

convenient words as adsorption used by the colloid chemists, since we see that purely physico-chemical laws find application to mineral colloids also, in this case the soil. The word colloid will then mean only a particle of special dimensions and not of special properties.

### Summary

It has been shown that clays of different origin and different reaction have the same iso-electric point and the curve obtained by plotting rate of settling against the hydrogen-ion concentration has the same course as that of gelatin. The clay acts as an amphoteric electrolyte and can therefore combine with either acid or base. This is also shown by the buffer action of the clays. The result is important theoretically, as well as practically.

The work has been carried out in the Laboratory of Plant Physiology of Harvard University. To Professor Osterhout I express my warmest thanks for his kind help and suggestions.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## SOLID THALLIUM AMALGAMS AND THE ELECTRODE POTENTIAL OF PURE THALLIUM

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This investigation was undertaken for the purpose of ascertaining the cause of the potential difference recently found to exist between pure thallium and saturated thallium amalgam. Several earlier investigators concluded that, as in the case of zinc, the solid phase in equilibrium with the liquid in the 2-phase amalgam consists of pure solid metal,—the solubility of mercury in solid thallium being regarded as practically zero, when, of course, the potential of the 2-phase amalgam would be identical with that of pure thallium. Lewis and von Ende,<sup>1</sup> in their excellent determination of the potential of the thallium electrode, assumed this to be the case, and used, in place of a pure thallium electrode, a 55% amalgam consisting of 2 phases. The basis for their assumption was the thermal analysis of Kurnakov and Puschin,<sup>2</sup> the electromotive force measurements of Sucheni,<sup>3</sup> and experiments of their own.

The experimental precautions employed, however, were evidently not adequate to prove the point, for the work of recent Harvard investigators

<sup>1</sup> Lewis and von Ende, *THIS JOURNAL*, **32**, 732 (1910).

<sup>2</sup> Kurnakov and Puschin, *Z. anorg. Chem.*, **30**, 86 (1902).

<sup>3</sup> Sucheni, *Z. Elektrochem.*, **12**, 726 (1906). See also Spencer, *ibid.*, **11**, 681 (1905).

has shown a real difference of electromotive force between pure thallium and thallium with a film of amalgam on its surface.<sup>4</sup>

The main objects of the present investigation were to confirm this difference of potential as well as to discover whether it is due to the formation of a solid solution of mercury and thallium, or to a crystalline compound. Incidentally, the electrode potential of thallium was revised.

### Experimental Details

The substances used were purified with adequate care: the water was twice distilled (from alkaline permanganate and very dil. sulfuric acid); hydrogen was generated electrolytically (from sodium hydroxide containing a little barium hydroxide) and thoroughly dried; and mercury was purified by treatment with mercurous nitrate solution and distillation. The preparation of the pure thallium must be described more in detail. This was chiefly at hand in the form of nuggets of crude metal containing perhaps 7% of lead and small amounts of other impurities. The thallium was dissolved in dil. pure sulfuric acid, leaving most of the lead, partly as a metallic powder and partly as precipitated sulfate. The cooled and somewhat diluted solution was filtered; to it was added dil. redistilled hydrochloric acid drop by drop, with constant stirring. Very little, if any, lead was found in the precipitated thallic chloride, which was washed several times by decantation. Pure conc. redistilled sulfuric acid converted the solid thallic chloride into sulfate. This thallium sulfate, which on dilution gave no precipitate of lead sulfate, was crystallized by cooling to 0°. The long needles of the salt were thoroughly dried, recrystallized at least twice (sometimes thrice) in a silica dish, by cooling with ice a solution almost saturated at the boiling point. The solubility curve is steep and the process efficient.

From this sulfate, which must have been amply pure enough for our purpose, metallic thallium was prepared by the electrolysis of the saturated solution of the sulfate in water; the electrodes were short platinum wires exposing not more than 1 cm. of their length to the solution. The anode was placed on the bottom of the beaker containing the solution (being protected above by a long glass tube into which it was sealed), while the cathode merely dipped beneath the surface. The heavy red-brown deposit of peroxide at the anode remained at the bottom of the beaker and therefore did not contaminate the crystalline spongy mass of thallium deposited on the cathode above. A current of about 1 ampere was used and the thallium was removed at frequent intervals from the cathode by means of a small glass fork, rinsed thoroughly with pure water, pressed together, and kept under pure boiled water until fused. A small further amount of thallium was obtained by electrolysis from pure liquid amalgam remaining from the work of Daniels, the amalgam being made the anode in dil. sulfuric acid solution. This thallium was found to contain traces of mercury, which were removed by fusing at a high temperature.

For use in the study of the amalgams, as well as of the pure metal, the thallium was fused into a compact mass. The sponge was pressed as free from water as possible, and dried in a vacuum desiccator. At first the dried thallium was pressed into one of three Pyrex glass bulbs connected by capillary tubes. After sealing and thorough evacuation of the tube, the thallium was melted; and, by tilting the apparatus, the molten metal was run through the capillary into the second bulb, leaving the solid impurities behind. The clean, bright metal was then heated to drive off volatile im-

<sup>4</sup> Richards and Daniels, *THIS JOURNAL*, **41**, 1732 (1919). Jones and Schumb, *Proc. Am. Acad.*, **56**, 199 (1921). See also Lewis and Randall, *THIS JOURNAL*, **43**, 247 (1921) (Footnote).

purities (if any) into the third bulb; after which the apparatus was sealed off between the second and third bulbs, leaving the pure metal in the second bulb. Here it could be kept indefinitely without fear of oxidation.

Later, with larger quantities of metal, another less elegant but more convenient technique was employed. The dried sponge was pressed into a large unglazed earthenware boat, which was slipped into the glazed porcelain tube of an electric furnace. The tube, wound with resistance ribbon and asbestos, was supported in a horizontal position by large clamps, and its ends were closed tightly with Hempel stoppers, through which constant streams of cold water were kept flowing. Air was at once removed by an oil pump and replaced by hydrogen, the exhaustion and replacement by hydrogen being repeated thrice. All heating was conducted in an atmosphere of hydrogen, which was kept flowing through the tube in a slow, but steady, stream. A temperature between 350° and 400° was maintained from 1 to 3 hours. Most of the oxide present was reduced to the metal, and volatile impurities were driven off. Usually a very thin scarcely weighable grayish coating of non-metallic impurities remained upon the surface of the compact ingot of pure metal, which was scraped clean and bright before using.

The same technique was adequate for the removal of mercury from very concentrated amalgams. When much mercury was evaporated, it was found to carry with it a trace of thallium,<sup>5</sup> so that the method is not a very good one for purposes of analysis, but the residual thallium appeared to be beyond reproach. In order to make certain of the expulsion of every trace of mercury, the ingot was reheated at least once in hydrogen after cleansing the furnace.

From this pure thallium, amalgams were prepared as follows. The desired amount of solid metal was scraped until thoroughly clean, weighed, and mixed with a weighed quantity of mercury. The amalgamation was at first effected by heat in a sealed glass tube, but the method had disadvantages and was abandoned in favor of a simpler one in which the mercury and thallium were brought together in a small porcelain crucible and immediately covered with molten paraffin, with which the crucible was almost filled. Gentle heating melted the thallium, and the metals were stirred together with a fine glass rod until they formed a homogeneous liquid amalgam. This was allowed to cool slowly. The layer of paraffin above the amalgam prevented oxidation of the thallium, and evaporation of mercury, and served also to render cooling more uniform, and to protect the bead of amalgam from air until needed. The solid bead after cleaning free from paraffin, showed a bright, clean surface.

The amalgams were analyzed by a method already described,<sup>6</sup> enough mercury being added to the solid amalgam to effect its solution, and the liquid being agitated with pure air and standard dil. acid. The method was tested by two preliminary determinations made with pure thallium in the same fashion. Thus 0.1309 g. of metal was estimated as 0.1307 g. and 0.2200 g. as 0.2201 g., indicating adequate precision.

Thallium is deposited electrolytically in hexagonal plates.<sup>7</sup> Whether or not these belong to the hexagonal system we did not decide. Solid amalgams containing over 10% of mercury were quite different in appearance and properties from the pure metal. When less than 10% of mercury was present, they could be cut smoothly with a knife, but amalgams with more mercury, especially those containing 12%, were distinctly brittle, breaking up into grains which appeared to be well formed cubic, or near-cubic,

<sup>5</sup> Compare Krafft and Knocke, *Ber.*, **42**, 202 (1909), and von Wartenberg, *Z. Elektrochem.*, **19**, 482 (1913).

<sup>6</sup> Richards and Daniels, *THIS JOURNAL*, **41**, 1732 (1919).

<sup>7</sup> Our observations on this matter agree with Kurnakov and Puschin, *Z. anorg. Chem.*, **52**, 430 (1907).

crystals. This implies the formation of a new solid phase, the nature of which will receive discussion later. When more than 12% of mercury was present, a trace of liquid amalgam was sometimes found on the faces of the freshly formed crystals. On standing, this excess of mercury seemed to have incorporated itself into the amalgam as solid. It must be remembered that these preparations had been solidified by cooling and that therefore the first formed crystals, when they actually separated, were in equilibrium with the liquid at a higher temperature than that of the room. Evidently thallium takes in more mercury in the solid form at a low temperature than at a high temperature; but an 85% amalgam (containing 15% by weight of mercury) contained between the solid crystals a permanent very thin layer which was not absorbed on standing. Of course, amalgams yet poorer in thallium contain still more of this liquid film. The crystals of the amalgam just mentioned are much harder than pure thallium. The pure metal is so soft that no considerable strain can exist in it at ordinary temperatures.

As regards microstructure, no satisfactory evidence could be obtained by polishing and etching the surfaces, for, of course, the mercury set free at once covered the surface with a shining layer of liquid amalgam. On solidifying, the solid amalgams showed delicate fern-like patterns on their surfaces, but these gave no evidence of the crystalline structure.

### The Electromotive Force between Amalgams

The measurements of electromotive force were made by the usual Poggendorf compensation method, a Wolff potentiometer and a highly sensitive galvanometer being used. The potentiometer was standardized by a Weston cell certified by the Bureau of Standards. All usual precautions were taken for obtaining results of high accuracy. The thallium cells were kept at 20.00° in an electrically regulated thermostat (with a cooling coil for hot weather). They were contained in vessels of the ordinary H type, the electrical connections being made through short platinum wires sealed into fine straight tubes which passed through paraffined corks. The electrolyte was at first a saturated solution of thallium sulfate with crystals of the salt in each arm, but afterwards a dilute solution was found to be more convenient, since the changes of temperature in the cells after removal from the thermostat caused changes of concentration when solid sulfate was present, which were slow in equalizing themselves. The most convenient standard of reference for all the thallium amalgams was the 2-phase amalgam containing 55% of thallium and 45% of mercury, as recommended by Lewis and von Ende. This is a very constant and reproducible electrode. A portion of 2-phase amalgam thus prepared was always placed in one arm of each H-cell; in the other arm was placed one of the various amalgams to be studied. Twenty or more cells were thus equipped at one time, and 76 in all were measured.

Electrodes of electrolytic thallium were prepared by electro-deposition from a thallos sulfate solution in several ways, the deposit being made upon a short platinum wire. The ordinary procedure was to use a very low current for an hour or two until the wire was well covered with a compact deposit of thallium, after which the current was increased so that a spongy deposit with a large surface formed rapidly. A few electrodes were prepared by running a very low current for 2 or 3 days, the small deposit thus obtained being very thin, adherent, and finely crystalline.

Electrodes were prepared also from pieces of the thallium which had been fused in hydrogen. The piece which, usually, had a maximum cross-sectional area of about 0.5 sq. cm., was cut with a knife, and into the deep slit thus formed the short platinum wire of a connecting tube was forced, the metal was pressed together over the wire, and a little paraffin was melted over the closed slit and over any exposed portion of the platinum wire. Connection with the electrode was thus made in such a manner

that the thalious sulfate solution in the cell could have no access to any metal other than that of the electrode. All the electrodes were rinsed several times with thalious sulfate solution before use in the cell. Solid thallium amalgams were mounted as electrodes in the way just described.

In all except the very first experiments, considerable precaution was taken against the presence of oxygen in the electrolyte above the amalgams, the gas above the liquid being repeatedly exhausted and replaced by pure hydrogen before the electrode to be studied was introduced, and this introduction was effected while the hydrogen was flowing in a rapid stream. In the first few cells only was there any considerable oxidation. The electromotive forces usually remain constant for a long time. This constancy was evidence also that mercury was not appreciably transferred from the 55% amalgam to the other electrode during the time of experimentation. In a few cases the electrolyte was found, after a long time, to have become alkaline to phenolphthalein, but what little alkalinity existed was equally distributed through the cell so as not to affect the electromotive force, which depends not upon the character of the electrolyte, if uniform, but upon the concentration in thallium of the two electrodes.

Preliminary measurements gave fairly constant results for spongy, electrolytically deposited thallium, varying from 2.60 to 2.81 millivolts when compared with the 2-phase 55% amalgam. Fused thallium gave 2.08 mv. Solid amalgams containing between 85 and 100% of thallium all gave lower results, as had been expected. The final values obtained (the averages of many measurements) are given in the following table. The individual determinations rarely differed more than 0.10 mv. from the average in the case of the most significant figures between 96 and 91%, the reproducibility of the electrodes increasing with increasing mercury content.

TABLE I  
ELECTROMOTIVE FORCE

Pure thallium or solid amalgams versus saturated amalgam								
Negative electrode	Tl %	E.m.f. Mv.	Negative electrode	Tl %	E.m.f. Mv.	Negative electrode	Tl %	E.m.f. Mv.
Elec. deposit (fresh): pure								
Tl	100	2.67		95	1.32		89	1.02
Fused: pure								
Tl	100	2.08	Fused amalgam	94	1.39	Fused amalgam	88	0.59
	99	1.80		93	1.26		87	0.39
Fused amalgam	97	1.47		91	1.30		86	0.15
	96	1.28		90	1.10		85	0.00

Let us consider first the behavior of the pure metal under different conditions. Electrolytically deposited thallium gave, when freshly prepared, a potential 0.6 mv. higher than that of thallium which had been fused—a difference seemingly too great to be accounted for on the ground of experimental error, since the lowest individual determination for fresh spongy, electrolytic thallium was higher than the highest individual determination for the compact form.

This difference might be ascribed to one or more of three different possible causes. It might be due to active hydrogen, released at the cath-

ode along with the metal during the electrolysis. Although thallium occludes ordinary gaseous hydrogen in quantities which can hardly be detected,<sup>8</sup> possibly hydrogen formed at a cathode during electrolysis might be occluded to a greater extent, as in the case of iron.<sup>9</sup> Accordingly, qualitative experiments were made to test the point. The samples to be tested were dissolved in mercury under water in a test-tube to form a dil. amalgam, in which hydrogen must have been practically insoluble. Fused thallium evolved no gas when thus treated, nor did electrolytic thallium which had been long prepared. Freshly made electrolytic thallium evolved a few bubbles, but unfortunately the results of this latter test were inconclusive, as they could not show whether the hydrogen was actually occluded in the metal, or merely held on its surface, or in cavities. At any rate the total amount of hydrogen was shown to be very small.

Another possible explanation for the difference of potential between fused and electrolytic thallium lies in the allotropy of the metal. When a metal capable of existing in more than one form is deposited electrolytically, the metastable form is likely to be deposited first.<sup>10</sup> This metastable form may change rapidly to the modification which is stable under the existing conditions, or may remain unchanged for a longer period of time. The metastable form has, of course, a higher potential than the stable.<sup>11</sup> Thallium has been known for some time to exist in two enantiotropic modifications,  $\alpha$ -thallium, the form stable at ordinary temperatures, changing to  $\beta$ -thallium at the transition temperature  $235.3^\circ$  (as described later); but  $\beta$ -thallium has never been observed at room temperatures. An attempt was made to obtain it by quenching the liquid metal, but the attempt was a failure, since the quenched metal showed the same potential as ordinary fused thallium and was therefore the  $\alpha$  modification. There is a remote possibility that electrolytic thallium may be a hitherto undiscovered modification lying between the  $\alpha$  and the  $\beta$  forms, but the lack of any thermal evidence of its existence, and the fact that X-ray photographs of sections of the metal taken at different temperatures show no change of structure below  $227^\circ$ ,<sup>12</sup> seem to render this possibility so remote as to deserve no serious consideration.<sup>13</sup> Complete knowledge of the

<sup>8</sup> Sieverts, *Z. Elektrochem.*, **16**, 708 (1910). Smith, *J. Phys. Chem.*, **23**, 188 (1919).

<sup>9</sup> Cailltet, *Compt. rend.*, **80**, 319 (1875). Johnson, *Proc. Roy. Soc. (London)*, **23**, 168 (1875). Bellati and Lussana, *Z. physik. Chem.*, **7**, 229 (1891). Shields, *Chem. News*, **65**, 195 (1892).

See also Richards and Behr, "The Electromotive Force of Iron under Varying Conditions, and the Effect of Occluded Hydrogen," *Carnegie Inst. Pub.*, **61** (1906).

<sup>10</sup> Smits, *Verslag. akad. Wetenschappen Amsterdam*, **22**, 642 (1913).

<sup>11</sup> Cohen, *Trans. Faraday Soc.*, **10**, 216 (1915).

<sup>12</sup> Nishikawa and Asahara, *Phys. Rev.*, **15**, 38 (1920).

<sup>13</sup> Werigin, Lewkojeff, and Tammann (*Drude's Ann.*, **10**, 647 (1903)), measuring the change with temperature of the "Ausflussgeschwindigkeit" of thallium thought that a transformation was indicated at  $180^\circ$ , but other investigators have been unable to discover any such transformation.

different crystal structures of thallium might make it possible to decide conclusively against the assumption that the higher potential of the electrolytic metal is due to metastability,<sup>14</sup> but at present this explanation seems unlikely.

A more probable explanation than either of these, is that the difference of potential between the compact and finely divided thallium is due to the degree of subdivision. This effect has long been well-known in other cases: the solution tension of a fine powder is greater than that of a flat surface.<sup>15</sup> The differences in potential ascribed to this cause, as found by others in various cases, have varied from a few tenths of a millivolt to several millivolts. The small difference of 0.6 mv. found by us may well be thus produced; the gradual elimination of the finest shreds of thallium on standing would be expected to reduce the potential to the normal value.

Clearly, since the 55% amalgam lacks 2.08 mv. of the true thallium potential, the true potential for the cell [Tl, (Tl<sup>+</sup> normal), calomel electrode] at 25° is 0.6192 instead of 0.6170.<sup>16</sup> The "single electrode potential" of thallium may be taken as about 0.055 with this concentrated solution,<sup>17</sup> or about 0.115 with a Tl<sup>+</sup> 0.1 *N* solution, neglecting the junction potential of the liquids (which may, however, be fairly large).

Turning now to the amalgams of thallium, we find that the e.m.f. determinations range themselves in a broken curve of definite character. With increasing concentration of mercury there is a decrease in the potential as far as 4% or 5%, then a fairly constant potential (within a reasonable limit of error) as far as 9%, and then a rapid falling off down to 14.5%, where the potential becomes that of the 2-phase amalgam. The cause of the striking double break in this curve will be considered after other phenomena have been studied. The curve furnishes further evidence that thallium which has been fused contains no atomic hydrogen, for otherwise its e.m.f. would lie above the extrapolation of the left hand end of the curve to the vertical axis. It likewise conclusively proves

<sup>14</sup> As the crystal structure of thallium is now under investigation by A. W. Hull, who is applying to it his highly developed method of X-ray analysis, the knowledge should soon be available.

<sup>15</sup> The literature upon this subject is very plentiful. A few references are given below.

Luedtke, *Wied. Ann.*, **50**, 678 (1893). Ostwald, *Z. physik. Chem.*, **34**, 495 (1900). Hulett, *ibid.*, **37**, 385 (1901). Richards and Behr, Ref. 9. Hering, *Met. Chem. Eng.*, **10**, 14 (1912).

<sup>16</sup> Ref. 1, p. 740. Our value 0.00208 volt for this difference was at 20°; but this would be increased to about 0.00217 at 25° (See Richards and Daniels, Ref. 4, p. 1743).

<sup>17</sup> The calomel electrode is assumed to give 0.564 volt at 25° and no allowance is made for the unknown solution-junction potential.

that thallium dissolves considerable mercury in the solid state. This curve is depicted as the lowest one in Fig. 3, given later.

### Thermal Analysis of Thallium Amalgam

For amalgams containing more than 50% of mercury the melting points have been studied by one of us in collaboration with F. Daniels.<sup>18</sup> The melting point<sup>19</sup> of pure thallium has been variously given in recent years between 299.4 and 303.0 and the transition point<sup>20</sup> between the  $\alpha$  and  $\beta$  modifications of thallium variously given between 225° and 238°. In the earlier investigation only a few points had been determined with

<sup>18</sup> Ref. 4. In this paper references to earlier work of this sort will be found. See also Pavlovitch, *J. Russ. Phys. Chem. Soc.*, **47**, 29 (1915).

<sup>19</sup> Determinations of the melting-point of thallium

Melting point °C.	Observer	Publication
288	Crookes.....	<i>Phil. Mag.</i> , [4] <b>21</b> , 301 (1861)
290	Lamy.....	<i>Ann. chim. phys.</i> , [3] <b>67</b> , 385, 418
303.7	Heycock and Neville.....	<i>J. Chem. Soc.</i> , <b>65</b> , 32 (1894)
301.7	Kurnakov and Puschin.....	<i>Z. anorg. Chem.</i> , <b>30</b> , 91 (1902)
301.2	Kurnakov and Puschin.....	<i>Ibid.</i> , <b>52</b> , 430 (1907)
301	Williams.....	<i>Ibid.</i> , <b>50</b> , 127 (1906)
303	Petrenko.....	<i>Ibid.</i> , <b>50</b> , 133 (1906)
301	Chikashigé.....	<i>Ibid.</i> , <b>51</b> , 328 (1906)
302	von Vegesack.....	<i>Ibid.</i> , <b>52</b> , 30 (1907)
299.4	Lewkonja.....	<i>Ibid.</i> , <b>52</b> , 456 (1907)
301.2	Kurnakov, Zemczuzny and Tararin.....	<i>Ibid.</i> , <b>83</b> , 200 (1913)
301	Pavlovitch.....	<i>J. Russ. Phys. Chem. Soc.</i> , <b>47</b> , 29 (1915)
301.5	Roos (Electrolytic Tl).....	<i>Z. anorg. Chem.</i> , <b>94</b> , 358 (1916)
301.7	Fuchs.....	<i>Ibid.</i> , <b>107</b> , 308 (1919).

<sup>20</sup> Determinations of the transition point of thallium

Trans. point °C.	Observer	Publication
225	Levin.....	<i>Z. anorg. Chem.</i> , <b>45</b> , 31 (1905)
226	Williams.....	<i>Ibid.</i> , <b>50</b> , 127 (1906)
227	Petrenko.....	<i>Ibid.</i> , <b>50</b> , 133 (1906)
231.6	Chikashigé.....	<i>Ibid.</i> , <b>51</b> , 328 (1906)
227	Kurnakov and Puschin.....	<i>Ibid.</i> , <b>52</b> , 430 (1907)
230.5	Lewkonja.....	<i>Ibid.</i> , <b>52</b> , 456 (1907)
234	Voss.....	<i>Ibid.</i> , <b>57</b> , 49 (1908)
238	Donski.....	<i>Ibid.</i> , <b>57</b> , 185 (1908)
229	Kurnakov, Zemczuzny and Tararin.....	<i>Ibid.</i> , <b>83</b> , 200 (1913)
226	Werner.....	<i>Ibid.</i> , <b>83</b> , 275 (1913)
234	Pavlovitch.....	<i>J. Russ. Phys. Chem. Soc.</i> , <b>47</b> , 29 (1915)
233	Roos (Electrolytic Tl).....	<i>Z. anorg. Chem.</i> , <b>94</b> , 358 (1916)
231-233	Fuchs.....	<i>Ibid.</i> , <b>107</b> , 308 (1919)
227	Nishikawa and Asahara.....	<i>Phys. Rev.</i> , <b>15</b> , 38 (1920).



certainty on the liquidus curve for thallium-mercury mixtures containing from 80-100% of thallium. This curve therefore seemed worthy of further study. Our experiments were carried out in a large test-tube jacketed by another still larger test-tube, the thermometer being immersed in the melted metal, a stirrer being provided and carbon dioxide being led into the space above in order to protect the metal from oxidation. The outer test-tube was heated by immersion in a bath of melted sodium and potassium nitrates suitably controlled in temperature. The thermometer was calibrated in precisely the same way with pure tin certified by the U. S. Bureau of Standards and an imported pure cadmium (melting points assumed as  $231.9^{\circ}$  and  $320.7^{\circ}$  respectively).

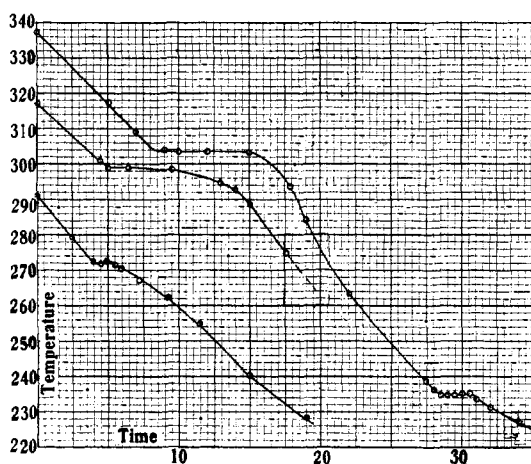


Fig. 1.—Typical cooling curves: pure thallium and two amalgams.

Temperatures are plotted as ordinates; times as abscissas. The unit of time is  $\frac{1}{2}$  minute for the uppermost curve; 1 minute for the two lower ones. The uppermost curve is for pure thallium, the middle curve for a solid solution containing 1.1% mercury, and the lowest curve for a solid solution containing 8.8% of mercury.

With this apparatus a number of cooling curves of pure thallium and of the various amalgams were made. They were usually started about  $15^{\circ}$  above the freezing points of the mixtures and continued to about  $40^{\circ}$  below. Three typical cooling curves are given in Fig. 1; one for pure thallium, one for an amalgam containing 98.9%; one for an amalgam containing 91.2% of thallium.

Discussing the pure thallium curve first, it is evident that at  $303.5^{\circ}$  the marked inflection occurs which indicates the freezing point (and melting point) of the pure metal. This temperature was found uniformly as  $303.5^{\circ}$  in all our pure samples. It is somewhat higher than the values

found by most of the other investigators, possibly because of greater purity of our specimens. At  $235.3^{\circ}$  comes another smaller inflection corresponding to the transition of  $\beta$  to  $\alpha$  thallium. This temperature also is higher than that of most other observations. Because of the small heat of transition, small quantities of impurity would tend to lower greatly the transition point, unless the impurity is isomorphous. This temperature is so near the standard temperature  $231.9^{\circ}$  (the melting point of tin) that it must have been accurately determined in our case.

Turning now to the cooling curves of the *amalgams*, we see, as would be expected, that the freezing point becomes less marked as the amount of mercury increases and that it is sometimes preceded by a slight depression

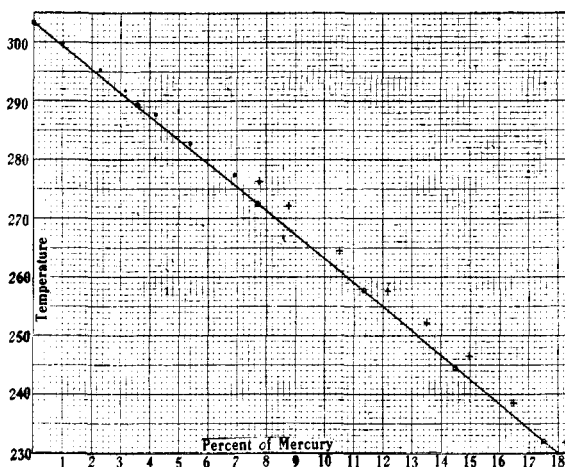


Fig. 2.—Liquidus curve (freezing points) of thallium amalgams.

The first breaks in three series of cooling curves (see Fig. 1) are here plotted to show the linear relation of temperature to mercury content. The last series (indicated by circles) was by far the most accurate.

due to supercooling. Instead of breaking sharply again at the downward turn, these curves show gradual decrease in freezing point as the freezing proceeds. This may be taken as definite evidence of the formation of a solid solution of mercury in thallium, agreeing essentially with the results of Pavlovitch and of Roos.<sup>21</sup> Of course the maximum temperature to which the mixture rose at the commencement of solidification after supercooling was taken as the freezing point, no measurable error resulting from the small amount of supercooling.

The results for the freezing point are sufficiently indicated by the accompanying graph, Fig. 2, in which they are carefully recorded, the graph

<sup>21</sup> Cf. Ref. 19.

taking the place of a printed table. In drawing the curve, the last most accurate and most comprehensive series (index 0) is given most weight. The other earlier series (from which small quantities of mercury had certainly evaporated during long heating) are indicated by other indices on the plot. These earlier values, lying closely together, serve to show that there is no minor inflection in the curve. The absence of inflection indicates that the solid phase produced at or in the neighborhood of the temperature of freezing with mixtures containing less than 20% of mercury consists of one or more solid solutions rather than a simple chemical compound.

At first sight, it might seem that the molecular freezing-point depression (*i. e.*, the depression produced by 1 gram-atom of mercury in 100 gram-atoms of solvent thallium) could be simply calculated from this curve, the result being 3.95°. Heycock and Neville,<sup>22</sup> from a study of the freezing points of dilute solutions of gold, silver, and platinum in thallium, concluded the molecular freezing-point depression for thallium to be 6.31°, from which they calculated the latent heat of fusion of thallium to be 5.12 calories per gram. Robertson<sup>23</sup> determined the heat of fusion of thallium as 7.2 calories per gram. The molecular freezing-point depression may be calculated from this datum by the well-known van't Hoff equation,

$$K = \frac{0.02 T^2}{L}$$

in which  $K$  is the molecular freezing-point depression,  $T$  the freezing point of the solvent on the absolute scale, and  $L$  the molecular latent heat of fusion of the solvent. In this case,  $T = 273^\circ + 303.5^\circ = 576.5^\circ$ ; and  $L = 7.2 \text{ calories} \times 204.1$ , therefore  $K = 4.53^\circ$ .

This result is much lower than the value, 6.31°, obtained by Heycock and Neville, but considerably higher than the value, 3.95°, obtained by direct experiment in the present investigation. The value 3.95° is doubtless too low because of the formation of a solid solution of mercury in thallium, as the formation of a solid solution may greatly change the freezing-point depression, tending to decrease it (even making it negative in the case of the solutions of lead in thallium).

If 3.95° is assumed to be correct, it leads to the value 8.3 for the latent heat of fusion of 1 g. of thallium.

Our solidus curve (melting point) agreed essentially with those obtained by Pavlovitch and by Roos by thermal methods.

#### Densities of Concentrated Thallium Amalgams

The densities of the solid thallium amalgams were determined by a method similar to that used in the Harvard laboratories in the determina-

<sup>22</sup> Heycock and Neville, *J. Chem. Soc.*, **65**, 31 (1894).

<sup>23</sup> Robertson, *ibid.*, **81**, 1233 (1902).

tion of the density of lead from radio-active minerals.<sup>24</sup> Great care was used in the determinations, which were conducted at  $20.000^{\circ} \pm 0.003^{\circ}$ . Very pure dry toluene was used as the liquid to be displaced and the volume of the pycnometer was determined by pure water. Successive readjustments and weighings of the same sample never differed by more than 0.3 mg. The metal was cut into small pieces which could be slipped into the pycnometer, and all oxide was scraped from its surface. The metal was covered as soon as possible, and air bubbles removed either in a vacuum or by shaking (which gave identical results). Amalgams rich in mercury, which crumbled into fine crystals, gave trouble from oxidation, due possibly to the large surface exposed; this error was avoided by rapid manipulation and by avoiding as much as possible the disintegration of the amalgam. A preliminary series made with old amalgams of somewhat doubtful composition and giving irregular results was rejected. The second series given below was made with fresh amalgams made for this purpose. The samples were prepared from the same specimen of pure thallium by the successive addition of mercury, melting the metals together and cooling slowly. A small amount of mercury was lost during the successive fusions, but the amount was too small to cause any error beyond the limits of experimental error. The densities and specific volumes of the several amalgams reduced to the vacuum standard are given in the following table, in which each figure represents the mean of at least two determinations. The last value (for 80.35% thallium) came from crystals formed slowly from a more liquid amalgam, and separated centrifugally as well as possible from the residual liquid. The separation was incomplete, as appeared under the microscope; but from the result (knowing that the liquid has a density of 12.647 and contains 43.3% of thallium<sup>25</sup>) it is easy to calculate that if the solid contains 85.4% (as indicated by the e.m.f. measurements) the percentage of liquid in the mix-

TABLE II  
DENSITIES AND SPECIFIC VOLUMES OF THALLIUM AMALGAMS

Wt.-% of Tl in amalgam	Density of amalgam Mean value	Specific volume of amalgams		Diff. $\times 10^8$
		Obs.	Calc.	
100	11.849	0.08440	0.08440	0
99	11.873	0.08422	0.08429	- 7
97	11.874	0.08422	0.08408	+14
95	11.861	0.08431	0.08386	+45
93	11.896	0.08406	0.08365	+41
91	11.920	0.08389	0.08344	+45
89	11.918 (?)	0.08391 (?)	0.08323	+68
85.4	12.021 (?)	(0.08341) (?)	0.08285	+56
80.35	12.082			

<sup>24</sup> Richards and Wadsworth, 3rd, *THIS JOURNAL*, **38**, 221 (1916),

<sup>25</sup> Richards and Daniels, Ref. 4.

ture was 12% and the density of the solid crystals 12.021. Since, as will be shown, the percentage 14.6 of mercury is probably less than the truth, this value is probably also somewhat too small. The fourth column gives values calculated on the assumption that no volume change occurred on amalgamation, and the last column indicates the extent of the expansion on amalgamation.

These results cannot be considered as very satisfactory; probably protracted investigation would be necessary to obtain exact values. Especially with amalgams poor in thallium the structure of the solid must vary with the speed of cooling; moreover, under the best conditions the first crystals which appear must come from an environment richer in thallium than the later ones. Hence the samples cannot be uniform in composition, and may well change in volume on aging. In spite of these disadvantages, however, two facts appear clearly from the figures; first, that a sharp break in the curve appears at the 95% point, (the density having been but slightly altered by the mercury until after 5% had been added), and secondly that marked expansion occurs as a rule on amalgamation. This latter fact was known before as regards liquid amalgams. We have extended it to the solid state. The results will be plotted later in comparison with the other properties.

### Hardness of Amalgams

Hardness is a characteristic physical property, but one which, dependent upon several quite distinct magnitudes, is not easily defined.<sup>26</sup> None of the methods for determining hardness has proved wholly satisfactory, because of the varying influence of the tendencies determining this property. The methods are as follows: (1) resistance to scratching or cutting; (2) resistance to indentation when stressed either gradually or suddenly; (3) elastic reaction; (4) plastic flow<sup>27</sup> (as regards soft materials).

With thallium amalgams the first method shows qualitatively a distinct increase in hardness with the addition of small quantities of mercury. This method, however, especially with soft materials, does not give satisfactory quantitative results. We have, therefore, depended primarily on the second method.

Our first tests were made by noting the diameter of the depression produced by the sudden impact of a small hammer with a hemispherical face. Originally it had been intended to measure the height of the rebound of this hammer, which was raised by the suction of a rubber bulb to the top of the glass tube where it was conveniently held, to be released,

<sup>26</sup> C. H. Desch, "Metallography," 1918, p. 243.

Walter Rosenhain, "Introduction to the Study of Physical Metallurgy," 1914, p. 218.

C. V. Boys, *Proc. Phys. Soc. (London)*, 30, 83 (1918).

<sup>27</sup> Kurnakov and Zemczuzny, *Jahrb. Radioakt.*, 11, 1 (1914).

when desired, by pressure upon the bulb. The rebound, however, was too small for accurate measurement. Accordingly the use of this instrument<sup>28</sup> was abandoned as regards its original intention and the diameters of the indentations were measured, thus using the apparatus in the sense of the second method of determining hardness. The hammer was very small and the depression in thallium only 1.0 mm. in diameter.

These preliminary results could not be translated into the usual hardness numbers, but since the energy of the falling hammer was always the same, they serve as a good index of relative hardness.

Three series of samples of thallium were used in this test; first the samples which had been for 4 months under saturated thallosulfate solution in the electrolytic cells; second, another set of similar samples which had been in the first place more slowly cooled during their original preparation; and third, 2 samples which had been carefully annealed for 18 hours at about 140°. Many measurements were made using both sides of the flattened samples. The annealing of the 97% and 93% samples was found to make no difference. Some of the samples, measured again after from 4 to 7 months, showed no significant change. A summary of average results is given in the following table.

TABLE III  
PRELIMINARY DETERMINATIONS OF HARDNESS  
(Shore scleroscope)

Wt.-% Tl	Average diameter of depression (in mm.)	
	First series	Second and third series
100	1.00	0.99
99	0.92	0.97
97	0.84	0.91
95	....	0.88
94	0.73	....
93	....	0.84
91	....	0.85
90	0.76	....
89	....	0.85
88	0.76	....

Evidently there is a marked increase in hardness up to about 6% of mercury, after which the hardness slowly diminishes in both series. The first series showed a greater increase with added mercury than the second. These results were qualitatively similar to those obtained by Pavlovitch,<sup>19</sup> but he found the maximum of hardness with 3% of mercury instead of with 6%.

The results, especially in view of the electromotive force and density measurements, were sufficiently interesting to warrant a more careful study. Accordingly, a more searching test of hardness was made by the

<sup>28</sup> The Shore scleroscope, dependent on elastic reaction.

Brinell method.<sup>29</sup> This is the most highly developed and generally used method and consists in pressing a hardened steel ball under a measured load into the surface of the material to be tested and measuring the diameter of the circular indentation produced.

We are indebted to Professor Albert Sauveur for his kindness in lending us his Brinell apparatus and in acquainting us with some of its subtleties.

If  $H$  = hardness number,  $L$  = load in kilograms,  $A$  = area in sq. mm. of the concave surface of the indentation, and  $R$  = the radius of the ball in centimeters, then  $H = L \sqrt[5]{R/A}$ , approximately.

We used a ball 1 cm. in diameter; hence the formula becomes  $H = L/A$ .

When a constant load is used the small actual deviation<sup>30</sup> of  $H$  from a truly linear relation to  $L$  becomes unimportant. An upward flow of material around the compression ball, forming a ridge on the rim of the indentation, sometimes complicates the matter. In our experiments this was unimportant except in the case of pure thallium, where the flow was downward instead of upward. Another but less serious complication (the deformation of the steel ball under the load) was not sufficient to affect our results seriously, and since we always used loads of either 50 kg. or 100 kg. in each of these series, the relative values in either series were entirely uninfluenced by it.

Time enters to some extent into the question since the indentation does not immediately attain its full magnitude. Experiments showed, however, that, with our specimens, the depressions produced in 10 seconds and in 30 seconds were essentially identical; therefore the latter period, always used in our work, was doubtless sufficient.

For the Brinell test large samples of the amalgams prepared for density determinations were employed. The cylinders of metal were about 2.20 cm. in diameter and from 0.8 to 1.8 cm. in thickness. They were provided with smooth parallel faces. The variation in thickness of the cylinders had no effect upon the results. Each sample to be tested was placed on a movable steel plate resting upon a heavy steel column and was carefully levelled. Contact between the surfaces of the specimen and the ball having been adjusted, the pressure was applied (by a hydraulic testing machine) attaining in 7 seconds its maximum, which was maintained for exactly 30 seconds. The diameter of the indentation was measured with a micrometer microscope. The higher pressure could not be used with the softer samples, since 100 kg. pressed the ball so deeply into

<sup>29</sup> Brinell, Communications, présentées devant le congrès international des méthodes d'essais de matériaux de construction. Paris, 3, 83 (1900). *Baumaterialienkunde*, 1900, p. 276.

<sup>30</sup> C. Benedicks, "Recherches Physiques et Physico-Chimiques sur l'acier au Carbone," Upsala, 1914, p. 75.

R. P. Devries, "Comparison of Five Methods Used to Measure Hardness," *Bur. Standards Tech. Paper*, 11, (1912).

the mass of thallium that a collar holding the ball was forced into the metal. The results were calculated with the help of a table giving  $L/A$  for different loads and diameters.<sup>31</sup> The diameters of depressions produced in thallium (with 50 kg. load) varied only between 6.0 and 6.1. The hardest amalgam (95% thallium) under the same pressure gave diameters of depression varying from 3.48 to 3.55 mm. Under 100 kg. load the diameters with this sample varied from 4.75 to 4.91. Below are given the averages of many determinations obtained in this way. The disintegrated crystalline macrostructure interfered with accuracy in the case of the 89% amalgam and entirely prevented the determination of hardness when more mercury was present.

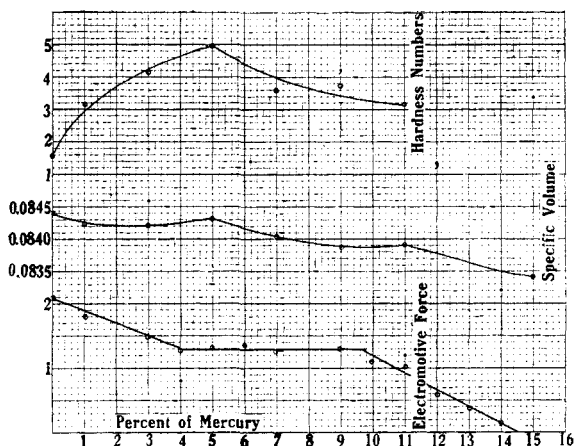


Fig. 3.—Hardness, specific volume, and e.m.f. of thallium amalgams.

The respective properties are plotted quantitatively as ordinates; the mercury contents of the several amalgams are plotted as abscissas. For hardness the usual Brinell numbers are used; the specific volumes are in cc. per gram; the unit of electromotive force is the millivolt.

TABLE IV  
HARDNESS OF SOLID THALLIUM AMALGAMS

Wt. % of Tl	Brinell hardness number	
	50 kg. load	100 kg. load
100	1.57	....
99	3.19	....
97	4.15	4.85
95	4.99	5.12
93	3.60	3.85
91	3.66	3.93
89	3.18	3.36

<sup>31</sup> Sauveur and Boylston, "Laboratory Experiments in Metallurgy," Cambridge, Mass., 1908, p. 54.



The hardness numbers show a marked maximum at 95% thallium under both 50 and 100 kg. load. The numbers with the different loads do not exactly agree. In general it has been observed in the past that with the Brinell test a heavier load is apt to give higher values for the hardness numbers. Possibly, moreover, the scale readings for the pressure were not exact, as the gage was not calibrated and the movement of the needle was small, since the gage was intended primarily for higher pressures. Nevertheless, the results are amply sufficient for our purpose. We were not concerned primarily with the absolute value of the Brinell numbers. Evidently the verdict of this method of testing hardness is essentially identical with that given by the improvised method with the Shore scleroscope.

The interpretation of the results is interesting. The hardness of a binary mixture depends not only upon the hardness of its constituents individually, but also upon the condition in which they exist in the mixture. Desch and Tammann have formulated rules which define some causes of the changing hardness of alloys.<sup>32</sup> Since mercury is much softer than thallium the mixtures should be softer than pure solid metal, supposing that no solution were formed. If a single solid solution is formed and no other complication exists the hardness of the mixtures should increase to a maximum with equimolecular proportions. Both of these suppositions are ruled out by our results, which show a maximum with 5% or 6% of mercury.

The appearance of a maximum at this place might be explained by assuming that the solid thallium molecule contains 15 to 20 atoms, but this explanation would demand that the second branch of the curve with increasing mercury should fall off much more rapidly in hardness than it actually does. A much more likely explanation, as will be seen, is that at 5% of mercury a new solid phase containing thallium in a different modification comes into existence. This is especially clear when the hardness numbers are compared with the results for electromotive force, density and melting point.

### Correlation of Results

Let us review the conclusions reached, in order to correlate them. The diagram (Fig. 1) will assist in the correlation. In Fig. 1 the more trustworthy values (except the linear freezing-point curve given in Fig. 2) are plotted in the same diagram. The horizontal axis represents the composition of the amalgams, and along the vertical axis are plotted first, the electromotive forces in millivolts, below, then the specific

<sup>32</sup> Desch, Ref. 26, p. 249.

Tammann, "Lehrbuch der Metallographie," 1914, p. 332. Cf. also Desch, *Trans. Faraday Soc.*, **10**, 251 and 254 (1915).

Kurnakov and Zemczuzny, *Z. anorg. Chem.*, **60**, 1 (1908).

volumes in cubic centimeters, and finally, above, the Brinell hardness numbers. All the properties unite in pointing to the existence of a solid solution of mercury in thallium up to 14.5%, which quantity appears to cause saturation. The linearity of the freezing-point (liquidus) curve had shown, as already stated, the absence of a definite compound at the melting temperature within this range. On the other hand, the three other curves in the diagram show striking inflections in the neighborhood of 5% of mercury, and two of them show inflections again with about 10% of mercury. What is the explanation of these inflections?

The electromotive force, representing free energy, is the most convenient starting place for the reasoning. Its curve (the lowest in the diagram) gives clear evidence of the existence at first of a single solid phase, which increased in mercury content until it contained about 4% of mercury. At this point, a second solid phase must have appeared, since the e.m.f. became constant.<sup>33</sup> This new solid phase existed in equilibrium with the first phase throughout the length of the horizontal portion of the curve down to 91% of thallium. At 96% the mixture must have consisted entirely of the first phase, while at 91% it must have consisted entirely of the second. As the thallium content decreased beyond this point, the second phase became manifest as a new crystalline form, and its composition changed until at 85.4% its potential became that of the 55% amalgam, showing that a liquid phase appeared at this point. Beyond this point the solid phase and the liquid phase must of course be in equilibrium until the solid disappears with less than 43.3% of thallium.<sup>34</sup>

The other properties confirm these conclusions. The data concerning hardness found in the present investigation likewise point to the solid solution of mercury in  $\alpha$ -thallium alone at 20° until about 5% of mercury has been added, and they are consistent with the assumption of the appearance of a second solid phase in the neighborhood of this point because here the hardness ceases to increase with added mercury.

The specific-volume curve reveals an increase of volume accompanying the mixing of mercury and thallium, which, as before, is an indication of the formation of a solid solution. The break in the continuity of the curve at 5% of mercury can only indicate a change in the number of phases at this point; and perhaps another change occurs also at about 11%. Thus it is essentially consistent with the two preceding curves. As al-

<sup>33</sup> The phase rule demands constancy of activity at constant pressure and temperature with 2 phases and 2 components.

<sup>34</sup> Richards and Daniels, Ref. 4. The appearance of the liquid phase between 86% and 85% was indicated also by the results of examination of the amalgam with a microscope, as an 85% amalgam was found to contain a small, but appreciable, quantity of liquid. A trace of liquid was found in freshly prepared 86% and 87% amalgams, but electromotive-force measurements showed that equilibrium had not here been established when the sample was examined.

ready stated, however, the experimental data concerning this property were not very satisfactory—more would be needed to make entirely sure of the slight breaks in the curve.

What now can be the second solid phase which exists in equilibrium with the first between the concentrations of about 4% or 5% and about 10% of mercury, and which afterward takes in more and more mercury until it finally dissolves?

A solid solution of mercury in  $\beta$ -thallium is the only substance which seems to be capable of producing effects consistent with the facts. The possible existence of this phase even at room temperatures under these conditions is easily shown. The transition temperature of the  $\alpha$  to the  $\beta$  enantiotropic form is, as has been said, greatly affected by impurities.

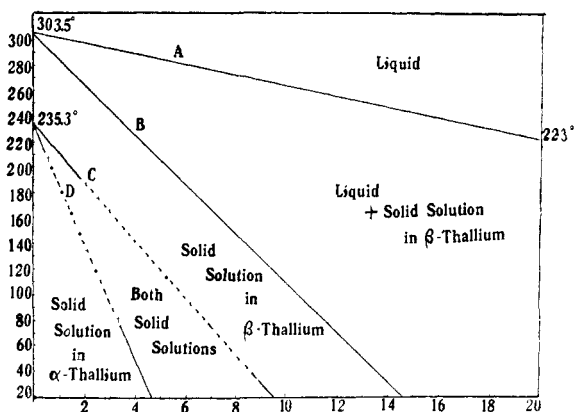


Fig. 4.—Phase diagram, showing freezing and melting temperatures, and analogously related transition limiting temperatures, in relation to mercury contents of concentrated thallium amalgams.

Pavlovitch showed that 1 atomic per cent. of mercury lowered it from 234.0° to 212°, at the same time decreasing markedly the intensity of the arrests in the cooling curves. With more mercury these arrests entirely disappeared, because of the gradual transition of the solid solutions. When in Fig. 4, the curve C, depicting change of transition temperature with concentration, is nevertheless extrapolated in a straight line (in analogy to the liquidus curve A in Fig. 4, which was shown to be very nearly linear), it appears that a 90.5% amalgam corresponds to transition at 20°. Hence any amalgam stable at 20°, poorer in thallium than about this amount, must contain only the  $\beta$  form of this metal. This is probably the new solid solution which appeared as the well-marked crystals of near-cubic form already mentioned. Evidently the solid amalgam in equilibrium with any liquid amalgam must be this  $\beta$  solid solution.

Along and immediately to the left of this curve C, the solid solution of mercury in  $\beta$ -thallium must be mixed and in equilibrium with the solid solution of  $\alpha$ -thallium,<sup>35</sup> which latter solution must, saturated as it is, be richer in thallium than the former. As the total percentage of mercury is diminished (between 10% and 5%) at any one temperature, the proportion of  $\alpha$ -thallium must increase, until the mercury present corresponds to the exact saturation point at 20° of the  $\alpha$ -amalgam (about 5% of mercury). At this point, with further decrease in mercury, the  $\beta$  phase will entirely disappear. The curve D represents this latter dividing line.

Thus, five fields are established in the thermal equilibrium diagram, each of which is duly labeled on the accompanying graph. This explanation seems to elucidate adequately all the widely diverse phenomena. Evidently the metals expand on adding mercury to form the  $\alpha$  solid solution, but no great change of volume of the constituents occurs when additional mercury gradually changes the  $\alpha$  into the  $\beta$  modification. Hence occurs the break in the specific volume curve at 95% thallium. Evidently, too, both solid solutions are harder than pure thallium, the  $\alpha$  solid solution being somewhat the harder of the two. That the new phase is a solid solution in  $\beta$ -thallium rather than a compound (such as  $Tl_7Hg$  or  $Tl_6Hg$ ) is probable, not only because a compound of this kind is *per se* unlikely, but also because it should have a lower potential than a solid solution in  $\alpha$ -thallium containing the same amount of mercury, whereas in fact the new phase, although containing much more mercury than the original  $\alpha$  phase, nevertheless is in equilibrium with it.

If the line in Fig. 3 which represents the potentials of amalgams constituting the second phase (containing presumably  $\beta$ -thallium) is produced to meet the electromotive-force axis at a composition of 100% thallium, it should give approximately the potential of pure supercooled  $\beta$ -thallium against a 55% thallium amalgam at 20°. The result obtained by this extrapolation is 3.8 millivolts, while the potential of pure compact  $\alpha$ -thallium against a similar amalgam has been found to be 2.1 millivolts. The difference between these values (1.7 millivolts) should be approximately the difference of potential between the two modifications of thallium at 20°. On account of the uncertainty of the extrapolation, the result cannot be regarded as accurate; but it should, at least, indicate the order of magnitude of the quantity. From this it may be calculated that at 20° the free energy content of supercooled  $\beta$ -thallium would be nearly 40 calories per gram atom higher than that of the compact  $\alpha$ -modification. This difference is nearly three times that found for spongy thallium, which could not, therefore, have been metastable  $\beta$ -thallium.

As already hinted, the nature of the case clearly prohibits great exact-

<sup>35</sup> Roozeboom has shown such a field as that included between the lines C and D in our diagram to be theoretically necessary. *Z. physik. Chem.*, 30, 417 (1899).

ness in the data for these solid amalgams. None of them could have been perfectly homogeneous, since the portion which first separated on cooling must have been richer in thallium than that which followed. The electromotive force would indicate the surface conditions, which might not represent the true average. The hardness, and especially the density, probably represent a fairer average of the whole mass, but even these latter phenomena may be much influenced by speed of cooling, which might affect not only the magnitude but also the position of the maxima of the curves. Possibly to such causes may be ascribed the difference in detail between our results for hardness and those of Pavlovitch, which nevertheless qualitatively agree with ours. More satisfactory results might be obtained by quenching the amalgams suddenly in very cold oil. For this extension of the work, time has not yet been found. We hope to continue the study later.

Similar considerations lead to the belief that the percentage of mercury, 14.5%, indicated for the saturation point of solid  $\beta$ -thallium at 20° may be less than the true value. Probably crystals separated from a large mass of saturated liquid amalgam immediately in the neighborhood of 20° would contain somewhat more than 15% of mercury, even if all the superficially adhering liquid could be removed.

In spite of these inherent experimental difficulties of the problem, which would not be easy wholly to eliminate, it seems probable that the picture here presented of the equilibria between mercury and large concentrations of thallium represents the essential characteristics of these equilibria, and that later investigations are likely to affect the outcome only in minor details.

We are indebted to generously granted funds from the Carnegie Institution of Washington as well as from an anonymous benefactor of the University for most of the apparatus and thallium employed.

### Summary

1. Pure thallium in compact form is definitely shown to possess at 20° an electrode potential 2.1 millivolts higher than saturated thallium amalgam. When immersed in a solution normal in thallos ions and connected with a normal calomel electrode, the total potential 0.6192 volt is indicated at 25°. The potential of pure thallium is not influenced by quenching the metal, which is so soft that no important strain can exist in it.  $\alpha$ -Thallium is the only phase of the pure metal stable at room temperatures.

2. Finely divided electrolytic thallium sponge gives a potential 0.6 millivolts higher than the compact fused form. The difference is probably due to the fine state of division, and disappears on long standing. The

difference of potential shown by  $\beta$ -thallium (if it could exist at ordinary temperatures) would probably be nearly three times as great.

3. Solid thallium amalgams may be made having potentials anywhere between that of pure thallium and the 2-phase amalgam. As mercury is added the potential decreases at first, then remains constant (between about 4% and 10% of mercury) and later decreases again until at about 15% of mercury the liquid phase becomes permanent at 20°. Crystals of solid amalgam separated centrifugally from the liquid containing more mercury showed as much as 20% of mercury, but some of this was undoubtedly adhering mother liquor.

4. The densities of solid thallium amalgams indicate an increase in volume of thallium on amalgamation. The corresponding curve shows a slight inflection at about 5% of mercury.

5. The hardness of solid thallium amalgams increases with added mercury until about 5% is present when it begins slowly to diminish.

6. From these phenomena it is inferred that  $\alpha$ -thallium dissolves mercury, increasing in hardness and volume up to about 5% of mercury. When more mercury is added, another solid phase of about the same hardness and volume, but containing more mercury, appears. These two phases appear to exist mixed together in equilibrium, over the range from about 5% to 10% of mercury at 20°. With more than about 10% of mercury the  $\alpha$ -thallium solid solution ceases to exist and the other phase continues to dissolve mercury in solid solution until it is saturated (with perhaps 15% of mercury). The other solid phase is probably a solid solution of mercury in  $\beta$ -thallium, which appears in definite crystalline form, making the amalgam friable after the admixture of  $\alpha$ -thallium has been eliminated.  $\beta$ -Thallium can exist at ordinary temperatures only in the presence of much mercury, but it is always the form present in equilibrium with the liquid amalgam.

7. Pure thallium is found to have a melting point of 303.5° and a transition point of 235.3°.

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