for the various temperatures, are calculated by the method suggested by Giauque and Wiebe. The entropy at $0°$ is found to be 44.04 or 43.72 Entropy Units per mole, depending upon whether the Tetrode or Lewis value of the chemical constant is used.

PITTSBURGH, PENNSYLVANIA

A RAPID METHOD FOR THE SEPARATION OF ALUMINUM AND BERYLLIUM

BY I. M. KOLTHOFF AND ERNEST B. SANDELL

From the voluminous literature on the subject of the separation of aluminum and beryllium it may be concluded that the estimation of these elements in the presence of each other is of great difficulty, and that there is no simple, satisfactory method for their accurate determination. An excellent summary of the older methods for the separation of aluminum and beryllium will be found in C. L. Parsons' "The Chemistry and Literature of Beryllium." H. T. S. Britton[1] concluded from an experimental study of the more important methods proposed that the only four which were capable of giving satisfactory results, if the details of the respective procedures were carefully adhered to, were the following. 1. Decomposition by boiling of sodium hydroxide solutions of aluminum and beryllium.[2] Sodium beryllate is hydrolytically decomposed, giving a precipitate of beryllium oxide; sodium aluminate remains in solution. 2. Parsons and Barnes' method.[3] Beryllium hydroxide is dissolved by hot sodium bicarbonate solution; aluminum hydroxide is not dissolved. 3. Method of Wunder and Wenger.[4] The oxides are fused with sodium carbonate and the residue is extracted with water. Aluminum goes into solution. 4. F. S. Havens'[5] ether–hydrochloric acid method. Beryllium chloride alone is soluble in a mixture of hydrochloric acid and ether saturated with hydrogen chloride. Of these methods, Britton considered 1 and 4 to be the most satisfactory. For discussion and criticism of these methods, see Hellmut Fischer[6] and also L. Moser and M. Niessner.[7] A method which appears to be superior to any hitherto proposed has recently

[1] Britton, *Analyst*, **46**, 359, 437 (1921); **47**, 50 (1922).

[2] R. Gmelin and Schaffgotsch, *Pogg. Ann.*, **83**, 175 (1843); Penfield and Harper, *Am. J. Sci.*, (iii), **32**, 110 (1886); Zimmermann, *Z. anal. Chem.*, **27**, 61 (1888).

[3] Parsons and Barnes, THIS JOURNAL, **28**, 1589 (1906).

[4] Wunder and Wenger, *Z. anal. Chem.*, **51**, 470 (1912).

[5] Havens, *Z. anorg. Chem.*, **16**, 15 (1898).

[6] Fischer, "Wissenschaftliche Veröffentlichungen aus dem Siemens–Konzern," **1926**, Band V, Heft 2, p. 99.

[7] Moser and Niessner, *Monatsh.*, **48**, 113 (1927).

been described by L. Moser and M. Niessner,[7] in which aluminum alone is precipitated by a saturated solution of ammonium acetate containing 3% of tannin. The tannin must be destroyed in the filtrate before the beryllium can be precipitated. The method which is described below is simpler and more rapid.

R. Berg[8] has recently introduced the use of o-hydroxyquinoline (called "oxine" by F. L. Hahn)[9] for the separation and determination of various metals. According to our own experience, this new reagent is very useful in many different analytical procedures.

In a solution weakly acid with acetic acid and containing ammonium acetate, aluminum is precipitated quantitatively by a solution of oxine as $(C_9H_6ON)_3Al$. Beryllium is not precipitated under these conditions. On the addition of ammonium hydroxide to the filtrate from the aluminum precipitation, beryllium gives a precipitate of indefinite composition which appears to be beryllium hydroxide containing adsorbed oxine. Addition of oxine and ammonium hydroxide to a solution of a beryllium salt containing sufficient sodium potassium tartrate to prevent precipitation of beryllium hydroxide gives a yellow precipitate, somewhat difficult to filter, which unfortunately cannot be used in the estimation of the element, both on account of its solubility and its variable composition.

The procedure adopted is based on the following facts. (a) From a weakly acid solution containing aluminum and beryllium, aluminum is quantitatively precipitated by the addition of an acetic acid solution of oxine and an excess of ammonium acetate. The precipitate of $(C_9H_6ON)_3$-Al is weighed after drying at 120–140°.

(b) In the filtrate from the aluminum precipitation beryllium hydroxide is precipitated by the addition of ammonia and ignited to the oxide.

Procedure

Reagent.—R. Berg,[8] F. L. Hahn[9] and I. M. Kolthoff[10] all worked with a 5% solution of oxine in 95% alcohol when precipitating aluminum. Kolthoff found the results with aluminum to be about 0.4% too low when thus precipitated. We confirmed these results and found the low values obtained to be due to the solubility of aluminum o-hydroxyquinoline in the warm dilute alcoholic solution from which it is precipitated. We therefore recommend that an acetic acid solution of oxine be used in the precipitation of aluminum and possibly also with other metals. Moreover, the acetic acid solution of the reagent has the added advantage over the alcoholic solution that it is more stable and may be kept for many weeks without change. The reagent is prepared by dissolving a

[8] Berg, *J. prakt. Chem.*, **115**, 178 (1927); *Z. anal. Chem.*, **70**, 341 (1927); **71**, 23 (1927).

[9] Hahn, *Z. anal. Chem.*, **71**, 122 (1927).

[10] I. M. Kolthoff, *Chem. Weekblad.*, **24**, 606 (1927).

sufficient amount of finely powdered o-hydroxyquinoline in 2 N acetic acid to form a 5% solution.   Ten cubic centimeters of reagent thus prepared are sufficient to precipitate one millimole of aluminum.[11]

Determination of Aluminum.—The solution of aluminum and beryllium salts (containing not more than 100 mg. of either oxide per 100 cc.) which should be only slightly acid is warmed to 50–60° and treated with an excess of the acetic acid solution of oxine.   A solution of 2 N ammonium acetate is slowly added until a permanent precipitate is obtained and then 20–25 cc. more of ammonium acetate is added to insure the complete precipitation of aluminum.   When the aluminum o-hydroxyquinoline has settled, the liquid is poured through a Jena glass or porcelain filter crucible (more convenient to use in this case than a Gooch crucible).   The precipitate is washed with cold water and dried at 120–140°.   It then has the composition $(C_9H_6ON)_3Al$ and contains 11.10% of Al_2O_3.

Determination of Beryllium.—The filtrate from the aluminum precipitation is heated nearly to boiling and ammonium hydroxide is cautiously added to the liquid until it smells faintly of ammonia.   The beryllium hydroxide thus precipitated is colored yellow or brown by adsorbed oxine.   It is filtered off and washed thoroughly with a hot dilute solution of ammonium acetate containing a few drops of ammonium hydroxide. The precipitate may be dried directly over a low flame and ignited (without the addition of oxalic acid) in a platinum crucible over a blast lamp.   The beryllium oxide thus obtained is somewhat more hygroscopic than the form ordinarily obtained by ignition of beryllium hydroxide precipitated in the absence of oxine and it must therefore be weighed quickly.   The single deflection method of weighing, as described by P. H. M.-P. Brinton[12] may be advantageously used.

Analytical Results

The standard solution of aluminum used was prepared by weighing out potassium alum obtained by recrystallization of a very pure product. The beryllium nitrate solution employed was standardized by careful gravimetric analyses according to the method of Parsons, the platinum crucibles used being reweighed after ignition.

In solutions containing only aluminum, or aluminum in the presence of alkali salts, results of a high degree of accuracy are obtained by the use of an acetic acid solution of o-hydroxyquinoline, as the following table shows.

TABLE I

RESULTS OF ANALYSES

Al_2O_3 taken, g.	Weight of oxine ppt., g.	Al_2O_3 found, g.	Error, g.
0.02691	0.2420	0.02686	−0.00005
.02691	.2424	.02691	.00000
.02691	.2422	.02688	− .00003
.02691	.2424	.02691	.00000
.02691	.2416	.02682	− .00009
.02691	.2431	.02698	+ .00007

[11] Most of the determinations were made with o-hydroxyquinoline obtained from the Amsterdamsche Superphosphaatfabrieken.   A good product—though rather expensive—is put on the market by the Eastman Kodak Company.

[12] Brinton, THIS JOURNAL, **41,** 1151 (1919).

The separation of aluminum and beryllium was carried out in volumes of about 200 cc. of original solution according to the directions given above.

TABLE II

SEPARATION OF ALUMINUM AND BERYLLIUM

Aluminum			Beryllium		
Al_2O_3 taken, g.	Al_2O_3 found, g.	Error, g.	BeO taken, g.	BeO found, g.	Error, g.
0.00834	0.00844	+0.00010	0.1854	0.1863	+0.0009
.02083	.02090	+ .00007	.1854	.1856	+ .0002
.02691	.02695	+ .00004	.2	. . .	. . .
.02691	.02700	+ .00009	.1	. . .	. . .
.02691	.02704	+ .00013	.1	. . .	. . .
.02691	.02688	− .00003	.0927	.0924	− .0003
.02691	.02706	+ .00015	.0927	.0924	− .0003
.1086	.1082	− .0004	.0927	.0929	+ .0002
.1086	.1084	− .0002	.0927	.0922	− .0005
.1086	.1084	− .0002	.0464	.0483	+ .0019
.1086	.1086	.0000	.0232	.0236	+ .0004
.1086	.1083	− .0003	.0464	.0469	+ .0005
.1628	.1620	− .0008	.0927	.0934	+ .0007

If ferric iron is present it will be precipitated with the aluminum. Two separations of beryllium from ferric iron were made. A solution containing 1 g. of ferric alum and 0.0927 g. of BeO in about 100 cc. was treated with an excess of oxine, as described in the aluminum precipitation, and the black ferric o-hydroxyquinoline was filtered off and beryllium determined in the filtrate in the usual way. The weights of beryllium oxide obtained were 0.0931 and 0.0937 g. The separation is therefore satisfactory.

From the table of results given above it will be seen that the weight of beryllium oxide found is a little high in most cases. This is partially to be ascribed to a slight solubility of aluminum o-hydroxyquinoline in water, which was found to be increased to some extent by beryllium salts. An excess of oxine will, however, reduce the solubility of the aluminum compound. Therefore in those cases where there is much beryllium and little aluminum present, it is advisable to add at least 50% of oxine in excess. In ordinary cases where aluminum, and not beryllium, preponderates, an excess of 10–20% of oxine is sufficient.

If the amount of beryllium is quite small, it is best to convert the oxide to the sulfate and weigh the latter. Anhydrous beryllium sulfate has already been proposed as a weighing form for beryllium by Taboury.[13] A few drops of sulfuric acid (1:1) are added to the oxide, and then the water and most of the excess sulfuric acid are evaporated off. The residue may be safely heated to constant weight at temperatures from 350 to 400°. Satisfactory results with known amounts of beryllium oxide have been obtained.

[13] Taboury, *Compt. rend.*, **159**, 180 (1913).

Summary

A simple and rapid method has been described for the separation of aluminum and beryllium by the use of an acetic acid solution of o-hydroxyquinoline. Beryllium is also separated from ferric iron by means of this reagent.

MINNEAPOLIS, MINNESOTA

A NEW DESIGN OF APPARATUS FOR THE MOVING BOUNDARY METHOD OF DETERMINING TRANSFERENCE NUMBERS[1]

BY EDGAR REYNOLDS SMITH[2]

During the past few years several designs of cells for the determination of transference numbers by the moving boundary method have been described.[3] In each of these, the boundary moves through a calibrated tube and the number of coulombs which pass through the circuit, while the boundary moves through a predetermined volume, is measured. The purpose of this article is to describe an apparatus which has two unique features. (a) A calibration of the measuring tube is not required. (b) After the boundary has traversed the length of the measuring tube, it can be returned to the starting point for a fresh determination. This operation can be repeated any number of times without changing the solutions.

Apparatus and Manipulation

The cell is shown in the figure. The boundary tube B (of approximately 0.3 cm. inside diameter), the electrode tube C and their connecting tube are filled with the solution to be measured. The tube H contains mercury and the remainder of the cell is filled completely with the indicator solution to a point well above the stopcock D. The method of forming the boundary, except for a slight modification, is the one described by MacInnes and Smith.[3a] In this modified cell the boundary tube B projects about 0.3 cm. into the indicator reservoir I and its opening is ground flat, thus presenting a true surface for contact with the plunger F. The latter is fitted with a rubber cap to which two small hooks are attached. Rubber bands stretched between these hooks and the glass projections J serve to hold the plunger firmly against the top of B before beginning the measurement. For precise work it would be safer to sub-

[1] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Associate Chemist, Bureau of Standards.

[3] (a) MacInnes and Smith, THIS JOURNAL, 45, 2246 (1923); (b) Smith and MacInnes, ibid., 46, 1398 (1924); (c) MacInnes and Brighton, ibid., 47, 994 (1925); (d) Smith and MacInnes, ibid., 47, 1009 (1925); (e) MacInnes, Cowperthwaite and Huang, ibid., 49, 1710 (1927).