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

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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).

are the simplicity of the equipment required and the sensitiveness and peculiar character of the end-point.

Details of the Apparatus and Procedure

Fig. 1 illustrates the arrangement of the apparatus used. G is a suitable galvanometer. In our experiments two types were used, one a Leeds and Northrup box with enclosed lamp and scale, and one the needle instrument which is part of the Wendt titration apparatus. R is a Beck Brothers rheostat, 50 ohms and 3.3 amp.; B is an Edison cell; C is a beaker for the titrations and E, E are platinum wire electrodes. A motor-driven stirrer that was used is not shown. The essential feature of the procedure is the adjustment of the resistance so that the potential difference between the electrodes is only 10 to 15 millivolts.

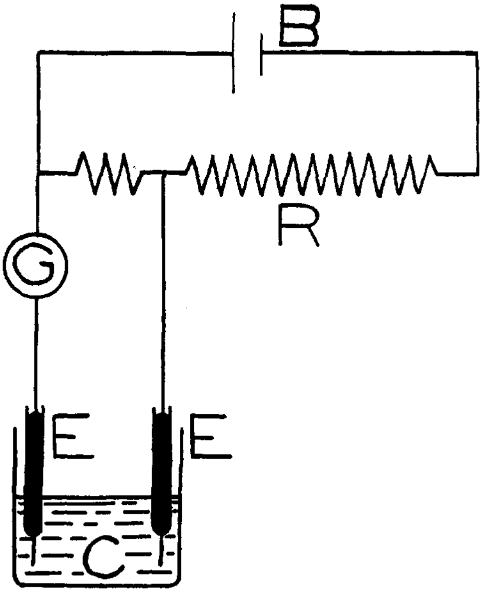

Fig. 1.—Apparatus.

When iodine, for example, is titrated by means of this simple apparatus with a thiosulfate solution it will be found that when nearly all of the iodine has been reduced the light spot of the galvanometer comes into view and, as successive drops of the thiosulfate solution are added, the spot approaches the zero of the scale until, coincident with the disappearance of the last trace of the iodine, it comes to rest at zero and remains there even when an excess of thiosulfate solution is added. When the reverse titration is made, that is, when iodine is added to thiosulfate, the nature of the end-point is reversed. During the early part of the titration the light spot of the galvanometer remains at zero but as the end of the reaction approaches, the spot makes temporary excursions returning, however, to its zero position as stirring proceeds. Finally, the end-point is indicated by a permanent displacement which is increased by further additions of iodine from the buret.

Since this type of end-point is characterized by the galvanometer coming to a dead stop or by its permanent displacement from a position of rest, the name "dead-stop" end-point is suggested.[3]

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[3] "Polarization" end-point would perhaps be a better name but it was not used because of probable confusion with other polarization applications in electrometric titrations; such, for example, as the work of Willard and Fenwick.

Theory of the Dead-Stop End-Point

Willard and Fenwick[4] and later Van Name and Fenwick[2] have shown that metallic electrodes of the type used here owe their effect in electrometric titrations to gas reactions taking place on the surface and have discussed in so exhaustive a manner the theory of the behavior of such electrodes that nothing need be added here excepting the details applying to the dead-stop end-point. By way of variety, however, and because we are concerned only with the practical application of this phenomenon to titrations, we shall depart from the conventional method of using mathematical equations to show the potential changes that occur at and near the end-point and shall discuss the situation in a purely qualitative way. Our point of view will at least be found adequate for predicting new applications.

The fundamental condition for the production of the dead-stop end-point is the use of so low a potential (10 to 15 millivolts) between the electrodes in the solution to be titrated that the back electromotive force of polarization[5] balances it and consequently no current flows, the galvanometer registering zero.[6] Under these conditions the dead-stop end-point will occur in the titration of all systems in which a sharp transition from the polarization of at least one electrode to the complete depolarization of both of them (or *vice versa*) coincides with the end of the reaction. We assume that polarization is due to oxygen adsorbed on the anode and hydrogen on the cathode and that the anode can, therefore, be depolarized by a suitable reducing agent and the cathode by a suitable oxidizing agent.

It is obvious that from the standpoint of the condition of the electrodes during a titration only three cases can exist. (1) One electrode only is polarized. The titrating solution from the buret must then depolarize this electrode. This is the situation in the titration of thiosulfate or of arsenite with iodine. The anode remains depolarized throughout the titration due to the reducing agents present and at the end-point the first trace of iodine in excess depolarizes the cathode. (2) Both electrodes remain depolarized. This presupposes the presence in the solution of both an oxidizing and a reducing agent which do not react with each other, or at any rate, not in an irreversible way. It is the situation in the titration of iodine with thiosulfate or arsenite. (3) Both electrodes are polarized. The titrating solution must then be capable of depolarizing them both.

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[4] Ref. 1, p. 2516.

[5] The first suggestion that simple polarization was the probable explanation of the dead-stop end-point came to us from Dr. W. G. France.

[6] The zero position of the galvanometer is not absolutely essential. It was found as a matter of practice that if the needle or light spot stood close to zero, this position would serve as the point of reference for this type of end-point. There was, however, no advantage in this.

This is possible because mixtures of reagents may be used as titrating solutions but, as a rule, Case 3 could be transformed into Case 1 by the addition of a suitable reagent.

In general, at least one of the main constituents of the reaction must be an efficient depolarizer and the products of the reaction must not act as depolarizers and thus vitiate the end-point. In iodimetric titrations, for example, the sodium tetrathionate and the sodium arsenate which form are not cathodic depolarizers. As in other titrations, the sharpness of the end-point is proportional to the degree of irreversibility of the reaction.

Finally, it should be pointed out that the necessary polarizing or depolarizing conditions are not limited to those directly produced by the constituents of the main reaction. They can be brought about indirectly by the action of one of these main constituents upon a suitable added substance or mixture of substances. For example, a sharp dead-stop end-point can be obtained on titrating a strong base with a strong acid if there is present in the solution of the base a small amount of iodide and a suitable oxidizing agent. This interesting application of electrometric titration to neutralization reactions is now being studied in the Ohio Laboratory.

Experimental Evidence on the Above Points

With the electrodes in a solution of potassium chloride no current flowed when iodine was added because the anode remained polarized. The addition of a little iodide at once caused a deflection of the galvanometer. In another experiment the iodide was added first but without effect. The electrodes were then tried in separate vessels containing iodide solutions of the same strength connected by a salt bridge. No current flowed unless a trace of iodine was present in the cathode vessel. If this electrode, though bathed in iodine, was made the anode, the current ceased.

Characteristics of the Dead-Stop End-Point

The dead-stop end-point possesses the three most desirable characteristics of an end-point. (1) It gives evidence of its approach by the behavior of the galvanometer. (2) If overrun the fact is at once apparent. (3) It is very sensitive. (The behavior of the galvanometer at and near the end-point and the effect of overrunning the end-point are described in an early paragraph above.) Finally, equilibrium is reached almost instantly, so that there is no tedious waiting in the neighborhood of the end-point.

The sensitiveness or response of the dead-stop end-point to slight changes in concentration of the main constituents of the reaction is remarkable. Under favorable conditions in the titrations of iodimetry two or three drops, more or less, of 0.001 *N* solution are sufficient to give an end-point. Under ordinary conditions, however, a drop of 0.01 *N* to 0.005 *N* solution is required. Colored substances, solids in suspension and various organic liquids have no effect unless, of course, there is direct reaction.

Application to Iodimetry

Titrations of iodine with either sodium thiosulfate or sodium arsenite and titrations of these two substances with iodine can be made with the apparatus shown in Fig. 1. A potential of 10 to 15 millivolts[7] between the electrodes should be used and a motor-driven stirrer must, of course, be provided.

The chemical conditions for the titrations should be the same as those used with starch as indicator. It will be found, however, that the dead-stop end-point is less affected by variations in conditions than is the starch blue. For example, the concentration of potassium iodide, sodium hydrogen carbonate and acid may vary within wide limits. Titrations can also be made in strong alcohol or glycerol solutions if 2% potassium iodide is present. Temperatures approaching 100° also have no effect.

The character and sensitiveness of the dead-stop end-point in iodimetry have been described above. It is perhaps more sensitive with arsenite solutions than with thiosulfate. The relation to the starch end-point is interesting, being the equivalent of about 4 drops of 0.001 *N* solution removed, in the sense that in titrating with iodine the electrometric end-point occurs before the starch blue appears and, conversely, in titrating iodine with thiosulfate or arsenite it occurs after the blue has disappeared. In other words the depolarization of the cathode under the conditions of the titration is a much more sensitive test for iodine than the reaction with starch. This also answers the question that should be raised about a new volumetric process, namely, what is its end-point error, or the amount of titrating substance required to produce the end-point? In this case it is easily seen that the excess of iodine to give the dead-stop end-point is negligible, less than the concentration needed for the starch end-point.

The reproducibility of the dead-stop end-point was tested by titrating a series of 25.00cc. portions of 0.001 *N* iodine solution in 2% potassium iodide solution (measured at the end of the titration) with approximately 0.002 *N* sodium arsenite solution. Twelve successive titrations were made, the average volume of arsenite required being 13.31 cc. The greatest deviation from this average was 0.06 cc. In another experiment five portions of from 25 to 33 g. of 0.1 *N* iodine solution were titrated with a somewhat more concentrated thiosulfate solution. Weighing burets were employed, the end-point being obtained in each case by the use of small amounts of 0.001 *N* solution. On calculating these five results to the common basis of 25.00 g. of iodine solution, the corresponding weights of thiosulfate were found to be 23.51, 23.52, 23.52, 23.52 and 23.53 g. These titrations were made with a Wendt apparatus which employs a needle galvanometer.

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[7] It is not necessary to use an instrument for measuring the potential. Adjustment of the resistance so that the galvanometer is just brought to zero with at least one electrode polarized is sufficient.

Another question that may be raised concerns reactions around the anode. Theoretically, the depolarization of this electrode with iodide should result in some free iodine and, indeed, after long standing a faint test for iodine can be obtained. During the period of a titration, however, such liberation of iodine at the anode is undetectable.

Electrometric Titration without a Battery

The following experiment is perhaps only a bit of chemical by-play, but it is presented because of its interest and because it may suggest some practical application.

If two vessels, one containing dilute and the other concd. potassium iodide solution, are connected by a salt bridge and a metallic circuit through a galvanometer as shown in Fig. 2, the vessel containing the weaker solution can be used for the titrations of iodimetry by the dead-stop end-point method because the concentration chain formed by the two iodide solutions gives a sufficient potential for the purpose. The anode in the stronger solution remains permanently depolarized and the cathode in the weaker solution is polarized in the presence of an excess of thiosulfate or arsenite and depolarized if iodine is present. Many titrations were made with this arrangement which may be considered the simplest that has yet been used in electrometric work.

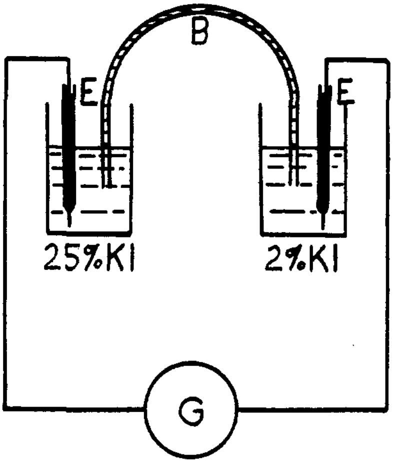

Fig. 2.—Concentration chain for titrating without a battery.

Other Applications

The dead-stop end-point scheme has been successfully applied to oxalate-permanganate titrations. It was also found, incidentally, that a very sharp end-point can be obtained in the direct titration of thiosulfate with permanganate and *vice versa*.

Summary

This paper contains the description and theory of a simple bimetallic electrode system for electrometric titrations, the fundamental principle of which is the use of a potential between the electrodes of the same order of magnitude as the counter electromotive force of polarization.

There is included a description of a novel arrangement which depends upon a concentration chain, composed of two potassium iodide solutions connected by a salt bridge, for the necessary impressed potential between

the electrodes. Iodimetric titrations can be made in the weaker of the two solutions without the use of a battery.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE VAPOR PRESSURE OF ETHANE NEAR THE NORMAL BOILING POINT[1]

BY A. G. LOOMIS AND J. E. WALTERS

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Introduction

For the design of an efficient plant to extract helium from natural gas it is necessary to know the thermodynamic properties of the several components of the gas. This investigation supplies the vapor pressure of ethane in the neighborhood of the normal boiling point, and is one of a series of investigations now being undertaken on the thermodynamic properties of the pure components of natural gas, and of their binary mixtures. The pressures recorded in this paper cover the range from 0.0245 atmospheres to 2.1441 atmospheres; Dr. Porter (see the following paper) has extended these measurements to the critical pressure.

Previous Investigations

Olszewski[2] reports the normal boiling point of ethane prepared from zinc ethyl as —93°.

Burrell and Robertson[3] measured the vapor pressure from 1 mm. to 760 mm., giving 183.8°K. as the normal boiling point. Temperatures were measured by means of a pentane thermometer, and two observers could check readings to 0.2° and in most cases to 0.1°. The cryostat of the Henning type could be held constant to 0.04° for the period of measurement of a vapor pressure. Pressure readings were reproducible to 1 mm. The limit of accuracy of reading the thermometers (0.2°) corresponds to 7.5 mm. near the normal boiling point. The ethane used was prepared from sodium acetate solution by electrolysis, purified chemically, fractionated and pumped free from traces of foreign gases. Moreover, portions were removed from time to time, so that the purity of their ethane was all that could be desired.

Maass and McIntosh[4] measured the vapor pressure from 288 mm. to 765 mm. and found 184.6°K. as the normal boiling point. Temperatures were read on a hydrogen gas thermometer; the cryostat could be held con-

[1] Published with the permission of the Director of the Bureau of Mines.

[2] Olszewski, *Berl. Ber.*, **27**, 3305 (1894).

[3] Burrell and Robertson, THIS JOURNAL, **37**, 1893 (1915).

[4] Maass and McIntosh, *ibid.*, **36**, 737 (1914).