Electrolytic metallic thallium, employed in one cell, in the form of a fine crystalline sponge, also gave a fairly constant potential.[1] Amalgamated thallium and solid amalgams at 20°, or above, gave electromotive forces fully as constant as those of the liquid amalgams. The solid amalgams of less than $33^1/_3\%$ at 0°, however, were not reproducible to millionths of a volt. The formation of mixed crystals may have introduced uncertainty here.

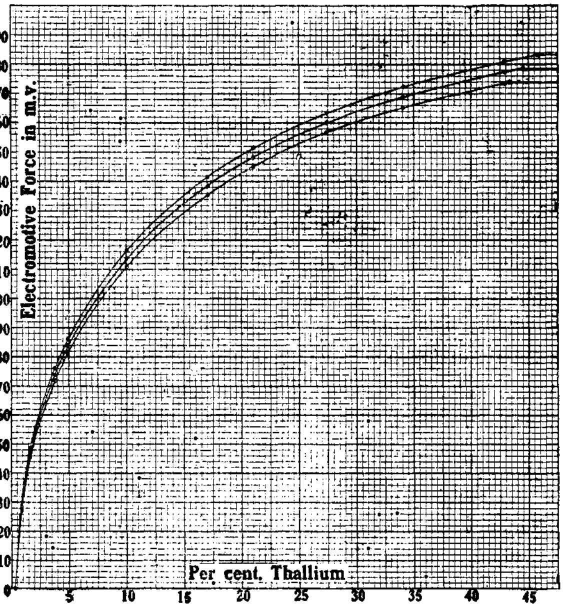

Fig. 3.—Electromotive forces of amalgam cells at 20°, 30°, and 40°. Uppermost curve 40°.

The preliminary measurments need not be recorded here. One of them has already been published.[2] It is enough to say that they were essentially identical with the results on p. 1740.

The accompanying graph (Fig. 3) pictures the final series of determinations at 20°, 30° and 40°, the weakest amalgam of this series (0.3315%)

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[1] Richards and Lewis, *Proc. Am. Acad.*, 34, 87 (1898). Lewis and Brighton point out that this is particularly the case with soft metals such as lead. Thallium is even softer than lead. THIS JOURNAL, 39, 1906 (1917).

[2] Richards and Daniels, *Loc. cit.*

being taken as the starting point with zero potential. They all (even the preliminary determinations) fall on a perfectly smooth curve; the error of plotting on coördinate paper as large as 44 × 53 cm. is much greater than the experimental error. The work of Richards and Wilson, below 2%, also falls exactly on the curve.

When the saturation point of the liquid amalgam has been reached, excess of thallium is without effect on the potential; the curve breaks into a horizontal straight line at a point giving the concentration at which solid and liquid are in equilibrium. A 43.3% thallium amalgam, then, has a freezing point of 20.00°. Similarly, the freezing points at 30° and 40° correspond to 44.5 and 45.8%, respectively. The horizontal line in the diagram indicates, of course, the coexistence of two phases in equilibrium.

Electrolytic thallium gave a potential somewhat more negative (2.49 millivolts at 20°) than amalgamated thallium. In an entirely independent more recent investigation (as yet unpublished) of Grinnell Jones and W. C. Schumb on the single potential of the thallium electrode, almost identical results were found. On the other hand, Lewis and von Ende[1] assumed from the results of Kurnakow and Puschin and of Sucheni (stating that their own experiments corroborated these results) that no difference in potential between thallium and the saturated amalgam exists. This apparent discrepancy will receive detailed discussion in a later communication.

The potentials of the liquid amalgams as given above are far greater than those demanded by any method of expressing the simple concentration law. For example, the observed potential between amalgams F and G above at 30° is 24.66, whereas the formula $(RT/F)\ ln\ C_1/C_2$ demands 13.88 and the formula $(RT/F)\ ln\ (1 + N_2)/(1 + N_1)$ demands 13.91.[2] This great discrepancy is even more highly interesting and important than the other. It will receive detailed consideration in the theoretical paper to which reference has already been made.

The Temperature Coefficient of the Cells and the Equation of Helmholtz.

The data in the table just given afford exact means of calculating the temperature coefficients of the several cells, and therefore of applying the equation of Helmholtz to them and calculating their heat effects.

The column before the last gives a quantity (the temperature coefficient of the potential of the cell divided by E_0, potential at 0°) which should equal the coefficient of expansion of a perfect gas, if the potential were due entirely to the concentration effect. The values of E_0 as far as the 17% amalgam could have been actually measured, but the amal-

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[1] G. N. Lewis and von Ende, THIS JOURNAL, 32, 732 (1910).

[2] See Richards and Daniels, *Loc. cit.;* Richards and Wilson, *Ibid.*, page 63; and Hildebrand and Eastman, *Ibid.*, p. 2456.

gams containing over 17% of thallium partly crystallized at 0°. In all cases the valves of E_0 were found by extrapolation from those at 20° and 40°. The minimum in this column at about 19% is very marked and is undoubtedly significant. Evidently the temperature coefficient is much less than that demanded by the gas law.

TABLE IV.

Temperature Coefficients and the Helmholtz Equation.

	$\Delta E/\Delta T$.				
Conc.	(20–30°).	(30–40°).	(Average).	$\Delta E/E_0\Delta T$ 20–40°.	U (joules).
0.3315	0.0001387	0.0001388	0.0001388	0.00325	470
1.704	0.0000656	0.0000654	0.0000655	0.00261	696
3.788					
	0.0000205	0.0000201	0.0000203	0.00215	370
4.935					
4.930					
	0.0000491	0.0000496	0.0000493	0.00173	1449
10.019					
	0.0000318	0.0000321	0.0000319	0.00135	1445
17.049					
	0.0000122	0.0000130	0.0000126	0.00135	568
21.025					
20.970					
	0.0000169	0.0000174	0.0000172	0.00149	631
27.362					
	0.0000163	0.0000157	0.0000160	0.00191	386
34.029					
42.858	0.0000186	0.0000187	0.0000187	0.00238	261
0.3315–42.86	0.0003697	0.0003708	0.0003703	...	6276
34.029					
	0.0001243	0.0001273	0.0001258		
49.418 (solid)					
Solid Amalg. Pure Tl	0.0000179	(0.00–20.00°) 0.0000142	0.0000160		

The values in the last column are calculated from the familiar equation of Helmholtz, as applied to a gram-atom of a univalent metal:

$$U = EF - FT\frac{\Delta E}{\Delta T}$$

They will be compared later with the actual values found thermochemically.

The agreement between the values at 20–30° and 30–40° is not perfect, since they represent small differences between large quantities; the temperature coefficient over the higher temperature range averages 0.28% higher than that over the lower range, and individual differences are in some cases much greater. Nevertheless, probably most of the average values given in the fourth column (and therefore those in the fifth) are within 1% of the truth.

The Densities of Thallium Amalgams.

Since, as one of us, with the help of J. H. Wilson, had already shown, thallium expands appreciably on amalgamation, the densities of the amalgams were needed in the theoretical consideration. These were determined as follows:

An Ostwald-Sprengel pycnometer, holding 1.0911 cc., was used in determining the densities. Determinations were made at both 20° and 30°, thus giving the coefficient of expansion, and furnishing an approximate mutual check on the results.

Table V.

Densities of Thallium Amalgams.

I. Thallium. %.	II. Obs. density 20°.	III. Obs. density 30°.	IV. Values from smooth curve 30°.	V. Average densities.	VI. Diff. V.-IV.	VII. Coeff. of exp.
0.000	13.5463	13.5218	13.522	13.522	0.000	0.000181
0.331	...	...	13.514	13.516	0.002	....
1.704[1]	...	...	13.484	13.493	0.009	....
3.788	...	...	13.440	13.459	0.019	....
4.930	13.439	13.415	13.415	13.439	0.024	0.000179
7.496[1]	13.383	...	...	...	...	....
10.019	...	...	13.306	13.354	0.048	....
17.040	13.190	13.167	13.167	13.237	0.070	0.000175
21.025	13.108	13.087	13.087	13.170	0.083	0.000161
21.16[1]	...	...	13.105	...	...	....
27.362	12.980	...	...	...	...	....
33.70[1]	12.854	...	...	...	...	....
34.029	12.846	12.828	12.828	12.953	0.125	0.000140
39.702	...	...	12.715	...	...	....
42.858	12.676	12.656	12.656	12.805	0.149	0.000157
44.30	...	...	12.629	...	...	....

Wilson's determinations at 20° gave, for amalgams containing, respectively, 0.793, 1.410 and 1.854% of thallium, densities 13.527, 13.515 and 13.504, respectively—values which fall precisely upon our curve.

These densities are plotted in the accompanying graph (Fig. 4). The curves are almost rectilinear; their slight lack of parallelism is due to the change of the coefficient of expansion indicated in the last column. The dotted line in Fig. 4 records the values which the densities would have possessed if there had been no expansion on amalgamation, taking 11.85 as the density of pure thallium. Evidently the expansion on amalgamation is 1.05% of the total volume in the case of the 40% amalgam, and others in proportion.

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[1] Our early determinations (1912). All the others given in the table were made more accurately in 1913.

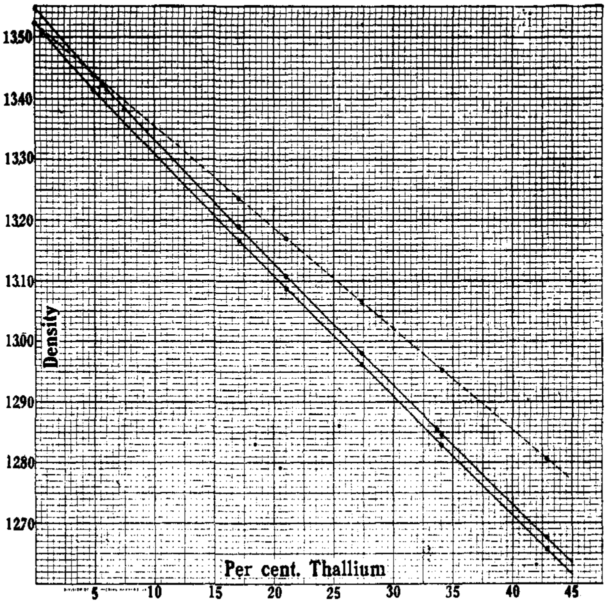

Fig. 4.—Densities of thallium amalgams at 20° and 30°. Upper curve 20°. Dotted line hypothetical.

The "solution volume"[1] of a gram-atom of thallium, *i. e.*, the excess in volume of an amalgam containing 204 g. of the solid metal over and above the volume of its mercury, is nearly independent of the concentration, varying only from 17.47, in the case of amalgams containing between 20 and 25% of thallium, to 17.51, in the case of very concentrated or very dilute amalgams. The following table exhibits the values at successive concentrations, the densities being taken from the smooth curve:

TABLE VI.

Solution Volume of Thallium in Mercury.

(Sp. Vol. of Mercury at 30° = 0.073955 = V_o.)

Per cent. b.	Density.	Sp. vol. (V).	$\frac{100\ V}{b}$.	$\frac{100-b}{b}V_o$.	Sol. vol. 1 g. Tl.	Mol. sol. Vol.
5	13.414	0.074549	1.49098	1.40515	0.08583	17.51
10	13.310	0.075131	0.75131	0.66560	0.08571	17.48
15	13.208	0.075712	0.50475	0.41908	0.08567	17.48
20	13.107	0.076295	0.38148	0.29582	0.08566	17.47
25	13.007	0.076882	0.30753	0.22187	0.08566	17.47
30	12.908	0.077471	0.25824	0.17256	0.08568	17.48
35	12.809	0.078070	0.22306	0.13735	0.08571	17.48
40	12.710	0.078678	0.19669	0.11093	0.08576	17.49

The values show a slight minimum at 22.5°, but otherwise, as already stated, are surprisingly constant. Whether or not this minimum truly exists, or is only an outcome of slight experimental defect, could hardly be stated positively without further very exact experimentation with a larger pycnometer, for which time was lacking.

The coefficients of expansion are less constant; they show a distinct decrease with increasing concentration.

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[1] See Bousfield and Lowry, *Trans. Faraday Soc.*, **6**, 85 (1910).

For further understanding of the situation, all the other thermal effects involved should also be carefully evaluated by experiment, including in addition to the temperature coefficient of the electromotive force (already detailed), the heat capacities and the heat of dilution of the several amalgams, and the heat of solution of thallium in mercury as well as in amalgams of increasing strength. These topics are considered in order below.

The Determination of Heat Capacities.

The procedure consisted in introducing a known quantity of heat into a weighed amount of amalgam and observing the rise in temperature. Electricity was passed through a heating coil of insulated manganin wire encircling the thermometer bulb in the amalgam, which was contained in a small adiabatic calorimeter, and the quantity of energy was determined by measuring the fall of potential across the coil and the quantity of electricity passing. The rise of temperature was measured on a sensitive thermometer. The calorimeter of the apparatus finally adopted and used with satisfaction for the determination of the heat capacities is shown diagrammatically in Fig. 5.

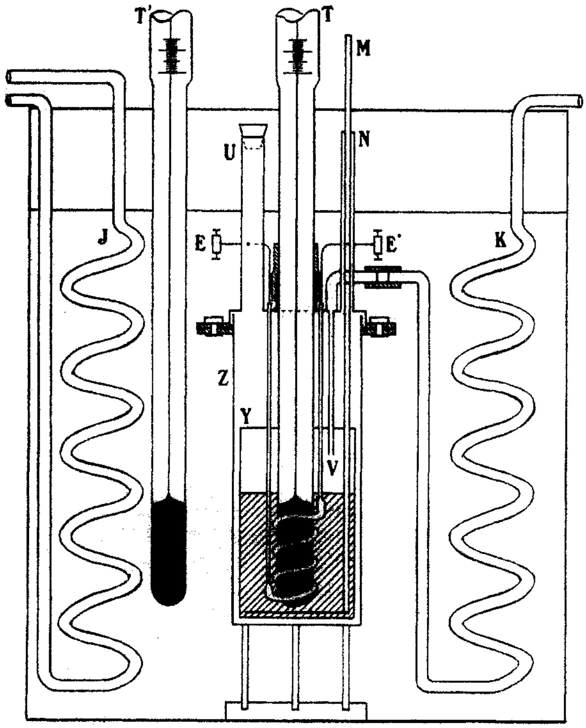

Fig. 5.—Calorimeter. E, E', binding posts. J, K, coils of brass pipe. M, stirrer fitting in bearing, N. T, T', Beckmann thermometers. U, tube for removal of amalgam and introduction of mercury. V, glass tube for entrance of carbon dioxide gas. Y, cylindrical brass can, surrounded by larger brass can, Z.

Thirty cc. of material from a special pipet was always taken for a determination. The substance to be measured was held in the cylindrical can Y, which was constructed of brass, 35 mm. in diameter and 51 mm. high. This fitted into a larger brass can, Z, and it was held in place by bits of cork, so that there was an air space of 2 or 3 mm. everywhere between the two cans.

A cover of brass with a wide flange was clamped securely to a similar wide flange on the can by means of 4 screws (binding posts from dry batteries). Each flange had cemented to it with shellac a washer of pure, soft rubber. The surface of each washer was smeared with paraffin rubber, and when the cover was screwed down firmly, this arrangement gave an oil-tight closure. The outer can, thus equipped, was securely fastened in a glass battery jar which was filled by a thin paraffin lubricating oil. The accurate Beckmann thermometer T was fitted in a short, copper tube soldered to the center of the cover, and was held firmly in position by shellac and a ring of heavy rubber tubing. This gave a secure setting, but allowed a certain amount of flexibility. The thermometer registered 6° and was divided into 0.01°, so that 0.001° could be estimated. The manganin coil, completely encased in glass, encircled (without actually touching) the thermometer bulb; and its leads, also encased in glass, came through two holes in the cover to the binding posts E and E′. It was securely fastened to the cover by means of de Khotinsky cement, which proved to be admirably suited to the purpose, after other cements had been found wanting. The small tube N, soldered to the cover, extended up above the oil level and allowed the manipulation of a stirrer, M. This stirrer consisted of a flat, copper ring, slightly smaller in diameter than the inner can, fastened to a glass tube which served as a handle. The other tube, U, projecting above the surface of the oil, was for the removal of amalgam and the introduction of mercury. During the heat capacity measurements it was closed by a stopper.

Since brass and copper are readily attacked by mercury, the interior of the inner can and stirrer were covered with a thin coating of asphalt varnish and thoroughly dried. The mercury did not work through this and was not soiled by it. Neither shellac, paint, nor collodion met these requirements.

The amalgam was protected from oxidation by a persistent atmosphere of pure, dry carbon dioxide. The stream of gas which had passed through a spiral brass coil immersed in the oil bath was delivered above the surface of the amalgam by means of a small glass tube, V, containing a fine aperture at the end. There was no danger of loss or gain of heat by the amalgam on account of this gas, since the oil bath was kept at the temperature of the amalgam. A fine capillary insured a uniform rate of flow (about 30 bubbles through the wash-bottles in a minute) during the entire day. At night a bit of paraffin was melted around the only free opening, where the stirrer fitted into the tube N, so that the calorimeter was gas-tight and the carbon dioxide current was thereby stopped. The continuous outflow of gas around the stirrer effectually prevented any access of exterior air, which might have otherwise been pumped into the inner vessel by the stirrer, with accompanying contamination of the amalgam and gain or loss of heat.

A second Beckmann thermometer, T′, exactly like the first, was placed in the oil bath near the calorimeter. The two thermometers were carefully set, so that at 20° they were within 0.01°.

The oil was heated during an experiment by means of an electric current passing through ribbon composed of a suitable alloy. About 3.6 meters of this were wound in a spiral around a glass framework just inside the glass battery jar. This is not shown in the figure. It was connected with the alternating lighting circuit of 110 volts through a knife switch, a suitable permanent resistance and a rheostat in which each stop corresponded to a rise of temperature in the oil of about 0.01° per minute. Thus it was easy to arrange the rheostat so as to obtain a rise which kept pace with that of the calorimeter. The oil was kept thoroughly mixed by a rapidly agitated stirrer. After a determination was finished, the oil was cooled again, so as to be ready for the next experiment, by passing cold water through the coil of brass pipe, J. One hour was usually required before the thermometer in the amalgam fell from 25.0° back to 20°.

The current for heating the coil in the amalgam was furnished by the lead storage cell. It was connected with the leads of the inner heating coil through a delicate relay, a sliding resistance, and a knife switch. The relay (which was of very low ohmic resistance to minimize heating and consequent changing of the current in the circuit) controlled a stronger, entirely separate current actuating a device for releasing a stop watch, which was stopped by a spring the moment that the currents ceased to flow. Thus the duration of the current was automatically timed to within a fifth of a second. There was also an amperemeter, which served to give an approximate idea of the current. The sliding resistance consisted of a heavy manganin wire mounted on a glass bridge. A slider with a platinum point moved back and forth on it, so that the resistance in the circuit could be changed at will, thus regulating the fall of potential across the heating coil. It was found necessary to polish the manganin wire with chamois skin every day to insure a good contact.

The fall of potential across the terminals of the heating coil EE′ was measured by an Ostwald-Poggendorff potentiometer, which was fed by a cell of cadmium amalgam, dil. cadmium sulfate solution, mercurous sulfate and mercury. It was balanced against a standard cadmium cell by slipping one of its connecting wires of fine manganin wire back and forth in the binding post until there was no deflection of the galvanometer. This simple method of adjusting the potentiometer is very convenient and sufficiently accurate. The shunt of the potentiometer box was connected through the galvanometer and a knife switch with the terminals of the coil EE′. The reading on the potentiometer box (0.7612 volt, kept the same in any given series, so that calibration was not necessary) was of a magnitude suitable for bringing all the factors to about the same order of accuracy. The mirror-galvanometer was read by means of a suitably arranged spot of light, which could be seen readily from the experimenter's position. Manipulation of the sliding contact of the heating circuit kept the galvanometer reading very near zero throughout the determination, and hence maintained a constant electromotive force at the terminals of the heating coil.

The complete insulation of the quantitative heating coil EE′ of manganin wire was attained by enclosing it in a very thin glass tube. Upon this the success of the method was dependent. Several glass tubes were drawn out to capillaries until one was obtained which just slipped over the wire and fitted it snugly. The two were then carefully heated to a faint red heat and bent into a coil. The glass melted around the wire at the same time. This coil was soldered to leads of large copper wire, encased in glass tubes, and larger glass tubes were melted in place around the two connections.

Since the arrangement was precisely the same in each experiment, and the method was a strictly comparative one, the exact resistances of the manganin wire and copper leads need not be accurately known. Neither need the small fraction of the heat developed in the leads which was communicated to the calorimeter be determined. Nevertheless, the resistance of the manganin wire was measured, and found to be 1.224 ohms (constant over wide range of temperature), and that of the leads 0.004 ohm. Making due allowance for the resistances in the lead wires (0.004 ohm), the effective potential was found to be $\pi = 0.7587$ volt. Hence the constant π^2/r, to be multiplied by the time in seconds in order to obtain the energy in joules, was 0.47035. The result divided by the rise of temperature (always nearly 5.000°) gave the heat capacity of the system, from which the heat capacity of the calorimeter was subtracted. This was determined by means of sixteen independent experiments made upon pure mercury, which gave as the value of the heat capacity the value 72.40 mayers, with an average deviation of 0.04. With such a large number of results a close approximation to the true value must have been obtained.

Assuming (with Bartolli and Stracciati) the specific heat of mercury to be 0.03344 between 20° and 25°, the heat capacity of the calorimeter, thermometer, and fittings must have been $72.40 - 408.16 \times 0.03344 \times 4.178$[1] $= 15.37$ mayers. This value was used throughout the following work.

Having thus found the constant of the apparatus and attained facility

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[1] The heat capacity of a gram of water at 22.5° in mayers.

in its use, we proceeded to carry out precisely similar experiments upon thallium amalgams. Two series were made, in each case starting with a concentrated analyzed amalgam, and going step by step to more and more dilute ones. At each step some of the amalgam was carefully withdrawn and weighed, and about an equal weight of mercury (also carefully weighed) was added by means of a peculiar pipet to be described later. Thus the concentration of the amalgam at each step could be easily calculated. As a check upon the chain of operations, from time to time the portions withdrawn were analyzed,[1] and, moreover, at the conclusion of each series the actual weight of the most dilute amalgam was determined. These checks were entirely satisfactory, and afforded satisfactory evidence that no accidental gross error in weighing had been made at any stage.

The results with thallium amalgam follow, the average for the mercury being placed at the head of the table.

TABLE VII.

Heat Capacities of Amalgams.

Designation of amalgam.	Thallium. %.	Weight. G.	Time. Seconds.	Temp. rise. ° C.	Total heat cap. Mayers.	Heat capacity of 1 g. amal.	Average (mayers).
		408.13			72.40		0.1397
A.........	40.92	382.85	802.4	5.000	75.48	0.15701	0.1571
	40.92	382.85	800.8	4.999	75.48	0.15701	
	40.92	382.85	802.2	4.995	75.54	0.15716	
B.........	37.21	382.21	793.2	4.980	74.91	0.15578	0.1557
	37.21	382.21	792.6	4.982	74.83	0.15557	
C.........	32.69	387.87	800.4	4.980	75.6	0.15528	0.1553
	32.69	387.87	802.2	4.990	75.61	0.15531	
D.........	27.69	400.295	815.6	4.990	76.87	0.15364	0.1534
	27.69	400.295	816.8	5.008	76.71	0.15324	
E.........	20.70	407.79	819.8	5.013	76.92	0.15094	0.1511
	20.70	407.79	817.6	4.992	77.03	0.15120	
F.........	15.40	420.14	831.0	4.996	78.23	0.14962	0.1496
	15.40	420.14	830.2	4.993	78.21	0.14957	
G.........	11.42	436.78	841.4	4.980	79.47	0.14676	0.1468
	11.42	436.78	841.8	4.980	79.51	0.14685	
H.........	11.42	400.54	788.0	4.992	74.25	0.14700	0.1470
	11.42	400.54	787.6	4.988	74.27	0.14705	
I.........	8.48	402.32	786.0	5.000	73.94	0.14558	0.1455
	8.48	402.32	785.4	5.002	73.85	0.14536	

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[1] Analyses of amalgams gave the following results: A = 40.97, 40.88, 40.91, average 40.92%. G = 11.42, 11.43, average 11.425% (calculated 11.42). L = 3.50, 3.49, average 3.495% (calculated 3.54). M = 34.91, 34.95, 34.84, 34.92, average 34.90%. U = 5.54, 5.53, average 5.535% (calculated 5.54). After each series the residual very dilute amalgams in the calorimeter were weighed, the weights being 405.7 and 401.9, respectively—reasonably near to the values calculated through the long chain of additions and subtractions.

TABLE VII (*concluded*).

Designation of amalgam.	Thallium. %	Weight. G.	Time. Seconds.	Temp. rise. ° C.	Total heat cap. Mayers.	Heat capacity of 1 g. amal.	Average (mayers).
J..........	6.30	403.95	784.2	5.008	73.65	0.14428	0.1441
	6.30		783.6	5.013	73.52	0.14395	
K..........	4.69	405.18	780.0	5.005	73.30	0.14299	0.1431
	4.69		780.4	5.003	73.37	0.14316	
L..........	3.54	406.32	780.0	5.020	73.08	0.14203	0.1423
			780.0	5.003	73.33	0.14264	
			778.2	5.020	73.21	0.14234	
			779.8	5.020	73.06	0.14200	0.1423
			780.4	5.010	77.27	0.14250	
M..........	34.90	386.17	800.0	4.999	75.27	0.15511	0.1550
				5.010	75.09	0.15465	
				4.998	75.29	0.15516	
N..........	29.49	388.86	801.0	5.019	75.06	0.15350	0.1534
			795.4	4.990	74.97	0.15327	
P..........	24.88	391.40	799.2	5.008	75.06	0.15250	0.1523
			798.2	5.010	74.94	0.15220	
Q..........	18.36	394.40	790.0	4.990	74.47	0.14985	0.1499
			790.2	4.990	74.48	0.14987	
R..........	13.58	396.54	787.0	5.002	73.93	0.14768	0.1478
		396.54	787.0	5.002	74.00	0.14785	
S..........	10.07	398.32	780.0	4.995	73.45	0.14582	0.1458
			781.8	5.005	73.47	0.14587	
T..........	7.47	398.93	778.2	5.029	72.78	0.14391	0.1444
			780.0	5.017	73.13	0.14479	
			775.6	5.012	72.79	0.14393	
			776.8	5.005	73.00	0.14446	
			778.4	5.008	73.11	0.14474	
U..........	5.54[1]	399.80	773.2	5.005	72.66	0.14330	0.1433
			775.0	5.015	72.69	0.14337	
V..........	3.07	400.71	765.8	4.988	72.21	0.14185	0.1418
			770.0	5.018	72.17	0.14175	
W..........	1.49	402.31	764.6	4.996	71.98	0.14071	0.1408
			764.8	4.995	72.02	0.14082	

These values are plotted in the accompanying graph (Fig. 6), which shows that only 2 of the 21 points are far distant from a smooth curve.

Schmitz[2] found the specific heat of solid metallic thallium (20–100°) to be 0.0324; hence the heat capacity of one g. is 0.1354 mayer—a value, as one would expect, not very different from that of lead. If no change of specific heat took place on amalgamation, a 40.9% amalgam should have the heat capacity of 0.1381 instead of the actual value 0.1571. The gain of 14% is unusually large, even taking account of the liquefac-

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[1] The portion of this taken out in preparation for the next amalgam was analyzed.

[2] *Proc. Roy. Soc. London*, **72**, 177 (1903).

tion of the thallium (for liquids usually, if not always, have a larger specific heat than the corresponding solids), and is especially interesting in view of the concomitant marked increase in volume. This adds another to the many cases in which these two changes go hand in hand—a category including the increase in volume and specific heat accompanying not only liquefaction in general, but also neutralization and other kindred phenomena involving the combination of ions. The most striking exception to the rule is the behavior of ice on melting.

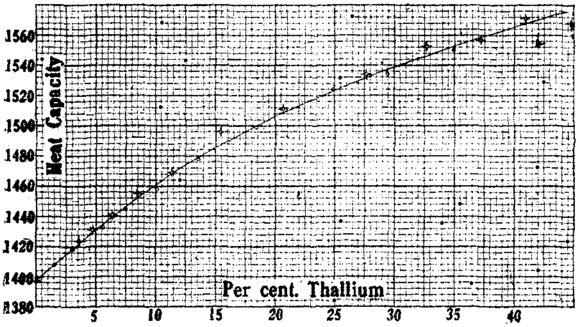

Fig. 6.—Heat capacities of thallium amalgams. Specific heat capacities (in joules/$t°$ = mayers) are plotted as ordinates, and percentage composition of amalgams as abscissas.

It is not without interest to refer the changes of heat capacity thus measured to a given constant quantity of thallium. This is most conveniently represented by determining a quantity which may be called the "solution heat capacity" of thallium, analogous to the "solution volume." The "solution heat capacity" is obtained by referring to the thallium all the change in heat capacity which occurs on amalgamation (although, of course, it is by no means certain that some of the change is not due to an effect upon mercury associated with thallium). This quantity gives another clue to the constitution of the solution, and is therefore of value.

The "solution heat capacity" may very simply be calculated by subtracting the heat capacity of the mercury $(100 - b)K_0/b$ of an amalgam having b % of thallium, from the heat capacity $100K/b$ of the amalgam. K_0 and K represent, of course, the heat capacities of a gram of mercury

TABLE VIII.

"Solution Heat Capacity" of Thallium.

(Heat Capacity of 1 g. of Mercury = 0.1397 mayer; of 1 g. Thallium = 0.1354.)

Composition of amalg. %.	Heat cap. per g. of amalg.	$\frac{100\,K}{b}$.	$\frac{100-b}{b}K_0$.	"Solution heat cap." per 1 g. thallium (mayer).
5	0.1431	2.862	2.654	0.208
10	0.1461	1.461	1.257	0.204
15	0.1486	0.990	0.792	0.198
20	0.1506	0.753	0.559	0.194
25	0.1523	0.609	0.419	0.190
30	0.1539	0.513	0.326	0.187
35	0.1552	0.443	0.259	0.184
40	0.1565	0.391	0.210	0.181

and of the amalgam, respectively. In this way the preceding table of solution heat capacities is easily calculated.

Evidently a gram of thallium produces less effect on the heat capacity in concentrated amalgams than in dilute ones, and we may safely infer that the circumstance or reaction which causes the greatly increased heat capacity occurs to a less extent in the concentrated amalgams than in the dilute ones. Presumably this effect is (at least in part) hydrargyration. In any case the increase is very striking, being from 34 to 53% of the original heat capacity of the solid thallium (0.1354).

The change in the "solution heat capacity" is interesting in contrast to the approximate constancy of the solution volume, already tabulated (see p. 1745). Although these phenomena parallel one another as regards sign and order of magnitude, they cannot be due entirely to the same tendencies.

The Heat of Dilution of Thallium Amalgams.

In the preceding extended series of experiments on the heat capacity of the amalgams, the heat of dilution with pure mercury, in the calorimeter, was carefully observed at the times of preparation of the successive amalgams.

Mercury is so good a conductor of heat, and the total heat capacity in the calorimeter was so small, that it was necessary to make sure that the added mercury possessed really the same temperature as the calorimeter at the moment of introduction. In order to accomplish this result, the mercury was introduced from a water-jacketed pipet with a very fine point. The whole length of the delivery tube as well as the body of the pipet was surrounded by a current of water kept at exactly 20°, the starting point of the experiment (Fig. 7). A weighed amount of mercury having been introduced into the pipet (the weight having been found by the loss of weight of a weighing bottle containing mercury, from which it had been drawn by suction), and time having been allowed for it to attain the proper temperature, the mercury was allowed to run into the calorimeter, diluting the amalgam there. At all times during the transfers, as well as during the thermal measurement, the amalgam was protected from oxidation by carbon dioxide gas in the manner already described, and the last drop of mercury was ejected from the pipet by pressure of the same gas.

Since mercury is more dense than the amalgams, the pure liquid diffused thoroughly through the liquid mass

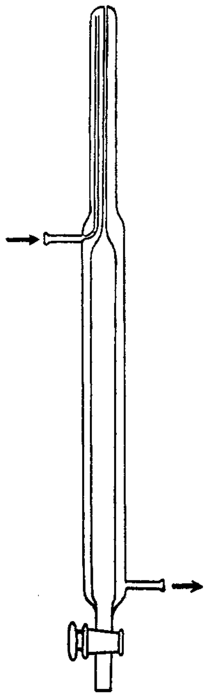

Fig. 7.—Water-jacketed pipet for delivering mercury isothermally.

almost immediately, and little stirring was needed, except in the case of the most dilute amalgams, where the densities of the two metallic liquids were nearly identical and somewhat more energetic stirring was needful.

The following table records the results:

TABLE IX.

Heats of Dilution at 20°.

Wt. of amalgam w_1. G.	Wt. of mercury w_3. G	% composition orig. amalg.	% comp'n resulting amalg.	Rise of temp.	Ht. cap. of system.	Heat evolved. Joules.	$U_{20°}$ Heat ev. per g. at. Tl.
First Series.							
347.56	34.65	40.92	37.21	2.240°	74.87	168	241
340.78	47.09	37.21	32.69	2.780	75.60	209	337
339.05	61.25	32.69	27.69	3.070	76.79	236	433
304.91	102.88	27.69	20.70	4.023	76.97	309	747
312.60	107.54	20.70	15.40	2.712	78.22	211	666
323.73	113.05	15.40	11.42	1.798	79.49	143	585
298.75	103.58	11.42	8.48	1.010	73.90	74.6	446
300.35	103.60	8.48	6.30	0.630	73.59	46.4	372
301.42	103.72	6.30	4.69	0.347	73.33	25.5	273
302.52	103.81	4.69	3.55	0.175	73.19	12.8	181
Second Series.							
322.83	64.03	34.90	29.49	3.250	75.02	243	435
330.54	60.86	29.49	24.88	2.810	75.00	211	441
291.17	103.22	24.88	18.36	3.483	74.47	259	731
293.15	103.39	18.36	13.58	2.250	73.97	166	631
295.37	102.94	13.58	10.07	1.375	73.46	101	514
295.99	102.94	10.07	7.47	0.810	72.96	59	405
296.43	103.37	7.47	5.54	0.480	72.67	34.9	321
297.55	102.88	5.54	4.12	0.273	(72.43)	19.8	245
297.88	102.83	4.12	3.07	0.130	72.19	9.4	156
296.26	106.04	3.07	1.49	0.130	72.00	9.4	319

At the close of the seventh experiment of the second series the final result was tested twice by heating the system through 0.480° quantitatively, by means of the spiral electrically heated coil. The values obtained (34.7 and 34.6) agreed as well as could be expected with the result computed from the heat capacity—34.9. Similar tests were made after the eighth and tenth trials, affording sufficient confirmation of these results also, within the limit of error of experimentation. Therefore it is safe to conclude that the values given represent closely the heats of dilution of the several amalgams.

Since the electromotive force and its temperature coefficient were both measured more carefully at 30° than at 20°, it is therefore convenient for comparison to recalculate the heats of dilution to the higher temperature—an easy task, since the heat capacity change during the reaction is known. According to the equation of Kirchhoff, $\Delta U = -\Delta K.\Delta T$ (or, in this case, $\Delta U = -10.\Delta K$), ΔK being the change in heat capacity involved in any given dilution where the total amount of thallium present was 204 g. (a gram-atom). Table VII contains the necessary data concerning the heat capacities, and the results of the calculation are contained in Table X following. The change in any one experiment was simply divided by the atom-fraction (n) present in order to give the value for the gram-atom. k and w mean heat capacity per gram, and weight, respectively; subscripts 1, 2 and 3, signify the stronger and the weaker amalgams, and mercury, respectively. The values of k_1 and k_2 were read from the smooth curve of Fig. 6 given on page 1752, since the smooth curve really represents an average value corrected for accidental experimental error. The values for ΔU were then plotted and were found to lie approximately on the curve given by Fig. 8.

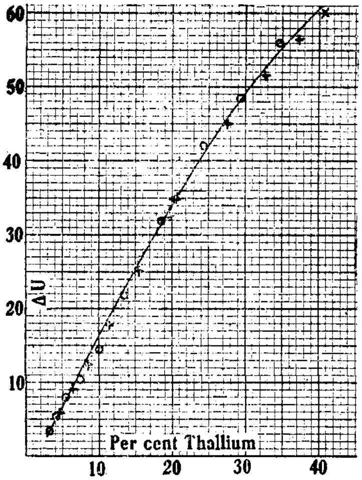

Fig. 8.—Change of dilution heat with 10° temperature change. ΔU (in this case the differences in kilojoules between the heats of dilution at 20° and 30°) are plotted as ordinates; and percentages of thallium are plotted as abscissas. Thus, for example, the curve shows that the dilution of a 40% to 20% amalgam (each containing 204 grams of thallium) evolves 26.5 kj. less heat at 30° than at 20°.

For later reference the values for the heat of dilution of amalgam with mercury at 325° were desirable. Unfortunately, no data exist as to the heat capacity change over that large range of temperature, and it is hardly safe to conclude that the change will be the same as at room temperatures. Nevertheless, in default of other data, the values for 325° also were calculated, and are given in the last column. They make no pretensions to exactness, whereas the values at 30° may be considered as being almost as exact as those at 20°.

TABLE X.

First Series.

Comp. amalg.	$k_1w_1 + k_3w_3$.	k_2w_2.	Δk.	ΔU.	$U_{20°}$.	$U_{30°}$.	$U_{325°}$.
40.92 37.21	59.303	59.548	0.245	3.5	241	237	136
37.21 32.69	59.671	59.965	0.294	4.7	337	332	196
32.69 27.69	60.974	61.326	0.352	6.5	433	426	238
27.69 20.70	61.084	61.495	0.411	10.0	747	737	450
20.70 15.40	62.163	62.475	0.312	10.0	666	656	372

TABLE X (*continued*).

Comp. amalg.	$k_1w_1 + k_3w_3$.	k_2w_2.	Δk.	ΔU.	$U_{20°}$.	$U_{30°}$.	$U_{325°}$.
15.40 11.42	63.932	64.119	0.177	7.0	584	577	368
11.42 8.48	58.326	58.418	0.092	5.5	446	440	281
8.48 6.30	58.084	58.138	0.044	4.0	372	368	252
6.30 4.69	57.864	57.894	0.030	3.0	273	270	198
4.69 3.55	57.732	57.780	0.048	7.?	181	174?	(?)
			Second Series				
34.90 29.46	59.048	59.456	0.408	7.5	435	429	255
29.46 24.88	59.306	59.610	0.304	6.4	441	435	201
24.88 18.36	58.765	59.119	0.354	10.0	731	721	431
18.36 13.58	58.387	58.648	0.261	10.0	631	621	334
13.58 10.07	58.066	58.193	0.127	6.5	514	508	319
10.07 7.47	57.625	57.685	0.080	4.0	405	401	282
7.47 5.54	57.305	57.331	0.026	2.5	321	319	249
5.54 4.12	57.041	57.061	0.020	2.5	244	242	169
4.12 3.06	56.813	56.821	0.008	2.0	156	154	102
3.06 1.49	56.824	56.641	0.183	6.	319	313	(?)

These results at 30° are plotted in the curve of Fig. 9. In plotting the two series together, the fifth experiment of the second series was made to lie exactly on the curve for the first set, for it is in this region that the results have the greatest accuracy and consistency. The origin was obtained by extrapolation. The graph gives at once the heat evolved by diluting an amount of amalgam containing one gram-atom from any given percentage to any other percentage, at 30.0°.

The Heat of Solution of Thallium in Mercury and in Thallium Amalgams.

A phenomenon closely related to that just treated, and of value in the verification of its significance, is the heat of solution of metallic thallium in liquid thallium amalgams. The explanation of the connection between the two diverse phenomena will be deferred until the second has been considered in detail.

Thallium dissolves easily and promptly in mercury, the first portion evolving considerable heat, and the later portion absorbing much more. The problem was to determine the magnitude of these thermal quantities.

The magnitude of the cooling effect may be determined simply by preventing the amalgam from being lowered in temperature, with the help of the quantitative heating coil described in the heat capacity experiments, noting the potential and quantity of the current. Through this isothermal method, a knowledge of the heat capacity is unnecessary. The amalgam is always at the temperature of the surroundings, and all cooling corrections are eliminated. The experiment may therefore extend over a considerable period of time, and equilibrium may be attained without rapid stirring. The method appears to be an extremely satisfactory one, but it can be used only for endothermic reactions. The apparatus consisted simply of a Dewar bottle (containing the amalgam, a heating coil, and a Beckmann thermometer) attached to the end of a large glass tube and submerged deep in a thermostat. The voltage across the heating coil was measured with a potentiometer, and a silver coulometer gave the quantity of electricity passing.

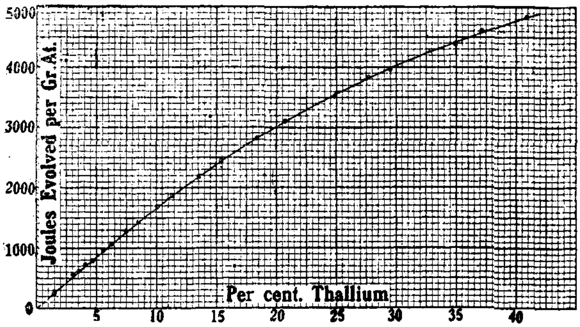

Fig. 9.—Heat of dilution of thallium amalgams at 30°. Ordinates indicate joules evolved on diluting a mass of amalgam containing one gram-atom of thallium. Abscissas indicate percentage composition.

The procedure, as evolved in the course of a few preliminary experiments, was as follows: A suitable quantity of mercury was put into the calorimeter, and when its temperature was the same as that of the thermostat (30°) it received successive weighed amounts of thallium. Occasional stirring with a small glass rod caused uniform mixing. Previously the oxide had been removed from the thallium by treatment with a little standard acid, due correction being applied to the weight taken. The thallium pieces had also been placed in a small bottle immersed in the thermostat, so that the whole system would be at the same temperature. Oxidation was nearly, but not completely, eliminated by a layer of purified kerosene in the calorimeter.

The heating of the coulometer with the passage of the current caused a rapid decrease in its resistance, and consequently a tendency to increase the fall of potential across the heating coil. Although this was corrected as rapidly as possible by the arrangement provided for that purpose, the compensation was not always exact, and the results must be regarded merely as preliminary. The arrangement described under the heat capacity determinations, including the stop watch, was far more satisfactory, and would have served the purpose better. It is intended not only to verify the present preliminary results by repeating the experiments with larger amounts of material, but also to extend the method to many other cases, both of amalgams and aqueous solutions producing endothermic reactions.

As already said, the first portions of thallium on dissolving in mercury caused a *rise* of temperature. This could not be measured accurately, since the heat capacity of the Dewar vessel was unknown. The procedure, therefore, until the concentration had attained 8.76%, was not thermally quantitative, but was interesting in showing that a considerable amount of heat was at first evolved. Every addition after the percentage just named caused a cooling effect and this could be accurately measured. These results are accordingly included in the table given below. After the amalgam reached the concentration of 38%, the liquid became so nearly saturated that the thallium dissolved very slowly and the results were of little value. Therefore they are not included in the table.

TABLE XI.

The Heat of Solution of Thallium in Mercury.

(240.546 g. of Mercury in the Calorimeter.)

Expt.	Tl present.	Tl added.	% Tl in resulting amalgam.	Per cent. of a g. at. of Tl added, 100n.	Per cent. of a g. atom present.	Heat involved in process, Δw.
1......	0.0000	15.9457	6.22	7.82	7.82	(150)[1]
2......	15.9457	7.1497	8.76	3.50	11.32	(50)[1]
3......	23.0954	6.2125	10.86	3.05	14.37	—1.0
4......	29.3079	13.9567	15.24	6.84	21.21	—52.8
5......	43.2646	14.6875	19.42	7.20	28.41	—116.2
6......	57.9521	16.5595	23.65	8.12	36.53	—188.5
7......	74.5116	16.4778	27.45	8.08	44.60	—219.0
8[2].....	64.6504	11.6705	30.87	5.72	37.41	—173.7
9......	76.3209	13.4104	34.43	6.57	43.99	—217.6
10......	89.7313	15.4190	38.09	7.56	51.54	—277.3

In tabulating these results, it was remembered that the concentration of the thallium in the amalgam increases as the thallium dissolves. Thus in any single experiment the first portion dissolved corresponds to the addition of thallium to an amalgam of the lower (original) concentra-

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[1] In giving these approximate values an approximate value was assumed for the heat capacity of the Dewar flask. Account was taken also of the extrapolation of the more certain part of the curve, and of the requirement of the Helmholtz equation.

[2] 99.0708 g. of the amalgam was removed at this point. 170.914 g. Hg now present.

tion, while the last portion corresponds to the addition of thallium to an amalgam of the higher (final) concentration. The heat evolved therefore corresponds approximately to the addition of thallium to an amalgam of the average concentration. For example, the heat evolved (—1614 joules) during the increase of concentration from 15.24 to 19.42% must correspond closely to the addition of a gram-atom of thallium to an amalgam of the average concentration 17.33% (as given in the middle column of the following table). This calculation assumes, of course, that the curve is practically a straight line between the two concentrations—an assumption which would be strictly permissible only for very small additions of thallium. Nevertheless, the small error thus introduced is clearly less than the probable experimental error. The middle column, and the method of arranging the figures, below, are obvious outcomes of these considerations. The heat evolved in each case is reduced to the gram-atom standard by dividing the heat evolved (nU) on the solution of the thallium in each case by the fraction (n) of a gram-atom added.

TABLE XII.

Heat of Solution a Gram-Atom of Thallium in Amalgams.

% Tl in successive amalgams.	Average % Tl during each additiou.	nU/n. Heat evolved in dissolving one gram-atom of Tl in amalgam.
8.76		
	9.81	— 32
10.86		
	13.05	— 771
15.24		
	17.33	—1614
19.42		
	21.53	—2321
23.65		
	25.55	—2711
27.45		
	29.16	—3036
30.87		
	32.65	—3310
34.43		
	36.26	—3670
38.09		

The average values from the middle column are plotted in relation to the heat values from the last column, in the accompanying graph (Fig. 10). The points do not lie on a perfectly smooth curve, but in drawing the curve the effort of compromise was made to distribute the errors by making the divergent points about equidistant from a reasonable locus. The error of the most divergent point is about 7% of the value; none of the other errors exceeds 5%. Although the accuracy leaves much to be desired, the present preliminary approximate curve will serve amply to illustrate the principles involved, and is therefore much better than nothing.

These values may be looked upon as containing separate factors; first, the heat absorbed when the solid melts or dissolves to form a saturated solution, and secondly, the heat evolved when the saturated solution becomes diluted to the resulting amalgam. When the dilution is great, the positive effects overbalance the negative and the net result is the evolution of heat, as seen at concentrations below 9.6%.

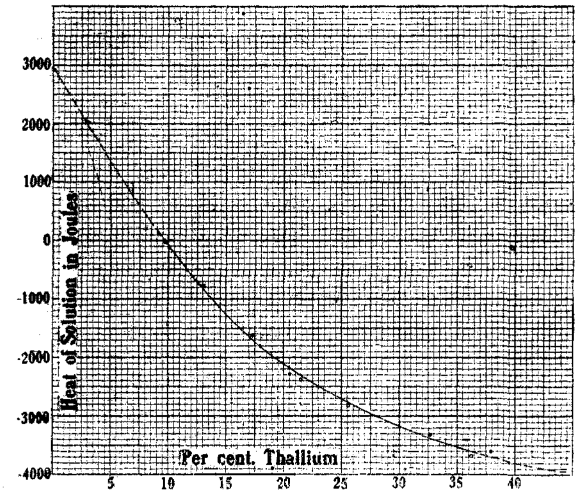

Fig. 10.—Heat of solution of a gram-atom of thallium in thallium amalgams. Abscissas indicate percentage composition of amalgams.

Since thallium increases greatly in heat capacity on amalgamation, it is evident that the thermal values given in the preceding table (XII) are subject to considerable change with temperature. Because the specific heats of the several amalgams are known, as well as the specific heat of thallium, this change is easily calculated by Kirchhoff's equation, in a manner analogous to that employed in the heats of dilution of thallium amalgam. For example, 100 g. of a 28% amalgam, on the addition of 4 g. of thallium produces 104 g. of a 30.77% amalgam. The heat capacity of the weaker amalgam and of the thallium separately aggregates 15.87 mayers; that of the concentrated product, 16.03 mayers. The gain in heat capacity corresponding to 4 g. of thallium is therefore 0.16 mayer. This, divided by n, the atom fraction, gives 8.16, which is $\Delta K = -\dfrac{\Delta U}{\Delta T}$. Three such results, all calculated from the smooth heat capacity curve (Fig. 6) are given below. The composition of the concentrated amalgam is represented by a; that of the dilute amalgam by b; K_4 signifies the heat capacity of a gram of thallium.

At first sight this table seems to be simply a repetition of that recording the solution heat capacity of one gram of thallium, with the heat capacity of the original thallium itself not included, and indeed it would be easy to show that the two tables are entirely parallel, representing, as they do, very similar phenomena. But they are not exactly alike; the earlier one records the gain in heat capacity when thallium is added to mercury, whereas the table just given records the gain in heat capacity when thallium is added to a thallium amalgam.

TABLE XIII.

b.	a.	Mean.	Wt. Tl added.	$K_2w_2 + K_4w_4$.	K_1w_1.	$\Delta K = \frac{n\Delta U}{\Delta T}$.	$\frac{\Delta U}{\Delta T}$.
40.00	42.31	41.16	4	16.19	16.34	0.15	7.6
28.00	30.77	29.39	4	15.87	16.03	0.16	8.2
18.00	21.15	19.58	4	15.52	15.70	0.18	9.2
10.00	13.46	11.73	4	15.15	15.37	0.22	11.2
5.00	8.65	6.83	4	14.85	15.11	0.26	13.3

The present table shows even more clearly than the other that the increase in heat capacity on adding thallium decreases as the concentration increases. The outcome is interesting in showing the large temperature coefficient, varying from 7.6 to 13.3 joules per degree, shown by the amalgamation of thallium, as well as the very considerable difference in heat capacity which must be suffered when thallium is transferred from a more concentrated to a more dilute amalgam, as during the operation of the amalgam cells under consideration. This last quantity is shown by the difference between the successive figures in the last column of the preceding table. The exhibition of this difference represents the main use of the table, and will be treated in detail later. Since the main comparison involved in the present work is made at 30°, the other possibilities of the table need not be discussed.

The Calculation of the Total Energy Change Involved in the Cell.

The total energy change (U of the equation of Helmholtz) involved in the cell has already been calculated from the temperature coefficient of the electromotive force. U is also to be found when the values given in the last column of Table XII, and plotted in Fig. 10, since the difference between any two of these values must give the heat of transfer of a gram atom of thallium from one to the other of the corresponding amalgams (*i. e.*, $U = \frac{n_1U_1}{n_1} - \frac{n_2U_2}{n_2}$).

Besides these two methods, yet a third method of calculating this quantity U exists, depending upon the heat of dilution of thallium amalgams with pure mercury. Formerly the assumption has often been made that the heat evolved in diluting an amount of amalgam containing a gram equivalent of dissolved metal is identical with the heat of transfer of the aforesaid gram equivalent between the initial and final amalgams.[1] This is far from being the case; indeed, the former is only about half of the latter. The presence of some sort of inconsistency here was recog-

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[1] See for example Cady, *J. phys. Chem.*, **2**, 562 (1898). Cady's actual measurements of the heat of dilution of sodium amalgams must have given much too high values.

nized in the earlier Harvard papers, and therefore the heats of dilution were rejected, without, however, attempting to discover its reason. In the sequel, the situation is fully explained.

When mercury is added to a liquid thallium amalgam, two processes occur simultaneously; first, some of the thallium is taken from the mercury originally present; second, this thallium is (at the same instant) dissolved in the new pure mercury. Only the first of these processes is parallel with anything that happens in the cell under consideration, since the cell has nothing to do with pure mercury.

Clearly, in order to calculate the heat-effect in the cell from the heat of dilution, the second of these two simultaneous processes must be eliminated. This may easily be done by causing two different concentrated amalgams to be diluted separately to the same final condition. Then, by multiplying each of the two heat values, thus found, by an appropriate factor corresponding to the amount of thallium transferred (so as to transform each into a value corresponding to the *transfer* of a *gram-atom* of thallium), two results are obtained which involve the formation of exactly the same amount of dilute amalgam made from newly added pure mercury. By subtracting these two values, the second of the two simultaneous processes is thus entirely eliminated. The difference between them becomes simply equal to the heat of transfer of a gram-atom of thallium between amalgams having compositions represented by the *average* compositions over the two respective ranges of dilution.

Since the problem is somewhat unusual, it may profitably be exemplified by a specific case.

In any given dilution let a equal the per cent. of thallium in the initial concentrated amalgam, b equal the per cent. of thallium in the resulting dilute amalgam, and x equal the amount of mercury added. Then $\frac{a}{100 + x} = \frac{b}{100}$, and $x = \frac{100\,a}{b} - 100$. Further, $\frac{(100 - a) + x}{(100 - a)} = 1 + \frac{100(a - b)}{(100 - a)b} = c$, (in which $c : 1$ is the ration of the total amount of mercury to that originally present); and the amount of thallium *transferred* must be the fraction $\frac{c - 1}{c}$ or $\left(\frac{100(a - b)}{a(100 - b)}\right)$ of a gram-atom, if the heat of dilution is calculated for the *total* amount of a gram-atom present. Hence this heat of dilution divided by the atom-fraction $\frac{c - 1}{c}$ gives the amount of heat involved in the *transference* of a gram-atom of thallium from the more concentrated amalgam into mercury, under such conditions that the product possesses the concentration of the more dilute amalgam. These expressions are exact. Such calculations are now carried out for the dilution of two concentrated amalgams to the same final concentration, and the heat-effect for each transfer is calculated for a gram-atom. In practise it is not necessary to calculate the values of x and c, since the fraction $\frac{c - 1}{c}$ may be expressed entirely in terms of a and b, as indicated above. As already stated, subtraction of the one result for the gram-atom from the other gives the heat of transfer from a solution corresponding to the average concentration over the first range to that of a solution having the average concentration over the second range. The detailed steps of the calculation for the two ranges, 40% to 30% and 35% to 30% follow, as an example of the method of calculation.

TABLE XIV.

Composition. %	G. Hg per 100 g. amalgam.	x = g. mercury added.	Dilution factor.	Observed heat of dilution.	Heat of dil'n per g.-atom of thallium.
a = 40.0	60.0	33.33	1.5555	740	2072
b = 30.0	70.0				
a' = 35.0	65.0	16.67	1.2565	400	1959
b' = 30.0	70.0				——
				U =	113

Algebraically, if q and r represent, respectively, the heat of removal of a gram-atom of thallium from the two concentrated amalgams, and m the heat of adding this thallium to mercury (the same in each case), then $q + m = 2072$ and $r + m = 1959$; subtracting, $q - r = U = 113$. Thus although we do not know, and have no means of knowing any one of the quantities q, r, and m individually, we are able to determine $q - r$ definitely. The result $q - r = U = 113$ joules represents the heat evolved when a gram-atom of thallium is transferred from an average concentration of 35% to an average concentration of 32.5%, the respective means (that is $^1/_2(a + b)$, and $^1/_2(a' + b')$) of the two ranges involved.

From the succession of pairs of values obtained in this way, step by step, the curve labelled SD in Fig. 11 was built up.

It is of course true that the curve SD, Fig. 11, thus produced does not exactly represent the true values, since it is rather made up of a series of straight lines than a strictly continuous curve. It is, however, very near the real curve, which would lie slightly above it (nearer to the curve H), and is probably accurate within the limit of error of the experiment. Greater accuracy could be attained by taking shorter intervals and more points, but this extra trouble is not warranted by the precision of the present experimental work.

Since this curve cannot be continued to infinite dilution, its origin must be found by extrapolation, but this is a matter of minor importance.

It should, of course, coincide with the values for U given by the Helmholtz equation (curve H, Fig. 11), and for great dilutions the latter is doubtless more accurate than the former can be. Therefore, instead of attempting an extrapolation, the curve D was started on the curve giving the values for the Helmholtz equation at about 8% amalgam.

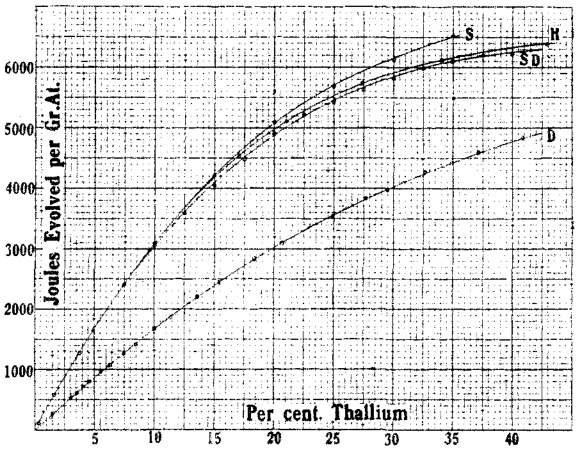

Fig. 11.—Heat of transfer of a gram-atom of thallium from one amalgam to another of different concentration. Curve S, as calculated from the heat of solution of thallium; Curve D, as calculated from the heat of dilution of thallium amalgam; Curve H, as calculated from the Helmholtz equation. Curve D gives the heat of dilution.

In order to show the degree of consistency of the 3 methods of calculating U, namely, from the heat of solution of thallium on the one hand, from the heat of dilution of thallium amalgam on the other hand, and from the Helmholtz equation (see page 1761), the following table is given, exhibiting values taken (as regards the first two methods) from curves plotted on a much larger scale than the appended diagram.

Table XV.

Heat Effect in Cell (U).

(In Joules Per Gr.-Atom of Tl Transferred.)

I. Conc. in cell.	II. Found from heat of solution of Tl.	III. Found from heat of dilution of amalgams.	IV. Calculated from Helmholtz equation.
0.3315– 1.704	..	..	470
0.1704– 3.788	..	..	696
3.788 – 4.935	..	..	370
			—
4.930 –10.02	1440	1420	1449
10.02 –17.05	1530	1400	1445
17.05 –21.02	625	570	568
20.97 –27.36	705	647	631
27.36 –34.03	460	400	385
34.03 –42.86	..	240	261
		——	——
Sum, 4.93 –42.86	..	4677	4739

The values in Col. II have a large probable error, and are valuable only as a general confirmation of the others. The values in Col. III are much more trustworthy, and those in Col. IV are probably even better.

Since the agreement of Cols. III and IV is within the limit of the series of experimental errors of the two columns, evidently the Helmholtz equation is confirmed in its application to these amalgam cells, taking account of the fact that the thermal effect to be considered is the transfer of thallium from a concentrated amalgam of definite concentration to an equally definite more dilute amalgam.

The Freezing Points of the Amalgams.

One other phenomenon which throws light upon the behavior of thallium, and therefore upon the nature of the solutions in mercury, deserves consideration, namely, their irregular freezing-point curve. There can be no doubt that these freezing points, through eutectic and dystectic breaks in the curve, indicate the existence of a solid compound. The work of Kurnakow and Puschin[1] seems to show a compound of the composition $TlHg_2$, but our experience (communicated below) indicates rather the formula Tl_2Hg_5. Some years after our determinations were made, but of course entirely independently, since our results had not been published, Roos[2] published results similar to ours.

Table XVI.

% Tl by weight.	Atomic %.	Temp. of freezing. °C
1913. First Series. (Small Quantities.)		
42.8	42.3	+1.6
38.8	38.3	5.3
34.0	33.5	12.0
31.7	31.3	13.9
29.1	28.7	14.9
26.4	26.0	14.3
24.2	23.8	12.3
19.5	19.2	3.0
1913. Second Series. (Small Quantities.)		
36.5	36.0	9.2
34.4	33.9	11.7
31.5	31.1	14.1
29.0	28.6	14.8
25.4	25.0	13.2
23.8	23.4	11.5
20.0	19.7	4.0
1914. Third Series. (Beckmann Freezing-Point Apparatus.)		
40.90	40.47	+0.9[3]
38.83	38.37	5.9[3]
37.19	36.71	9.5[3]
32.63	32.31	12.8[3]
27.60	27.24	14.3
20.63	20.31	5.7
18.27	17.97	—0.9
16.92	16.65	—6.5

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[1] Kurnakow and Puschin, *Z. anorg. Chem.*, **30,** 86 (1902).

[2] Roos, *Ibid.*, **94,** 358 (1916); *C. A.*, **10,** 1479 (1916).

[3] In these experiments there was not enough amalgam to submerge the whole of the thermometer bulb.

In 1913 crude experiments were performed with concentrated amalgams from the electromotive force experiments. A small glass bulb containing the amalgam was slipped over the thermometer bulb and tightly held with a rubber ring. The thermometer was read when the amalgam started to freeze upon being plunged into cold water. After complete solidification the bulb and thermometer were removed from the cold bath and the instrument was read again as the last portion of the solid amalgam was disappearing. With each amalgam several trials and successive readings were made. Successive portions of mercury were added and the process repeated again and again.

A year later further experiments were made, using a Beckmann freezing-point apparatus with large quantities of amalgams from the calorimetric determinations. These confirmation determinations are much more accurate than the preceding.

In Fig. 12 these values are represented by small circles. The curve attains a maximum in the neighborhood of 28.5 atomic % of thallium. This dystectic point shows then that a compound of thallium and mercury is formed corresponding to the formula Tl_2Hg_5. Convincing proof of such a compound lies in the fact that amalgams of approximately this composition gave a sharply defined melting point and remained stationary at this temperature (14.9°) during the whole time of freezing. All other amalgams (including those (corresponding to $TlHg_2$) or 33.3 atomic %) gave ill-defined freezing points, which changed during solidification. For instance, the 36.71% amalgam started to freeze at 9.5°, but was not completely solid even at 5.0°. Solid amalgams of approximately 28.5% consisted of perfect crystals, while all the other amalgams gave ill-defined crystals. This is to be taken as further evidence of the existence of a compound Tl_2Hg_5.

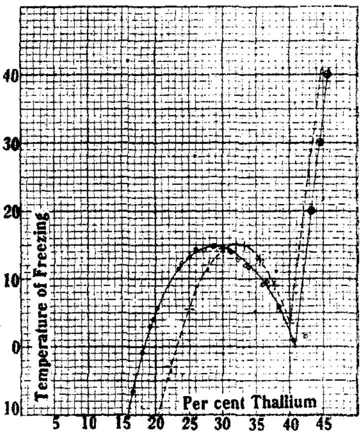

Fig. 12.—Freezing points of thallium amalgams. Dotted curve indicates results of Kurnakow and Puschin. Abscissas indicate atomic %. (In all other diagrams abscissas indicate per cent. by weight.)

The double circles represent freezing points as determined from the electromotive force measurements, being the breaks in the curve already illustrated in Fig. 3. Freezing points at 40°, 30° and 20° were found, respectively, to be at 45.8, 44.5, and 43.3%. This line extrapolated crosses the curve of the freezing point of the weaker amalgam at about 40.8%, the temperature being about 0.5°, and thus giving a wholly consistent picture.

The dotted line in Fig. 12 indicates the freezing points of thallium amalgams as determined by Kurnakow and Puschin.[1] This curve shows a maximum of 15.0° at $33^1/_3\%$ instead of at 28.5%, and seemed to its authors to indicate the existence of the compound $TlHg_2$. The eutectic point at 40% is likewise not in agreement with ours. Experimental details are not given and the cause of the serious discrepancy cannot be determined. Certainly the purity of the materials in the present research is beyond question, and the fact that our electromotive-force measurements (Fig. 3) gives a perfectly regular curve shows that the concentrations must be correctly known. Cohen and Inouye[2] have repeated Puschin's work on the zinc amalgams and found it considerably in error, and they suggest that his work on other metals may be in need of revision. The erroneous freezing-point curve for thallium amalgams has been copied in a text-book[3] as an example of the indication of a compound ($TlHg_2$) by a dystectic point.

The conclusion that the formula of the solid compound is really Tl_2Hg_5 is of interest as regards the constitution of the liquid amalgams, because it shows that thallium has a tendency to form diatomic molecules. If diatomic molecules thus exist in the solid state, it is not unreasonable to believe that the same tendency may exist in solutions.

Conclusion.

Thus a great variety of data concerning the nature of thallium amalgams has been provided, and some of the essential thermodynamic relations between these phenomena have been pointed out. The more detailed hypothetical analysis of these varied data is capable of furnishing much light on the nature of amalgams as well as on the nature of solutions in general; but this is a large subject, involving the discussion of bicomponent systems in its widest bearings, and is reserved for a later paper, now almost ready for publication.

We are much indebted to the Carnegie Institution of Washington for financial support in this investigation, and to Dr. W. C. Schumb for assistance in the manifold and time-consuming calculations involved.

Summary.

In this paper the following contributions to the experimental study of thallium amalgams have been made:

1. The electromotive forces between amalgams ranging from 0.33% to saturation (over 40%) have been measured within a few microvolts, at 20°, 30°, and 40°. These potentials are far greater than those demanded by the simple concentration law.

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[1] Kurnakow and Puschin, *Z. anorg. Chem.*, 30, 86 (1902).

[2] Cohen and Inouye, *Z. phys. Chem.*, 71, 627 (1910).

[3] Findlay, "The Phase Rule," p. 225, Longmanns Green and Co., New York (1915).

2. The temperature coefficients of the electromotive forces of these amalgams have been computed from these results. These temperature coefficients are less than the requirement of the gas law, and vary as the concentration increases.

3. The densities of the liquid amalgams and the solution volume of thallium in mercury have been determined over the whole range. The solution volume is remarkably constant, varying only from 17.47 to 17.51, but is somewhat in excess of the specific volume of thallium, 17.21. Thus thallium expands on amalgamation.

4. The coefficients of expansion of the various amalgams were computed from these results. They diminish with increasing concentration.

5. The heat capacities of the amalgams were determined by a somewhat new method over the whole range. They were found to be distinctly in excess of the sum of the heat capacities of the thallium and mercury taken separately; that is, the "solution heat capacity" of one gram of dissolved thallium is greater than the heat capacity of one gram of solid thallium. This excess is greater in dilute than in concentrated amalgams.

6. The heats of dilution of thallium amalgams with mercury at 20° were determined over the whole range of concentrations. With the help of the heat-capacity values these results were corrected to 30° (and approximately to 325°).

7. The heats of solution of thallium in mercury and in thallium amalgams of increasing concentration were measured.

8. Although the heat of dilution of thallium amalgam is a very different effect from the transfer of thallium from one amalgam to another, one of these effects can be computed from the other. The necessary steps are indicated.

9. It is shown that, within the limit of error of the experiment, the heat effects in the cells of which the electromotive forces were measured may be computed from either the heat of dilution of the amalgams, or the heat of solution of thallium in the amalgams, or the temperature coefficient of the electromotive force—each of these 3 methods giving essentially identical results within the limit of error of the experiment.

10. The freezing points of amalgams from 16 to 45 atomic % were repeatedly determined, and were found to give a curve indicating conclusively the existence of the solid compound Tl_2Hg_5.

11. The single potential of pure electrolytic thallium was found to be about 2.5 m. v. more negative than that of saturated thallium amalgam at room temperatures.

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