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.

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

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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-

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[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).

stitute ground glass stoppers in place of the rubber stoppers on the closed side of the apparatus.

As soon as the electrical circuit is closed, the rubber bands are removed and, with stopcock E closed and D open, F is gently loosened. When the boundary appears in B, F is carefully raised to about a centimeter above the top of B. Stopcock D is then closed and E is opened. Just as the boundary reaches a mark m, a coulometer is connected into the circuit. After the boundary has moved through a suitable volume, depending on the deposit desired in the coulometer, mercury is slowly withdrawn from H into a weighing flask until the boundary has been raised slightly above m. When the boundary again crosses m, the coulometer is disconnected and at the same time a second coulometer can be connected into the circuit for a second measurement.

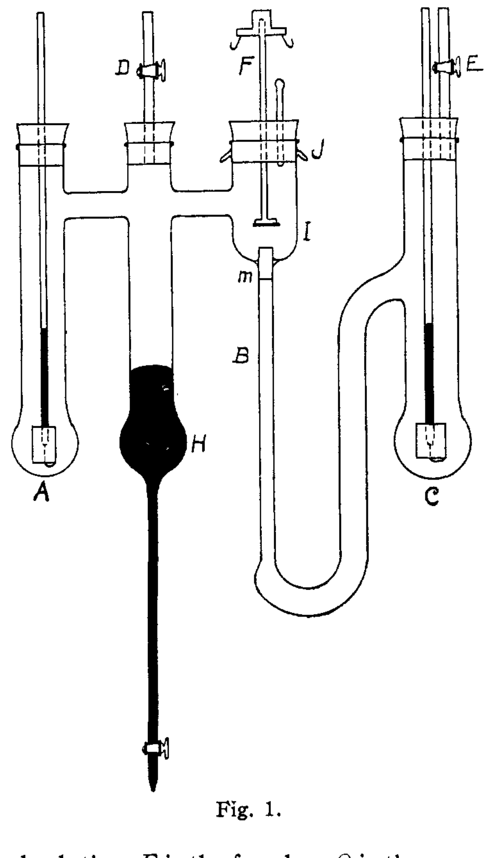

Fig. 1.

From the weight of mercury and of the deposit in the coulometer, the transference number is calculated by means of the equation[3d]

$$T = \frac{VF}{\phi Q} \pm \frac{\Delta v}{\phi} \qquad (1)$$

where V is the volume through which the boundary has moved (the observed weight of mercury divided by its density), ϕ is the equivalent volume of the measured solution, F is the faraday, Q is the number of coulombs passed and Δv is the correction[4] for the volume change per faraday due to the electrode reaction and to transference in the closed side of the cell.

Experimental Test

A preliminary experiment showed that the boundary could be raised any desired number of times without distortion provided the rate of withdrawal of the mercury was not fast enough to produce turbulence. An

[4] Lewis, THIS JOURNAL, 32, 862 (1910).

attempt to hold the boundary stationary at a definite position by withdrawing the mercury at exactly the rate of motion of the boundary was abandoned because of the constant attention required.

Since the object of this investigation was to test the practicability of the apparatus, a measurement of the cation transference number of 0.1 weight normal potassium chloride was performed with 0.065 weight normal lithium chloride for the indicator solution. This combination has been well investigated by other methods[3,ab,c,d] which give a value of 0.492, and it furnishes a reliable check on the present method. The anode was a piece of platinum gauze coated with silver and the cathode was the same with an additional coating of silver chloride. Dried salts of analytical reagent quality were used without further purification. The silver coulometer was of the porous cup type.

The coulometer was thrown into the circuit when the boundary reached m. After the boundary had moved through a volume of about 1 cc. it was raised and then allowed to continue down the tube through about 1.7 cc. It was then raised to a position slightly above the mark and when it again reached m the coulometer was disconnected. By this manipulation the motion of the boundary after having been raised is included. The weight of the mercury withdrawn was 36.65 g. and the silver deposited in the coulometer weighed 0.0588 g. From these weights the values of V/ϕ, F/Q and of T_K (uncorrected) were, respectively, 0.0002688, 1835 and 0.493. Since the anode side of the cell was closed, the correction ($\Delta v/\phi$ in equation 1) to be applied in this case is calculated as follows. Per faraday at the anode, 1 molecular weight of silver chloride is formed, 1 atomic weight of silver disappears and T_{Li} equivalents of lithium chloride are lost by migration. The accompanying volume change is an increase of approximately 14 cc. and the correction, which in this case is appreciable, amounts to 0.001 and must be subtracted. The corrected value of the transference number is therefore 0.492, identical with the value by other methods. However, the experiment was carried out at room temperature (22°) without the use of a thermostat, and the result obtained is not to be considered as an accurate determination of the transference number but merely as a satisfactory test of the apparatus.

Summary

A moving boundary cell in which the boundary may be returned to the starting point for a new measurement any number of times has been described. The measurements with this apparatus are independent of any tube calibration. The method consists in closing one side of the cell and withdrawing mercury from the closed side so as to oppose the motion of the boundary. The mercury withdrawn is weighed to obtain the volume through which the boundary has passed.

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