

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE DETERMINATION OF THORIUM IN MONAZITE SAND BY AN EMANATION METHOD.

By HOMER H. HELMICK.

Received March 21, 1921.

Historical.

In a recent paper,¹ Cartledge described an "emanation method" for the determination of thorium in monazite sand which was based on the facts: (1) thorium is the first member of the series of radioactive elements now known as the Thorium Series; (2) one of the members of the series, thorium emanation, is a gas. As a further basis for his method, he assumed: (1) on account of the great age of monazite, the elements of the thorium series have reached "radioactive equilibrium," (2) in an acid solution of monazite sand, the emanation is in such a condition of availability that it can be practically completely swept out by bubbling air through the cold solution. In our work on this problem, we have accepted the same facts and made the same assumptions.

Cartledge states that his method "by a triplicate analysis will give the thorium content within 1.5% of its true value," and pointed out that the inability of the method to give results of a higher degree of accuracy was probably due to the adsorption of thorium X by the undissolved material in the final solution, by the filter paper employed in the process of making the solution, and on the walls of the vessels used. Assuming that he was correct as to the sources of error, it was obvious that a much greater degree of accuracy could be obtained if a method could be perfected which would produce a complete solution of the sand without filtration and which would require the use of but one vessel. A thorough study of this problem led to a very satisfactory solution.

Proposed Method and Apparatus.

The method developed in this paper involves the following experimental steps: (1) preparation of the sample, (2) fusion, (3) solution of the melt, (4) transfer to solution vessel, (5) measurement of the ionization due to the sample. The preliminary investigation of each step will be recounted in order.

(a) **Preparation of the Sample.**—No difficulty was experienced in connection with this step, the same method being used throughout the experiments and in the final method. The sample was simply weighed out from a quantity of well-mixed, finely divided and dried monazite sand. Details are given under the description of the final method in the latter part of this paper.

¹ Cartledge, *THIS JOURNAL*, 41, 40 (1919).

(b) **Fusion.**—It occurred to us that a fusion of monazite sand with a suitable flux might prove a satisfactory substitute for the acidified water solution used by Cartledge, inasmuch as a fusion would eliminate loss of thorium X through filtrations and use of several vessels. Fusions were therefore made of monazite sand with (1) potassium hydrogen sulfate, (2) equal parts sodium carbonate and potassium carbonate, (3) anhydrous metaphosphoric acid. We were unable to sweep any emanation out of the potassium hydrogen sulfate melt, so it was eliminated from further consideration. The alkali carbonate melt was also abandoned because of the considerable percentage of sand remaining undecomposed, the violent effervescence, and the high temperature necessary. The fusion with anhydrous metaphosphoric acid appeared most promising, proceeding fairly quietly at about 700° , giving a melt only moderately viscous and leaving very little material undecomposed. Many experiments in our later work showed that this small amount of undecomposed material, chiefly silica and ilmenite, was the probable cause of disturbing effects on account of adsorption of thorium X. This difficulty was overcome by the addition of potassium hydrogen fluoride and metaphosphoric acid during the fusion in such a way that hydrogen fluoride was produced in the fused mass at a high temperature as well as practically continuously for some time, these conditions being found necessary for the removal of the objectionable compounds of silicon and titanium in the form of volatile fluorides. The detailed procedure is given in the latter part of this paper.

(c) **Solution of the Product of the Fusion.**—Our original plan had been to sweep the emanation directly out of the fused mass by bubbling air through it; but we were unable to find a vessel which would be inexpensive and at the same time both withstand the action of the hot fused material and resist deformation by pressure necessary to force air through the fused mass. It seemed that a platinum vessel would be necessary; but at this point a consideration of the chemical nature of monazite sand and the appearance of the cold metaphosphoric acid melt prompted us to attempt to dissolve it in water. This was found possible but extremely slow. To speed up solution a solvent was needed which had a high boiling point. Ordinary orthophosphoric acid immediately suggested itself, and experiment showed that our fusion of monazite sand could be fairly rapidly dissolved in 80% orthophosphoric acid at $240\text{--}250^{\circ}$ in a platinum crucible, the product consisting of a slightly viscous liquid, easily poured, and the crucible being readily washed out clean with water. Subsequent addition of a small amount of water with stirring produced a practically complete solution. Thus, by fusing monazite sand with metaphosphoric acid and potassium hydrogen fluoride in a platinum crucible, then heating and stirring the resultant mass with 80% orthophosphoric acid, and finally

adding water, we achieved our original goal of a complete solution (without filtration) in a single vessel. It remained to be seen whether the emanation measurements would justify our expectations of increased accuracy.

(d) **Transfer to the Solution Vessel.**—It would have been ideal if the solution of monazite sand made in a single vessel, as outlined above, could have been left in that vessel during the emanation measurements. We found, however, that this was impracticable on account of the cost of a platinum vessel of the necessary size. We decided, therefore, to transfer the solution as finally produced in a platinum crucible of moderate size to a glass vessel specially designed for the emanation withdrawal. Results have shown that this can be done at a negligible sacrifice of accuracy. Throughout this paper this special glass vessel is called the "solution vessel," and is shown diagrammatically in Fig. 1. It is important that this vessel be made of good glass and have a thin bottom to enable the hot solution (which becomes viscous on cooling) to be poured in without danger; that it be tall and narrow to give maximum deemanation by the stream of air bubbles; that it have ground-glass connections to prevent leakage and to insure constant length and volume of air line, as well as constant depth of air inlets below the surface of the solution; that it have a trap to prevent mechanical carriage of solution droplets into the ionization chamber; and that the bottom of the stopper be so high above the surface of the solution that only a negligible portion of the solution can be thrown against it by the bursting bubbles. Our experience also showed the most efficient air inlet jets to be those directed upward. The details of the technique used in transferring the hot solution from the platinum crucible to this glass vessel are given in the complete description of the method in the latter part of this paper.

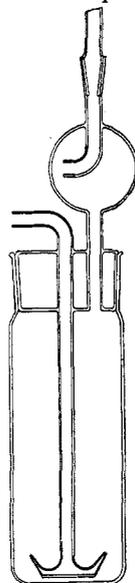


Fig. 1.—Solution vessel ($\frac{1}{2}$ actual dimensions).

(e) **Measuring Apparatus.**—We have used, with the changes and additions described below, the electroscope and accessories set up by Cartledge. A full description is given in his paper mentioned above, and we will therefore describe only the new parts.

Insulation Protector.—In the measuring apparatus as set up by Cartledge it was necessary to dry the stream of air after it had bubbled through the monazite solution before it entered the ionization chamber, in order to prevent the formation of a conducting film of moisture on the amber insulator separating the charged system from the grounded parts of the electroscope and ionization chamber. Cartledge dried the air stream

by means of a tube filled with granular calcium chloride. We examined the effects on the measurements of, respectively (1) this ordinary calcium chloride tube, (2) a much longer tube held horizontally with only the lower

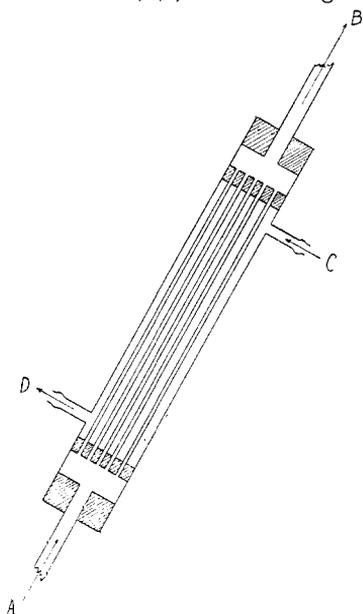


Fig. 2.—Multiple condenser.

A—Air inlet; B—Air outlet; C—Water inlet; D—Water outlet.

half filled with granular calcium chloride, (3) a multiple condenser consisting of many short, small-bore condensers combined in parallel and cooled with running tap water (see Fig. 2), (4) an ordinary short condenser filled with glass beads. None of these driers was entirely satisfactory because of either formation of moist surfaces which apparently adsorbed some emanation, or changes in area of cross-section of air line on account of deposition of water in interstices between granules of drying agent or in interstices between beads, or in small tubes. Since it thus appeared extremely doubtful whether the air stream could be dried without undesirable effects, we abandoned all attempts to do so and directed our attention to direct protection of the insulator.

An arrangement was accordingly devised whereby the insulator was directly protected by calcium chloride. The modification of the apparatus is shown in Fig. 3. The air gap between the rod R and the amber A_2 constitutes a better resistance than amber itself. Circulation or diffusion of air through this gap must be slight, and whatever air does reach the amber insulator A_1 is thoroughly dried by the calcium chloride in the wire-gauze basket B. Determinations made with this modification of the apparatus were much more satisfactory in every way than those made when the air was dried before entering the ionization chamber. There were, however, the following objectionable features: (1) the calcium chloride basket had to be taken out and refilled frequently, (2) the capacity of the electroscope seemed to change very slowly and very slightly during a determination, probably on account of the gradual wetting of part of the calcium chloride (mainly near the air gap), (3) uncontrollable and irregular effects due to minute quantities of emanation getting into the insulator chamber (in this article, by insulator chamber we mean the chamber fixed between the electroscope proper and the ionization chamber in this modification of the apparatus). In the apparatus which we have finally adopted, these

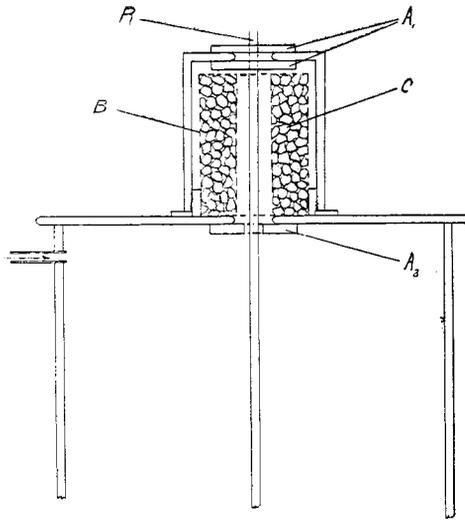


Fig. 3.—Insulator protection (first form).

R—Rod to electroscope; *A*₁—Amber insulator; *B*—Wire basket; *C*—Calcium chloride; *A*₂—Amber plug.

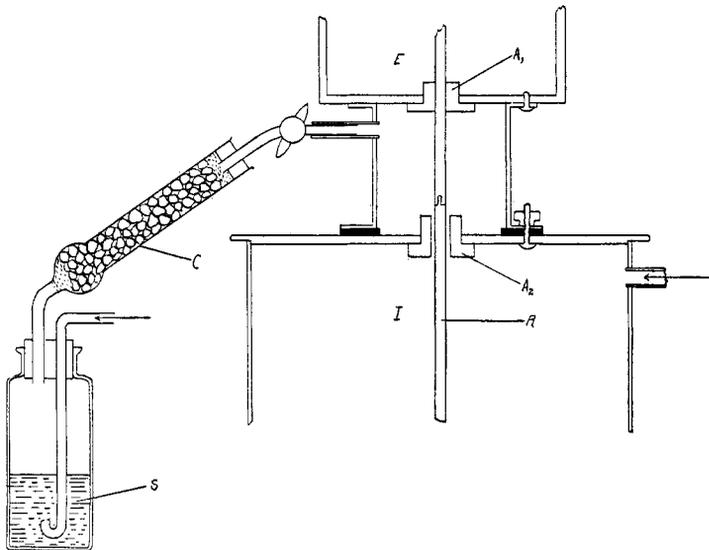


Fig. 4.—The insulator protection.

E—Electroscope; *I*—Ionization chamber; *A*—Amber insulator; *A*₂—Amber plug; *R*—Rod (brass); *S*—CaCl₂ solution (sat.); *C*—Calcium chloride tube.

objectionable features are entirely eliminated by the use of the insulator protector shown in Fig. 4. Outside air is drawn, by the suction from the main "line," very slowly through calcium chloride solution *S*, thence through calcium chloride tube *C*, then through the insulator chamber, and finally out through the air gap. The insulator is thus kept constantly in an atmosphere of dry air. This protector functions perfectly, is extremely simple, and requires practically no attention.

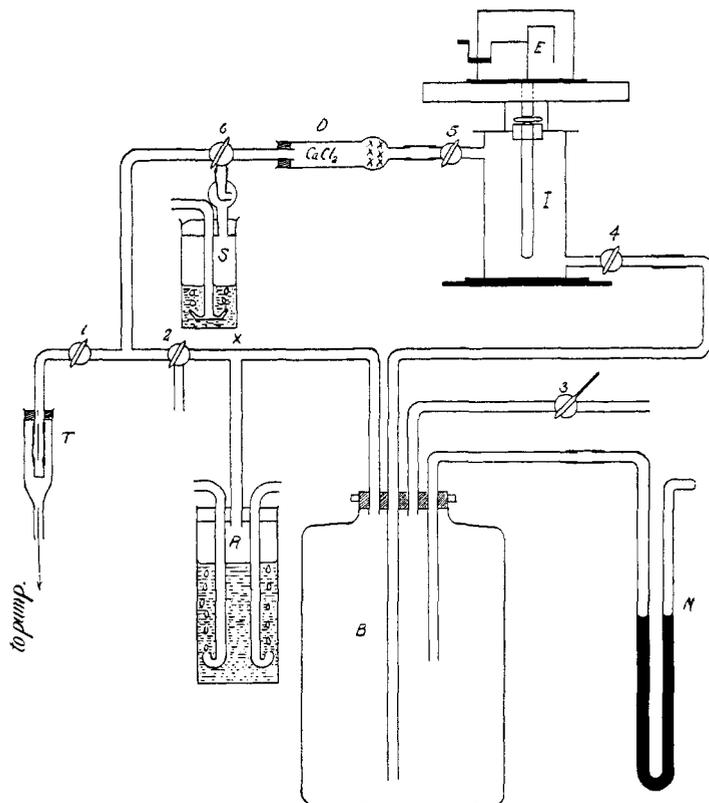


Fig. 5.—Diagram of set-up for emanation measurements.

E—Electroscope; *I*—Ionization chamber; *D*—Drying tube; *S*—Solution vessel; *M*—Manometer; *R*—Pressure regulator.

Pressure Regulator and Optimum Pressure Gradient.—Our method depends on comparing the rate of discharge of an electroscopical assembly by the emanation from a solution of the "unknown" sample with the rate produced by the emanation from a standard solution. In order that these rates may be directly comparable, it is necessary that the speed with which the emanation is drawn from solution to ionization chamber be the same,

within narrow limits, in both cases. Therefore a constant pressure gradient must be maintained along the suction line. This we have done

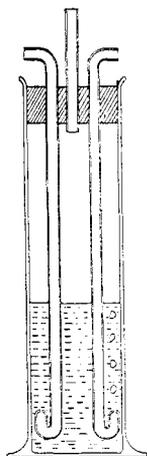


Fig. 6.—Pressure regulator.

by introducing a short branch from a point in the main line (farther from the solution than the ionization chamber) to a pressure regulator. Its relation to the rest of the setup is shown in Fig. 5. For a detailed drawing of the piece, see Fig. 6. Although the drawings show but 2 air inlets, the regulator actually used had 7, all admitting air under almost the same pressure conditions. The liquid used in the regulator is water, and adjustment to desired functioning pressure is attained by adding or subtracting water.

It is desirable, of course, to operate at that pressure at which the pressure coefficient of the rate of discharge of the electroscope is a minimum. A solution of monazite was therefore placed in the apparatus and the rate of discharge of the electroscope determined through the range of practical working pressures (our manometer readings). The results were plotted, the electroscopic readings being taken as ordinates and the pressure (manometer) readings as abscissas. The curve, Fig. 7, shows that the pressure coefficient of the rate of discharge of the electroscope is (for our apparatus) zero when the manometer reading is 11.5 cm. (of olive oil). (For the relation of the manometer to the remainder of the apparatus see Fig. 5.) By working at this pressure we therefore practically eliminated all error due to small pressure variations, attaining at the same time, as the curve shows, the extremely desirable effect of the maximum rate of discharge attainable. Thus, greater accuracy and maximum speed were attained.

Detailed Procedure.

The Sample.—About 50 g. of the well-mixed monazite sand is weighed out and ground to pass

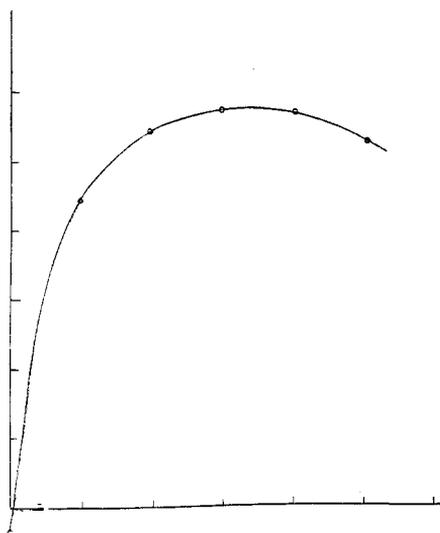


Fig. 7.—Pressure-discharge curve.

through a sieve with 40 wires per cm. It is then thoroughly mixed, placed in a weighing bottle, and dried to constant weight at 115–120°. For a determination a 2.0g. sample is weighed out to within 0.001 g.

The Fusion.—The sample is well mixed, by pouring back and forth between sheets of glazed paper, with 5 g. of potassium hydrogen fluoride and 5 g. of anhydrous (recently fused) metaphosphoric acid. The mixture is placed in a 35cc. platinum crucible and brought slowly to the highest temperature of the Meker burner, and heated until no further reaction is apparent. With continued heating, 5 g. more of the metaphosphoric acid is added in small portions, the reaction being allowed to come to completion each time before another portion is added. After the last of the metaphosphoric acid has been added, the mass is allowed to cool, the crucible being rotated in such a way that, when cool, the material is distributed as evenly as possible over the surface of the lower half of the inside of the crucible. The cooled mass is practically transparent and is colorless, and glasslike.

Solution of the Melt.—After allowing the fused mass to cool, 20 cc. of 80% orthophosphoric acid is added to the crucible, which is then placed in an air-bath where it is heated to 250–255° and maintained at that temperature for 3 hours. During that time it is stirred by a platinum wire stirrer attached to a motor. The liquid resulting from this treatment is, at 200–250°, about as viscous as light oil.

Transfer to Solution Vessel.—The solution vessel is suspended, to about $\frac{1}{3}$ its depth, in a bath of conc. sulfuric acid at 190–200°. The stirrer is lifted just above the liquid in the crucible and rotated for a few seconds to free it of most of the liquid adhering to it. Then the liquid is quickly poured out of the crucible into the solution vessel. The latter is now taken out of the hot bath, placed on an asbestos board, and allowed to cool. Twenty cc. of water is run into the crucible, the liquid stirred vigorously for a minute or two and the washings poured into the cooled solution vessel. This operation is repeated with a second 20 cc. of water. Any heavy particles of undecomposed sand and occasionally a little ilmenite still remaining in the crucible are then washed into the solution vessel by using 5 cc. of water blown from a small wash-bottle holding just that amount. The mixture in the solution vessel is now rapidly stirred for at least 15 minutes. The same stirrer is used throughout the experiment. Finally the stirrer is lifted just above the liquid, rotated for a few seconds, and washed with 5 cc. of water from the small wash-bottle, the wash-water being caught in the solution vessel. Water is then carefully added to bring the volume of the solution up to 75 cc. as indicated by a line etched on the vessel. The stopper carrying the inlet tube is then fitted into the solution vessel. A little desiccator-grease is used to insure an air-tight joint.

The Measurement.—(For diagram of the apparatus see Fig. 5. The calcium chloride tube D is omitted in our final apparatus.) Measurements are made on 3 different solutions, the blank, the standard, and the "unknown."

The blank is run first. This solution may be used for an indefinite number of determinations. It is prepared according to the method for an "unknown" sample as above, except that the monazite sand is omitted. The solution bottle containing the blank is attached to the line in place of Bottle S shown in the diagram. The pump is started, Cocks 1, 3, 4 and 5 are opened wide, Cock 6 is opened wide between S and I, and then Cock 2 is opened between Cock 1 and X. The cock admitting dry air to the insulation chamber (shown in Fig. 4 only) is then opened until the inlet tube through the calcium chloride solution is allowing bubbles to pass in slowly, at the rate of about 10 per minute. Cock 3 is then gradually closed until half the inlets of the pressure regulator are admitting air. We have the regulator so adjusted that the manometer, M, which contains olive-oil, then shows a difference between the pressure in Bottle B and the atmospheric pressure of 11.5 cm. This is best for the reasons given above. Under these conditions air bubbles through the monazite solution at a rate sufficient to stir it rapidly and thoroughly. The time of discharge of the electroscope is then noted.

The Standard.—Cock 2 is turned so as to admit air through the side-tube and close the line to the pump. The standard solution is substituted for the blank. Cock 6 is opened between the solution and the pump and a moderate stream of air drawn through the solution for 6 minutes to rid it of radium emanation. The cocks are then adjusted exactly as they were for the blank and readings of the time of discharge taken until constant within the allowable limits for the degree of accuracy desired.

The Unknown.—Exactly the same procedure is followed as for the standard.

The ionization chamber is then evacuated for $\frac{1}{2}$ hour and the pump stopped.

Calculation of Results.—The percentage of thorium in the "unknown" may be calculated from the equation,

$$X = A \frac{T_s(T_b - T_u)}{T_u(T_b - T_s)},$$

where X is the percentage of thorium in the unknown, A the percentage of thorium in the standard, T_s the time of discharge of the electroscope by the standard, T_u the time of discharge of the electroscope by the unknown, and T_b the time of discharge of the electroscope by the blank. The percentage of thorium in the standard is determined by gravimetric analysis.

Results.

In the table below are given the results of a series of determinations, showing the separate results of the triplicate analyses of each lot by our emanation method, and the average result from the triplicate analyses of each lot by the gravimetric method of Carney and Campbell. The agreement of the results obtained by our emanation method with those obtained by the gravimetric method is very close.

TABLE OF RESULTS.

Lot no.	Source of monazite.	ThO ₂ emanation method. %.	Av. ThO ₂ emanation method. %.	Av. ThO ₂ gravimetric method. %.
20	India	8.71
		8.75	8.74	8.76
		8.76
		8.69
22	India	8.70	8.70	8.70
		8.72
		8.49
23	India	8.53	8.51	8.50
		8.53
		8.66
26	India	8.67	8.69	8.69
		8.73
		8.73
28	India	8.77	8.77	8.76
		8.80
		8.67
30	India	8.68	8.70	8.70
		8.74
		6.37
A	Brazil	6.38	6.38	6.38
		6.40
		4.37
B	Carolina	4.37	4.39	4.40
		4.43

Suggested Further Improvement.

The transfer of the viscous solution of the fused mass in 80% orthophosphoric acid from the platinum crucible to the glass "solution vessel" should be eliminated for the following reasons: (1) it is difficult to carry out successfully, even after much practice; (2) it consumes time, requiring about $\frac{1}{2}$ hour; (3) probable loss of some thorium X on the surface of the platinum and practically inseparable from it even by washing a great number of times. These objectionable features can easily be avoided by the use of a platinum vessel of such size and shape as will allow the final electroscopic determination to be made with the solution in it instead of in the special glass vessel we have used. We suggest, therefore,

that if a great many analyses are to be made, a special platinum vessel be used. Fig. 8 shows the dimensions which we believe such a vessel should have, and a method of connecting the vessel to the line of apparatus.

Comparison of Methods.

In order that a method of quantitative determination may be useful, it must give results sufficiently accurate for the purpose at hand. Our method does this. In addition to accuracy, the next most desirable feature in a method is speed. In this respect our method is far superior to any other; a complete analysis by any gravimetric method requires approximately 20 hours, whereas our method requires somewhat less than 8 hours. The technique involved is extremely simple except when the transfer from platinum crucible to glass vessel is made, and, as has been suggested above, that would probably not be done if a great many determinations were to be made.

The disadvantages inherent in the emanation method as compared with gravimetric methods are (1) the apparatus required is somewhat costly; (2) the electroscope must be attached to a support practically free from vibration; (3) the electroscopic determinations must be made in a room free from unusual radio disturbances. If a great many analyses were to be made, these disadvantages could be disregarded, since the saving in time attained by the use of this emanation method would soon more than compensate for the initial cost and for the inconvenience in installing and protecting the apparatus.

Summary.

The main sources of error in Cartledge's emanation method of determining thorium in monazite sand apparently were adsorption of thorium X by suspended matter in final solutions, by filters, and by walls of vessels used. We have avoided these by producing a complete solution of the sand without filtration and in a single vessel. This involves (a) fusion of the sand with metaphosphoric acid and potassium hydrogen fluoride; (b) solution of the resultant mass in hot 80% orthophosphoric acid. Other improvements made are (1) use of a highly efficient form of vessel to contain

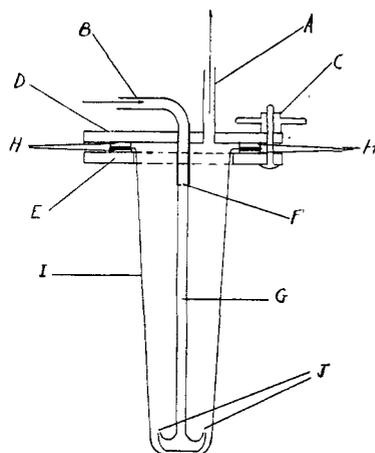


Fig. 8.—Platinum "solution vessel" and connections ($\frac{1}{2}$ actual dimensions).

A—Outlet tube (brass); B—Inlet tube (brass); C—Thumb-screws (3); D—Cover plate (brass); E—Brass circle; F—Cemented joint; G—Glass tube; H—Rubber washers; I—Platinum vessel; J—Jets (4).

the solution during deëmanation; use of an automatic regulator to maintain constant pressure in the ionization chamber during measurements; maintenance of optimum pressure gradient along air-current line through the measuring apparatus, thus assuring minimum error on account of pressure variations, and maximum speed of measurement; protection of the insulation of the electroscope by means of a current of dry air. Analyses by this method gave results agreeing very well with results obtained by gravimetric methods, and required much less time for each determination.

In concluding, the writer wishes to express his sincere appreciation of the valuable criticisms of Dr. Herbert N. McCoy at whose suggestion this research was taken up.

CHICAGO, ILL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE HEAT OF FORMATION OF SILVER IODIDE.

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Received March 29, 1921.

A discrepancy, amounting to 600 calories, exists between the determinations of the heat of formation of silver iodide as measured by Jones and Hartmann¹ using electrometric methods and the calorimetric determinations of Braune and Koref.² The values obtained are 14,565 and 15,100 calories respectively, so that the divergence represents a difference of some 4% which is much greater than would be anticipated from the reproducibility of either set of experimental measurements. Certain electrometric determinations by Taylor³ and Perrott, involving the iodides of silver, lead and cadmium, have shown agreement with the calorimetric data of Braune and Koref and favor the adoption of the higher value for the heat of formation of silver iodide.⁴

¹ Jones and Hartmann, *THIS JOURNAL*, **37**, 752 (1915).

² Braune and Koref, *Z. anorg. Chem.*, **87**, 175 (1914).

³ Taylor, *THIS JOURNAL*, **38**, 2295 (1916); Taylor and Perrott, *ibid.*, **43**, 484 (1921).

⁴ Since the communication of the present paper an article by O. Gerth has appeared in *Z. Elektrochem.*, **27**, 287 (1921), in which new electrometric measurements of the free energy and heat of formation of silver iodide have been made. By substituting a direct experimental method in place of a calculation of liquid junction potentials in the silver|silver iodide|iodine cells, Gerth has demonstrated that it is in the calculation of such liquid junction potentials that the discrepancy above mentioned has arisen. The value obtained by Gerth for the heat of formation of silver iodide is 15158 calories, in good agreement with the value of 15150 calories obtained by one of us (H. S. T.) at an earlier date. The present communication confirms the correctness of these results and of the earlier calorimetric measurements of Braune and Koref.