

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

RAPID ELECTROLYSIS WITHOUT ROTATING ELECTRODES

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Introduction

Within recent years various methods of "rapid electrolysis" for the estimation of metals have been developed and have become widely used. An extensive bibliography seems unnecessary, but it may be noted that Gooch and Medway¹ proposed rotation of the cathode; Exner² proposed rotation of the anode; Fischer³ showed that vigorous stirring of the electrolyte by any means achieved the desired result; and Frary⁴ utilized the effect of a magnetic field to stir the electrolyte. The present paper describes a simple glass apparatus in which stirring of the electrolyte is effected indirectly by a current of air, and with which results have been obtained, as rapid and as accurate as those afforded by the use of rotating electrodes.

Description of Apparatus

Preliminary experiments were carried out in a glass cylinder with a cathode of platinum gauze and an anode of coiled platinum wire, the electrolyte being stirred by a current of air bubbled through the liquid. The results were not altogether satisfactory, and it was obvious that the stirring was not uniform, and that the fine bubbles of gas liberated at the electrodes had a tendency to form a spray which was carried out of the cylinder by the air current, causing loss of the solution. Furthermore, there seemed to be the possibility, in some cases at least, of causing oxidation by exposing the cathode to the air.

After a number of trials the apparatus illustrated in Fig. 1 was developed, which has proved altogether satisfactory.⁵

It consists essentially of a tube of Pyrex glass (31 mm. in diameter) to which are sealed 3 glass "air lifts,"

¹ Gooch and Medway, *Am. J. Sci.*, [IV] **15**, 320 (1903).

² Exner, *THIS JOURNAL*, **25**, 896 (1903).

³ Fischer, *Z. angew. Chem.*, **20**, 138 (1907).

⁴ Frary, *Z. Elektrochem.*, **13**, 308 (1907).

⁵ This apparatus may be purchased from Messrs. Eimer and Amend, 205 Third Ave., New York City.

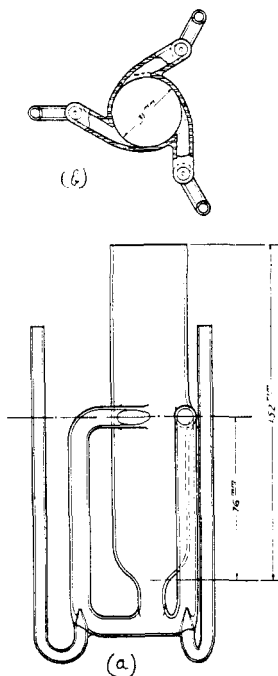


Fig. 1.

connecting in a single tube at the bottom, and entering symmetrically about half way up the wide tube, the upper seals being made tangentially. Fig. 1 (a) shows 1 of the 3 air lifts in detail, and Fig. 1 (b), which is a cross-section through the apparatus at the level of the upper entrance of the side tubes into the wide tube, illustrates the general plan.

If this apparatus is half filled with liquid and a current of air is forced (or drawn by suction) through the injectors, it is quite obvious that stirring is effected in two ways. In the first place, a continuous current of liquid is carried upward by the air lifts, causing vertical stirring; in the second, this liquid (with the air bubbles) is delivered into the wide tube in such a way as to cause rotational stirring. By suspending fine solid particles in the liquid it can be seen that the rotational stirring is very rapid, while the vertical movement is also considerable. Furthermore, the air bubbles are thrown centrifugally against the walls of the cell, so that no spray is carried out, even when a rapid air current is employed. In using the cell for an electrolytic determination the wide tube is fitted with a rubber stopper carrying a glass tube and the electrodes. These consist of a cylindrical platinum gauze cathode (2.5×5 cm., having about 50 sq. cm. surface) and a spiral platinum wire anode.

Experimental Technique

In carrying out a determination the following technique has been employed.

Rubber caps are slipped over the air inlets (to prevent the solution from running back into them), the solution to be electrolyzed is introduced, the stopper with its electrodes is inserted, the exit tube is connected to a water aspirator and suction is applied. The caps are then removed and a little water is added from a wash-bottle to each of the air inlets to rinse out any liquid which may have run back into them. The level of the solution is adjusted so that it just reaches the level of the upper entrance of the air lifts while the air current is flowing. The electric circuit is then closed. When the electrolysis is nearly complete the suction is increased for a moment to wash down the walls of the vessel, and is then reduced to the normal flow. At the end of the electrolysis the stopper is lifted and the electrodes are washed partially with a jet of water from a wash-bottle, without breaking the current. They are then transferred at once to a beaker of water, washed thoroughly with water, then with alcohol, and are finally dried as usual and weighed.

Most of the actual determinations have been made upon solutions of copper sulfate, to which have been added acids, ammonia, salts, etc., in varying amounts, as in the customary analytical procedures for electrolysis with rotating electrodes. Determinations have also been made of copper in the presence of zinc and lead, and a few estimations of other

metals⁶ have been included as shown in the table. Characteristic experimental data are given in Table I. Carefully standardized solutions, calibrated volumetric apparatus and weights were employed, and all ordinary precautions of good analytical work were taken. The 110-volt lighting circuit, reduced by resistance lamps was used as the source of current.

TABLE I
TOTAL VOLUME OF SOLUTION, 60 CC.

Metal present G.	Metal found G.	Error G.	Current Amps. ^a	Time Min.	Reagent added Cc.	Other metals present G.	Solution becomes colorless Min.
Conc. HNO ₃							
Cu							
0.1983	0.1982	-0.0001	0.5	60	3	...	20
0.1983	0.1984	+0.0001	1.0	30	3	...	12
0.1983	0.1981	-0.0002	3.0	15	3	...	4
0.1983	0.1982	-0.0001	2.0	20	3	0.1 Zn	5
0.1983	0.1982	-0.0001	3.0	15	3	0.1	4
0.1983	0.1983	=0.0000	3.0	15	3	0.2	4
0.1983	0.1982	-0.0001	2.0	20	1	0.1	5
0.1983	0.1984	+0.0001	2.0	25	5	0.1	5
0.3966	0.3968	+0.0002	3.0	20	3	...	6-7
0.1983	0.1984	+0.0001	1.0	25	3	{0.1 Zn 0.003 Pb	8-10
Conc. H ₂ SO ₄							
0.1983	0.1983	=0.0000	1.0	20	1	...	7
0.1983	0.1985	+0.0002	2.0	15	2	...	3-4
0.1983	0.1985	+0.0002	3.0	10	2	...	2
0.1983	0.1984	+0.0001	1.0	25	2	0.1 Zn	7
Conc. NH ₄ OH							
0.1983	0.1985	+0.0002	2.5	15	6	...	8
Zn							
0.1833	0.1834	+0.0001	2.0	30	NaOH 4.5 g.
Fe							
0.1896	0.1898	+0.0002	3.0	30	{(NH ₄) ₂ C ₂ O ₄ 5 g.	...	20
Fe							
0.1890	0.1888	-0.0002	3.0	30	{H ₂ C ₂ O ₄ .2H ₂ O 0.3 g.	...	20
Ni							
0.1999	0.1998	-0.0001	3.5	15	{Conc. NH ₄ OH 25 cc.	...	8
Ni							
0.1999	0.1999	=0.0000	3.5	20	{(NH ₄) ₂ SO ₄ 1.5 g.	...	8

^a Since the surface of the cathode was about 50 sq. cm. the current density (N.D.₁₀₀) is given approximately by multiplying these figures by 2.

Inspection of the data shows that the time necessary for a determination and the accuracy of the results obtained, compare favorably with those obtained with rotating electrodes, under a wide variety of experimental conditions.

⁶ In addition to the data recorded in Table I, satisfactory determinations have been made of Ag, Co, Cd and Pb.

Summary

A simple glass apparatus for electro-analysis has been described in which the solution is stirred indirectly by a current of air, and in which rapid electrolytic determinations may be made.

Data illustrating applications of the apparatus are presented.

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

THE MOLECULAR REARRANGEMENT OF SYMMETRICAL BIS-TRIPHENYLMETHYLHYDRAZINE

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Organic hydrazine derivatives resemble derivatives of hydroxylamine in all fundamental characteristics, except that, with a single exception, they have not been found to undergo molecular rearrangements of the same type as the Beckmann rearrangement of oximes or the Lossen rearrangement of hydroxamic acids. Stieglitz and Senior,² who called attention to this difference, made a series of attempts to effect such rearrangements of hydrazine compounds, but all their efforts were unsuccessful except when they used *sym.-bis*-triphenylmethylhydrazine, $(C_6H_5)_3C.NH.NH.C(C_6H_5)_3$. When they heated this compound to 250° to 300° with anhydrous zinc chloride and hydrolyzed the reaction product, aniline was obtained, which proved conclusively that one of the phenyl groups of the triphenylmethyl radicals migrates under these conditions from carbon to nitrogen, which is the typical shift of the Beckmann-Lossen rearrangements, and of the analogous rearrangements in the triphenylmethane series discovered by the one of us and his collaborators.³ The only other product identified in the preliminary investigation was triphenylmethane, a product of a parallel thermal decomposition of the hydrazine.

The present paper reports the results of a continuation of the investigation, which was carried out to throw light on the mechanism of the rearrangement. Unexpected results obtained toward the end of the investigation have made it impossible, at the present moment, to give a complete theory of the reaction, but as the one of us (Brown) was called to service in the U. S. Army, we wish to present now the lines of thought

¹ This report forms the basis of a dissertation submitted by Ralph L. Brown in part fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Chicago, 1917.

² *Proc. Nat. Acad. Sci.*, **1**, 207 (1915); and *THIS JOURNAL*, **38**, 2727 (1916).

³ See the literature references in *THIS JOURNAL*, **36**, 272 (1914) and **38**, 2051 (1916).