Summary

The electromotive forces of the cell Hg | HgCl, KCl (satd.) | HCl, sucrose, AgCl | Ag with flowing junction and of the cell Pt, H_2 | HCl, sucrose, AgCl | Ag have been measured at 25° with 0.1012 *N* acid and sucrose concentrations ranging from 0 to 700 g. per liter.

The potentials at both hydrogen and silver-chloride electrodes change during the process of inversion. The potential at the hydrogen electrode is also affected by a hydrogenation of sucrose or of the products of its inversion. The liquid-junction potential appears to be considerably changed by the addition of sucrose.

This last phenomenon, and to a smaller extent the second one, introduces a large uncertainty into the measurement of single-ion activities in these solutions, and therefore into the determination of the mechanism of the inversion process.

The values of the second cell are interpreted by theory, and some theoretical implications of the measurements with the first cell are discussed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF THE INFLUENCE OF THE ELECTRODES ON THE FORMATION OF OZONE AT LOW PRESSURES IN THE ELECTRICAL DISCHARGE

BY PHILIP T. NEWSOME[1]

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The electrolysis of gases constitutes a field of investigation which is important because it connects ionization with chemical reaction. Lind[2] has pointed out that electrolysis in solution is a special case of electrolysis, and that it is simpler than the electrolysis of gases. In solution, all the chemical reaction occurs at the surface of the electrodes, and there is a simple relation between the number of molecules reacting and the number of electrons passing through the circuit. This relation finds expression in Faraday's law, which is one of the most exact laws in science.

In the case of gases, chemical reaction is brought about partly in the gas space between the electrodes by ions that combine before they can reach the electrodes. Under these conditions the number of electrons, *n*, recorded by the ammeter in the circuit is considerably less than the total number of ions, *N*, involved, and less than the number of molecules, *M*, reacting.

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[1] This communication is based on a thesis presented in 1926 at the University of Wisconsin for the degree of Doctor of Philosophy. The investigation was carried out under the direction of Farrington Daniels.

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).

Anderegg[3] observed an aging effect in ozonizers and drew the important conclusion that part, at least, of the ozonizing reaction occurs at the surface of the electrodes. The present investigation was undertaken with the idea of reducing the pressure of the gas and increasing the area of the electrodes so that most of the reaction would occur at the electrodes. It was reasoned that under these conditions the electrolysis might be similar to electrolysis in solutions, and that the ratio of the number of molecules reacting to the number of electrons registered in the circuit might have theoretical significance.

The electrical discharge in gases is so complicated that it was necessary to eliminate as many variables as possible. The composition of the gas was kept constant by a constant-flow method. Fluctuations in the discharge were eliminated by including a very high external resistance in the circuit. The geometrical arrangement of the electrodes was designed to give a minimum of field distortion, a large metallic cylinder being coaxial with a large wire. The wire was large enough to prevent the intense potential drop around a point, but small enough so that there was a pronounced difference in area between the two electrodes. This difference was necessary in drawing conclusions concerning the specific action of the electrode material. The input of energy was so low that there was no appreciable heating of the chamber. There was always a bead of light on the negative electrode, sometimes stationary and sometimes wandering, but since the results checked closely regardless of the position of the bead this was not considered to be a variable.

In this communication the results on ozone are reported. It was found that under the conditions of these experiments the electrodes played a fundamental part in the chemical actions, and that under certain conditions there seemed to be a relation between the number of electrons reaching the electrodes and the number of reacting molecules.

Description of Apparatus

The arrangement of the apparatus is shown in Fig. 1. The gas was stored over concentrated sulfuric acid in the large bottle at the left of the figure, and drawn through the system by a vacuum pump (not shown). By carefully adjusting the stopcock H it was possible to maintain any desired pressure in the discharge chamber, as measured by the manometer, M. The rate of flow under any conditions was measured by the flowmeter F. When it was necessary to measure the rate of flow of mixtures of ozone and oxygen, the flowmeter was kept at a specified level while the sample of the gas was passed through the side tube I and analyzed.

After passing through the discharge chamber, the ozone was absorbed in a solution of potassium iodide contained in a tall absorption bottle A.

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[3] Anderegg, *Trans. Am. Electrochem. Soc.*, **44,** 203 (1923).

All connections were of fused glass tubing except the connection K to the absorbing bottle, which was constructed with overlapping joints covered with wax. After an experiment, the solution was acidified with sulfuric acid and titrated with 0.0025 *N* sodium thiosulfate solution, using a starch indicator.

A constant current of two milliamperes was maintained through the discharge chamber by a set of radio dry batteries of 2200 volts connected through a variable resistance **R** and a calibrated galvanometer G. The resistance contained a screw adjustment whereby one could vary the distance between a fixed platinum disk and a mercury level in a 50–50 mixture of absolute ethyl alcohol and xylene.

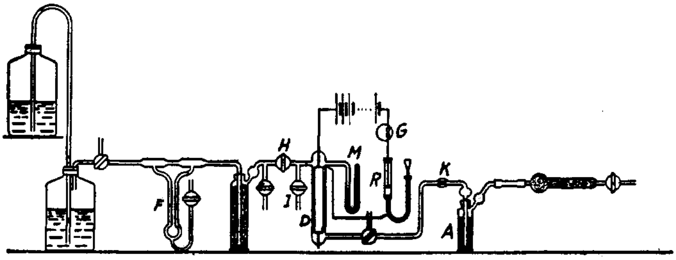

Fig. 1.—Apparatus for measuring the production of ozone at low pressures.

The vertical discharge chamber D consisted of a heavy copper cylinder 23.5 cm. long and 3 cm. inside diameter, slipped into a large glass tube. The tube was provided with inlet tubes and outlet tubes and a mercury manometer. Copper wire, 2.057 mm. in diameter, was strung through the center and set in position with de Khotinsky cement.

The silver and gold electrodes were made by electroplating the copper electrodes. The oxygen used in the experiments, taken from a commercial tank, was stored over sulfuric acid. The rate of flow of gas was about 27 cc. per minute, measured under 760 mm. pressure at 20°.

The inlet tube was above the copper cylinder and the bead of light stayed near the top of the cylinder. The incoming gas went downward through the bead of light and then came into contact with the large electrode area before passing out.

The relation between chemical action and ionization in these experiments is reported as M/n ratios, where M is the number of molecules reacting and n is the number of electrons reaching the electrodes. The number of electrons was determined by multiplying the amperes by the number of seconds to give coulombs, and dividing the coulombs by the charge of one electron (1.59×10^{-19} coulomb). The number of molecules was determined by converting the cubic centimeters of thiosulfate solution into moles of ozone and multiplying by the Avogadro number. Any M/n

ratio may be changed back to moles of ozone per coulomb by dividing by the factor 96,500.

It was gratifying to find that duplicate experiments checked closely. In most cases they agreed within the limit of the analytical accuracy and showed that the conditions of the discharge were completely reproducible. The average values, only, are given in the tables and the following examples, taken at random, are included to show the agreement in the *M*/*n* ratios: 0.21, 0.22, 0.21; 0.67, 0.67, 0.67; 2.73, 2.73, 2.75.

The Influence of Pressure on the Formation of Ozone

The pressure was varied from 14 mm. to 33 mm. Experiments could not be carried out below this range on account of the vapor pressure of the water in the absorbing solution, and above this range the discharge did not operate smoothly with the batteries which were available. The results of the experiments are summarized in Tables I and II and in the corresponding curves of Fig. 2.

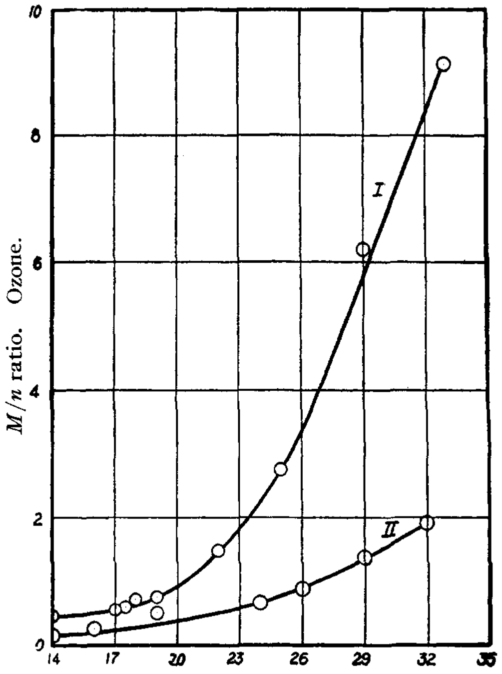

Fig. 2.—The influence of pressure on the *M*/*n* ratios. Cylinder negative. Upper curve—copper electrodes; Table I. Lower curve—gold electrodes; Table II.

As seen in the upper curve of Fig. 2, at low pressures the *M*/*n* ratio appears to approach a constant value of 0.5, which is the value corresponding to Faraday's law. This number suggests that two electrons are involved in the formation of ozone. In view of the later experiments, however, it is not certain that this ratio is significant.

In the case of gold electrodes a value considerably less than 0.5 is indicated for the *M*/*n* ratio at low pressures. The best explanation seems to be that gold catalyzes the decomposition of ozone. It is more effective in this decomposition when the electrode of larger area is charged positively, as shown by the last two results.

The greater production of ozone with the cylinder negative does not agree with the results of other investigators at atmosphreic pressure,

TABLE I

INFLUENCE OF PRESSURE. COPPER ELECTRODES

Time, min.	Current, milliamp.	Charge on cylinder	Pressure, mm.	Molecules of ozone formed per electron
5	2.19	−	33	9.14
5	2.15	−	29	6.20
10	2.03	−	26	3.53
5	2.19	−	25	2.75
10	2.15	−	22	1.48
10	2.15	−	19	0.75
15	2.15	−	18	.72
10	2.15	−	17.5	.59
10	2.15	−	17	.55
5	2.15	−	14	.46
		+	26	.25
		+	24	.14

TABLE II

INFLUENCE OF PRESSURE. GOLD ELECTRODES

10 minutes 2.19 milliamperes

Charge on cylinder	−	−	−	−	−	−	−	+	+
Pressure, mm.	32	29	26	24	19	16	14	24	23
M/n	1.91	1.38	0.881	0.670	0.513	0.258	0.153	0.365	0.305

shown in Table III, but it must be emphasized that the different conditions make a direct comparison impossible. Apparently no work has been done before on the electrolysis at low pressures. The influence of the electrodes is probably more important at the lower pressures.

TABLE III

RESULTS OF OTHER INVESTIGATORS AT ATMOSPHERIC PRESSURE

	Kunz and Rideal[4]		Warburg[5]		Anderegg[6]	
Charge on cylinder	+	−	+	−	+	−
M/n	90.54	48.29	86.52	34.20	36.35	30.00

The Aging of the Electrodes

It was soon found that the yield of ozone changed with time, a phenomenon discovered by Anderegg.[6] Table IV and Fig. 3 show that an increase in the duration of the experiment increased the efficiency of the production of ozone, when the cylinder was positive, but that time was not a variable when the cylinder was negative.

The upper curve, *A*, of Fig. 3 with the cylinder negative is a straight line, showing that the amount of ozone formed is directly proportional to the time, or to the input of electrical energy (current constant). The results are high indicating little, if any, de-ozonization. The lower curve,

[4] Kunz and Rideal, *J. Phys. Chem.*, **24,** 379 (1920).

[5] Warburg, *Ann. Physik,* **13,** 464 (1904).

[6] Anderegg, THIS JOURNAL, 39, 2581 (1917).

TABLE IV

DURATION OF DISCHARGE. COPPER ELECTRODES

A. Cylinder negative 26 mm. pressure; 2.03 milliamperes			B. Cylinder positive 26 mm. pressure; 2.33 milliamperes		
Time, min.	Ozone, millimoles	M/n'	Time, min.	Ozone millimoles	M/n'
5	0.0222	3.51			
10	.0446	3.53	10	0.00367	0.25
15	.0653	3.45	20	.0100	.34
20	.0898	3.56	30	.0276	.63

B, with the cylinder positive shows a considerably smaller yield of ozone, probably because the large positive cylinder decomposes the ozone, but as the discharge continues to pass, the decomposition becomes less and the yield of ozone, per *minute*, increases. This gives to the curve an increasing slope. The aging effect with the cylinder positive was only temporary. When the discharge was stopped and another experiment started within an hour, the M/n ratio was again low, and the data of Table IV could be repeated as often as desired. These facts suggest that the copper atoms of the positive electrode decompose ozone, but that the discharge causes them to become covered with a film of protecting material (possibly a higher oxide). The "poisoning" of the electrode surface tends to reach a maximum, and increased exposure gives less increase in the M/n ratio after the discharge has been operating for some time. The protecting material must be unstable, for the de-ozonizing effect quickly returns to its original value when the current is turned off.

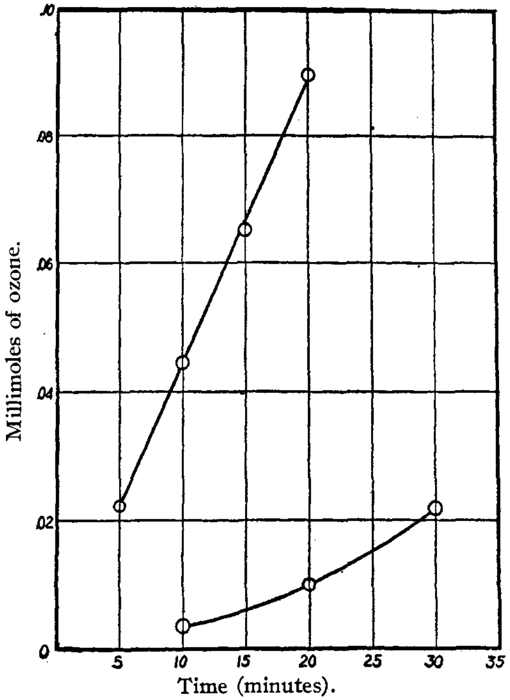

Fig. 3.—The influence of time of discharge on efficiency of ozone production. Copper electrodes. *A*. Upper curve—cylinder negative. *B*. Lower curve—cylinder positive.

A similar aging effect was observed with gold electrodes, and the M/n ratios increased with the duration of the discharge. In this case it was found that rinsing the electrodes with distilled water, caused the M/n ratio to fall to its original low value.

In order to study the influence of the electrodes from a different angle, the copper electrodes were given absolutely fresh surfaces by etching with nitric acid, and a series of five-minute exposures was made. The results are given in Table V.

TABLE V

FIVE-MINUTE EXPOSURES OF FRESHLY-ETCHED COPPER ELECTRODES

Cylinder negative; 26 mm. pressure; 2.15 milliamperes

Exposure no.	1	2	3	4	5	6	7
M/n	0.422	1.25	1.82	2.00	3.26	3.53	3.45

Apparently the new copper surface is active in decomposing ozone, even though it is charged negatively, but after being in the discharge a short time its efficiency is impaired and after 30 minutes it is rendered completely inactive. The M/n ratios increase (on account of a lessening of the deozonizing effect) until they reach a maximum value which agrees with the third experiment of Table I. The whole series was checked closely after etching a second time and repeating the experiment. After the copper surface became sufficiently aged to be inactive in decomposing ozone, when acting as the cathode, it was nevertheless active when made the positive electrode in the discharge, and the M/n ratios with the cylinder positive were again low as in the last experiments of Table I.

The Influence of the Electrode Material

Gold, silver and aluminum were used as well as copper, in studying the influence of the electrodes on ozone formation. By the use of mixed electrodes it was possible to gain additional information concerning the place where the ozone is formed and decomposed. The results are summarized in Table VI.

TABLE VI

INFLUENCE OF ELECTRODE MATERIAL

24 mm. pressure 1.9–2.2 milliamperes

Cylinder	Charge	Wire	Charge	M/n
Cu	+	Cu	−	0.14
Cu	−	Cu	+	2.35
Au	+	Au	−	0.36
Au	−	Au	+	.67
Au	+	Ag	−	.24
Au	−	Ag	+	.69
Ag	+	Ag	−	.13
Ag	−	Ag	+	.14
Ag	−	Cu	+	.21
Al	+	Al	−	.10
Al	−	Al	+	.10
Al	+	Cu	−	.10
Al	−	Cu	+	.09

These results may be interpreted on the hypothesis that the ozone produced is fairly constant, but is decomposed at the metallic surface of the electrodes. The area of the cylinder is so much greater than the area of the wire that the effect of the cylinder largely overshadows that of the wire. The catalytic de-ozonation is greater when the metal is charged positively. All the ozone yields are low except the one where the copper cylinder is negative, for in this case the copper cylinder appears to be inactive in decomposing ozone and the positive copper wire is small in area. The de-ozonizing effect seems to increase in the order copper, gold, silver, aluminum. The greater effect of the metal, when positively charged, is pronounced in the case of copper and gold, but it is not evident in the case of silver and aluminum because the decomposition is so great with these metals anyway, that any difference is minimized.

The Decomposition of Ozone

To test further, the hypothesis already proposed, the influence on ozone decomposition of electrode material and positive or negative charge was studied. Oxygen containing about 2% of ozone was passed through the discharge chamber under conditions similar to those already described. The results are summarized in Table VII.

TABLE VII

THE DECOMPOSITION OF OZONE

Current, 2.19 milliamperes; time, 10 minutes

Electrodes		Charge on cylinder	Pressure mm.	O_3 entering, millimoles	O_3 leaving, millimoles	O_3 decomposed %
Cylinder	Wire					
Au	Au	none	28	0.1685	0.1685	00.00
		−	28	.1428	.0278	80.5
		+	28	.1357	.0119	91.2
Au	Ag	none	27	.1155	.1104	4.4
		−	24	.0584	.00492	91.6
		+	24	.0584	.00275	95.3
Au	Cu	+	24	.0990	.00647	93.5
		+	24	.0702	.00468	93.3
Cu	Cu	none	24	.0960	.0948	1.2
		−	24	.1018	.00972	90.4
		+	24	.1018	.00965	90.5
Al	Al	none	21	.0646	.0642	0.3
		−	21	.0646	.0043	93.3
		+	21	.0646	.0042	93.5

An examination of the table shows that there is very little decomposition of ozone in passing through the chamber in the absence of the electrical discharge, except in the case of silver, and silver is known to be an excellent catalyst for the decomposition of ozone. When the discharge is passing, the decomposition is usually 90% or more complete. The decomposition is so great that the influence of the different factors is partly lost. It is evident, however, that the decomposition of ozone increases in the order copper, gold, silver, aluminum. The results with the gold cylinder support strongly the hypothesis that the decomposition of ozone is greater when the cylinder of larger area is charged positive.

The Voltage Factor

Although the potential drop across the chamber is not involved in the determination of M/n ratios, it is an important factor in ozone formation, particularly from the practical view of energy consumption. Good ozonizers working at atmospheric pressure yield about a gram molecule of ozone for a kilowatt hour input of electrical energy. Even this is a very low yield calculated on the thermochemical basis. It seemed worth while to determine the relation between ozone production and input of electrical *energy* under these new conditions of low pressure and chemically active electrodes.

The potential drop across the electrodes was determined with an electrostatic voltmeter. With copper electrodes the voltage, V, required to maintain a current of 2.19 milliamperes is given by the following equations in which P represents the pressure of oxygen in mm. of mercury: $V = 305 + 6P$ (cylinder —); $V = 265 + 6P$ (cylinder +). These equations are valid only for the particular discharge chamber used in these investigations and for the pressure range from 15 to 35 mm. The measurements were made with a constant stream of oxygen passing through, under the conditions of the previous experiments. The addition of 2% of ozone to the oxygen did not appreciably affect the voltage required to maintain the current and the voltage was constant within the limits of experimental measurement no matter how long the discharge was passing.

The yield of ozone in moles per kilowatt hour can readily be calculated from the M/n ratios by dividing by the faraday (96,500) and the voltage drop and multiplying by the number of joules in a kilowatt hour (3.6×10^6). With the copper cylinder charged negatively the highest values of M/n were obtained. Under these conditions at 24 mm. the efficiency was 0.2 mole of ozone per kilowatt hour. With the other electrode arrangements the yield was lower. At higher pressures the yields on the energy basis are greater.

Conclusions

The experimental results have been interpreted on the hypothesis that an important factor influencing the yield of ozone in these experiments is the de-ozonizing action of the electrodes, particularly the positive electrode. The mechanism of the destruction of ozone at the electrodes is not clear, but the experiments with aluminum electrodes are significant. It is known that aluminum is completely covered by a protecting film of oxide and that ozone is not decomposed by this coated aluminum. In fact, aluminum was used in the experiments because it was thought that with it there would be no de-ozonation at all. It was a surprise, then, to obtain the very low concentration of ozone, when the discharge was operating.

It seems likely that the bombardment of electrons on the positive aluminum electrode disintegrates the film of aluminum oxide and leaves free or partly free aluminum atoms at the surface, which then are immediately oxidized by the ozone (and by the oxygen) with the resulting destruction of the ozone. This hypothesis may also be applied to the other metals.

The conditions for the formation of ozone are more obscure. In the electrical discharge at these pressures the fall of potential is greatest near the negative electrode if the electrodes are of the same dimensions. The bead of light was always more intense at the negative electrode. These facts suggest that the ozone may be formed by electronic bombardment at or near the negative electrode. The present data do not enable one to decide whether the material of the electrodes influences the quantity of ozone actually synthesized, or whether it influences the final quantity only by decomposing part of the ozone that has already been formed.

It is a striking fact that under the conditions which give the highest yield of ozone, the M/n ratio, extrapolated to zero pressure, is practically 0.5 and corresponds to one molecule of ozone for every two electrons. Further experiments are necessary before it can be decided whether or not this ratio is significant. Certainly in the other cases, the de-ozonization process destroyed the theoretical significance of the M/n ratio, and it remains to be seen whether de-ozonation is still taking place to an appreciable extent when the copper cylinder is negative. It may be more than a coincidence that the ratio of the inside of the copper cylinder to the area of the wire is 14.5, and that the ozone production is fourteen times as great with the cylinder negative as with the cylinder positive. This ozone ratio of 14 to 1 was obtained only with copper electrodes, although the dimensions of the other electrodes were identically the same. In these cases, however, it is certain that some de-ozonization was taking place, even with the cylinder negative, for the M/n ratios are lower.

Experiments similar to those just described with ozone were carried out with ammonia. In both cases the gases passed through the chamber fairly rapidly and equilibrium conditions in the discharge were not reached. The thermal equilibrium in the two cases was different, that of ozone being a decomposition and that of ammonia being a synthesis. The catalytic effects of the electrodes were also different.

Each experiment lasted for 20 minutes, and the current was kept constant at 1.9 milliamperes and the gas velocity at 9 cc., per minute. The results are summarized in Table VIII.

Starting with hydrogen and nitrogen under the same conditions practically no ammonia was synthesized.

Table VIII

The Decomposition of Ammonia

			Positive wire		Negative wire	
Wire	Cylinder	Pressure, mm.	NH_3 decomposed, %	M/n	NH_3 decomposed, %	M/n
Al	Al	25	3.1	11.0	1.9	6.6
Fe	Al	22	2.2	7.1	1.6	5.6
Cu	Cu	23	3.4	12.1	2.9	9.9

The author wishes to express his appreciation to Professor Farrington Daniels for the assistance and instruction given during the course of this research.

Summary

1. The production of ozone has been investigated at pressures from 14 mm. to 33 mm. under conditions designed to emphasize the action of the electrodes.
2. The quantity of ozone produced per coulomb of electricity passing through the circuit decreased with decreasing pressure and approached a constant value.
3. The production of ozone was largely influenced by the material of the electrode. The efficiency decreased in the order: copper, gold, silver, aluminum. Experiments were also carried out with mixed electrodes.
4. Under certain conditions the yield of ozone increased as the electrodes became aged in the electrical discharge.
5. The results are in accord with the hypothesis that part of the ozone formed in the discharge is decomposed at the positive electrode.
6. Calculated as moles of ozone per kilowatt hour the efficiency is rather low.

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[Contribution from the Department of Chemistry, Ohio State University]

A NEW TYPE OF END-POINT IN ELECTROMETRIC TITRATION AND ITS APPLICATION TO IODIMETRY

By C. W. Foulk and A. T. Bawden

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The scheme of electrometric titration offered in this paper is a special case of the bimetallic electrode systems described by Willard and Fenwick[1] and discussed later by Van Name and Fenwick.[2] It was, however, not inspired by these investigations but was discovered accidentally by one of us in the preparation for the titration of iodine electrometrically in the conventional way. The suggestion thus offered by chance was then followed. The characteristic features of this scheme as finally worked out

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[1] Willard and Fenwick, This Journal, **44**, 2504 (1922).

[2] Van Name and Fenwick, *ibid.*, **47**, 9, 19 (1925).