the approach of the end-point or to predict the voltage range in which the end-point change will occur in any given case.

Summary

A brief study of the use of the Pt-Au electrode system has shown that it gives a sharp change in e.m.f. at the end-points of some oxidation-reduction reactions in 0.1 or 0.05 *N* solutions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A SIMPLE CONTINUOUS READING METHOD OF ELECTROMETRIC TITRATION WITH BIMETALLIC ELECTRODES

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Introduction

Electrometric methods of determining the end-points of volumetric oxidation-reduction reactions are accurate and convenient. Many varieties of systems have been developed to follow changes in the e.m.f. of a suitable pair of electrodes during the progress of a titration,[1] but not all of them possess the advantages of simplicity, economy of apparatus and speed. The system that is described in this paper combines these advantages and is, in addition, continuous reading.

Experimental

Apparatus.—The electrical system consists of a platinum electrode, a tungsten electrode,[2] a galvanometer and a high resistance that can be varied. The electrical connections are shown diagrammatically in Fig. 1. The platinum electrode was a wire of 0.33 mm. diameter (No. 28 B. and S. gage) and of 6–8 cm. length. The wire was soldered to a copper wire with gold; the platinum was sealed through the end of a glass tube (see Fig. 1). The end of the tungsten wire (No. 28 B. and S. gage; actual diameter 0.32 mm.) was dipped into the solution to a depth of 2–3 cm. The dimensions of the electrodes seem to have no very marked effect upon the behavior of the apparatus. A platinum wire of the size given seems somewhat more reliable than one of very small surface. The

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[1] For a review of these systems, see E. Müller, "Die Elektrometrische Massanalyse," 4th ed., Steinkopf, Dresden, **1926**; I. M. Kolthoff and N. Howell Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, **1926.**

[2] Qualitative studies have been made using tantalum, platinized platinum, copper or gold instead of tungsten. The Pt-Au system was the best of these combinations. It gave excellent end-point indications in the reaction between permanganate and ferrous sulfate but was, in general, far less sensitive than the Pt-W system.

electrodes must be clean. The solution should be effectively stirred (motor stirrer).

A handy resistance unit was assembled from inexpensive radio grid-leak mountings. The resistances were of the cartridge type, and were rated at 10,000, 18,000, 20,000 and 100,000 ohms.[3] By making one or two interchanges of resistors it is possible to vary the resistance in steps of about 10,000 ohms each up to 160,000 ohms. A resistance of about 50,000 ohms served for most titrations.

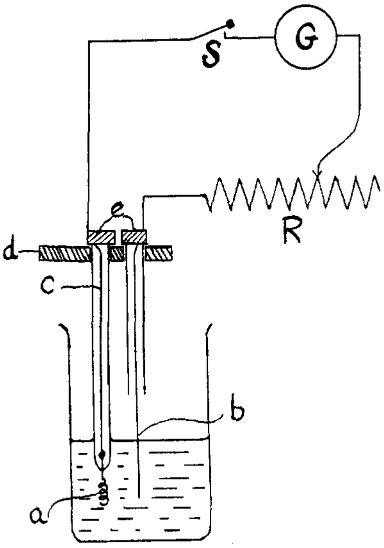

Fig. 1.—Apparatus. (a) Platinum electrode; (b) tungsten electrode; (c) copper wire. The copper and tungsten wires are wrapped around the glass tubes and held in place by the rubber tubes at (e); (d) is a Bakelite support for the electrodes. S, switch; G, galvanometer; R, variable high resistance.

The galvanometer was a Leeds and Northrup Company portable instrument (Type 2320D) of current sensitivity 0.5 micro-ampere. Any galvanometer of approximately similar characteristics should serve.

End-points.—Operation of the apparatus is very simple. The end-point is the largest single permanent deflection (usually 2–10 divisions) of the galvanometer that is produced by a single drop of the reagent, for all of the reactions that we have studied (ferrous sulfate-permanganate; ferrous sulfate-vanadic acid; ferrous sulfate-bichromate; iodine-thiosulfate). The galvanometer usually reads zero, or a low value, on the reducing side. As oxidizing agent is added, there is a slight increase in the galvanometer deflection. As the end-point is approached the needle gives temporary deflections that serve as convenient warnings. At the end-point there is a maximum permanent shift (2–10) divisions per unit volume of reagent. Further addition of oxidant produces relatively slight changes.

In the reverse titration there is a high initial galvanometer deflection, a maximum permanent downward shift in reading at the end-point and little further deflection on the addition of excess of reducing agent. Occasionally the end-point deflection is divided into two nearly equal parts. The maximum change per unit volume of reagent corresponds to the end-

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[3] The resistances were "Aerovox Lavite" resistors (Aerovox Wireless Corp., New York). A suitable unit can be assembled at a cost of $3 to $5. It was found that the resistors were in some cases as much as 10% higher than rated. We are indebted to Mr. W. S. Niederhauser for the resistance measurements.

point, as is the case in potentiometric procedures. Graphs with galvanometer readings as ordinates and cc. of reagent as abscissas are analogous to those obtained potentiometrically. In any case the end-point is definitely determinable by a slightly experienced operator.

Accuracy.—Approximately 0.1 or 0.05 *N* solutions of the reagents were prepared and standardized. Starch indicator was used in the iodine–thiosulfate reaction. In other cases the potentiometric method was employed. A large number of quantitative determinations were made for the ferrous sulfate–dichromate, ferrous sulfate–vanadic acid and iodine–thiosulfate reactions. In many of these titrations simultaneous observations were made by the potentiometric method and the new "galvanometric" method. The outstanding fact of such determinations was that in every instance the end-point determined with the galvanometer checked exactly with the potentiometer end-point; that is, the same drop of reagent produced the greatest relative change with both systems.

In order to determine whether the presence of the Pt-W system caused any change in the position of the end-point, determinations were made with the standard (Pt-N calomel) method alone. The errors thus found were no greater than the natural experimental errors; in fact, deviations from the average were as great for the standard method as for the galvanometer method.

Permanganate-Ferrous Sulfate Reaction

A preliminary orientation study showed that the Pt-W system gave excellent results. The galvanometer deflections at the end-points were large. There was, in every case, agreement with the usual potentiometric end-point.

Bichromate-Ferrous Sulfate

The solutions that were titrated contained 10–15 cc. of 12 *N* hydrochloric acid or 25 cc. of 6 *N* sulfuric acid in a total volume of 45–75 cc. Assuming that the average values obtained with the Pt-N calomel system were correct the errors found in the titration of 0.1 *N* bichromate were: +0.07, ±0.00, +0.04, +0.05, +0.06 cc. of 0.1 *N* ferrous sulfate. In these and subsequent determinations the amounts of solution that were pipetted out ranged from 10 to 50 cc.; the resistance was approximately 70,000 ohms. The end-point deflections per 0.05 cc. of reagent were 7–9 galvanometer divisions in hydrochloric and 3–5 divisions in sulfuric acid solution. In the reverse titration the errors found were: −0.04, +0.02, −0.06, ±0.00, ±0.00 cc. of 0.1 *N* bichromate. The end-point breaks were less pronounced than in the reverse titrations, being about 5 divisions in hydrochloric and about 4 in sulfuric acid solutions. The calculated cc. of bichromate are the average of three concordant determinations (Pt-N calomel).

The data for more dilute (0.05 *N*) solutions are presented in Tables I and II.

TABLE I

TITRATION OF FERROUS SULFATE WITH APPROXIMATELY 0.05 *N* BICHROMATE

	1	2	3	4	5	6	7
Bichromate, calcd. cc.	23.07	23.07	23.07	23.07	23.07	9.22	46.14
Bichromate found, cc.	23.10	23.03	23.09	23.09	23.11	9.27	46.18
Error, cc.	+0.03	−0.04	+0.02	+0.02	+0.04	+0.05	+0.04
Resistance, 1000-ohm units	58	58	40	100	50	58	58
Galvanometer defl. div. at end-point per 0.05 cc.	4.9	3.1	3.0	1.5	3	3.9	1.5

Acid present: Nos. 1, 2, 25 cc. of 6 *N* H_2SO_4; Nos. 3–7, 10–15 cc. of 12 *N* HCl. Initial volume, 50–65 cc.

Large variations in the resistance, therefore, do not change the order of magnitude of the sensitivity of the method.

TABLE II

TITRATION OF BICHROMATE WITH APPROXIMATELY 0.05 *N* FERROUS SULFATE

	1	2	3	4	5	6
Ferrous sulfate found (Pt-W), cc.	27.17	27.14	10.94	37.94	27.16	37.98
Ferrous sulfate found (Pt-N calomel)	27.17	27.14	...	...	...	...
Ferrous sulfate calcd.	...	...	10.86	37.99	27.16	37.99
Error, cc.	...	...	+0.08	−0.05	+0.00	−0.01

The general conditions were those of Table I except that the resistance was 58,000 ohms.

Unfortunately no independent comparisons of the bichromate and ferrous sulfate by the usual potentiometric method had been made within several hours of the time when these determinations were carried out. One of us (F.) made up solutions Nos. 3–6, and the other (W.) made the titrations without any knowledge as to the relative strengths of the solutions.

The Iodine-Thiosulfate Reaction.—The solutions were approximately 0.1 *N*.

TABLE III

TITRATION OF THIOSULFATE WITH IODINE (APPROXIMATELY 0.1 *N*)

	1	2	3	4
Iodine calcd., cc.	26.69	26.69	26.69	26.69
Iodine found, cc.	26.68	26.64	26.69	26.70
Error, cc.	−0.01	−0.05	±0.00	+0.01

The calculated values are the average of several concordant determinations with starch as indicator. The resistance was 86,000 ohms. The reverse titration was studied by simultaneous determinations with Pt-W, Pt-N calomel and starch. All three methods gave the same end-point within 0.05 cc. It is perhaps worth noting that in a few instances the electrical end-point by either system was a distinct fraction of a drop different from the color end-point. It appears that minute traces of iodine loosely combined with starch do not affect the electrodes as would free iodine. There appeared to be no immediate diffusion of iodine out of the complex, because the color remained faint blue while the potential was decidedly on the reducing side. The galvanometer deflections, per fraction of a drop of reagent at the end-point, were very large. Occasionally the change was distributed over two drops of reagent. The maximum rate of change per drop invariably checked with the potentiometer.

The Vanadic Acid-Ferrous Sulfate Reaction.—A 0.05597 *N* vanadic acid solution that had been standardized potentiometrically was used. The solution contained 30 cc. of sulfuric acid sp. gr. 1.84, per liter. In instances marked with an asterisk (*) the quantity of vanadic acid was unknown to the operator.

TABLE IV

TITRATION OF 0.05597 *N* VANADIC ACID WITH FERROUS SULFATE

	1	2	3	4*	5*	6*	7*
$FeSO_4$ calcd., cc.	28.76	28.76	28.76	28.76	11.61	11.61	11.61
$FeSO_4$ found, cc.	28.77	28.72	28.70	28.75	11.50	11.62	11.61
Error, cc.	+0.01	−0.04	−0.06	−0.01	−0.11	+0.01	±0.00

NOTE.—Some time elapsed between determinations No. 4 and 5, and the ferrous sulfate was restandardized. The resistance was 58,000 or 30,000 ohms. The initial volumes ranged from 35–50 cc., with either 5–10 cc. of concd. HCl, or 25 cc. of 6 *N* H_2SO_4 present.

The galvanometer deflections were the smallest per drop of reagent at the end-point of any case thus far investigated. The sensitivity was somewhat increased by dropping the resistance to 30,000 ohms.

Discussion

The chief possible source of error in this method seems to be the continuous production of current, which must occur at the expense of some reaction in the solution. Assuming that all of the current drawn is produced by the reduction of the oxidant (and this is not necessarily the sole source of current), and assuming that 10 galvanometer divisions represent 5 micro-amperes, it appears that this deflection could be maintained for one hour at the expense of about 0.05 cc. of 0.1 *N* reagent. Only a few minutes are required for the titration.

The relation of the potential difference between Pt-W and the difference between each wire and a N-calomel electrode is shown for a typical instance in Fig. 2. The slight current that is drawn does not affect the graph of the readings Pt vs. N calomel to any very considerable extent.

The authors have not thus far attempted to secure new evidence to establish the theoretical basis of the method. Analogous phenomena (persistent differences in oxidation potential) have been reported.[4] The gen-

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[4] Van Name and Fenwick, THIS JOURNAL, **47**, 11 (1925).

eral characteristics of the Pt-W systems have been previously studied.[5] It is planned to study the behavior of the Pt-W system further to see how far polarization effects account for the phenomena observed, and to study this and other systems in conjunction with vacuum tube amplifiers. Preliminary experiment has shown that polarization effects due to grid current may play an important role in its application.

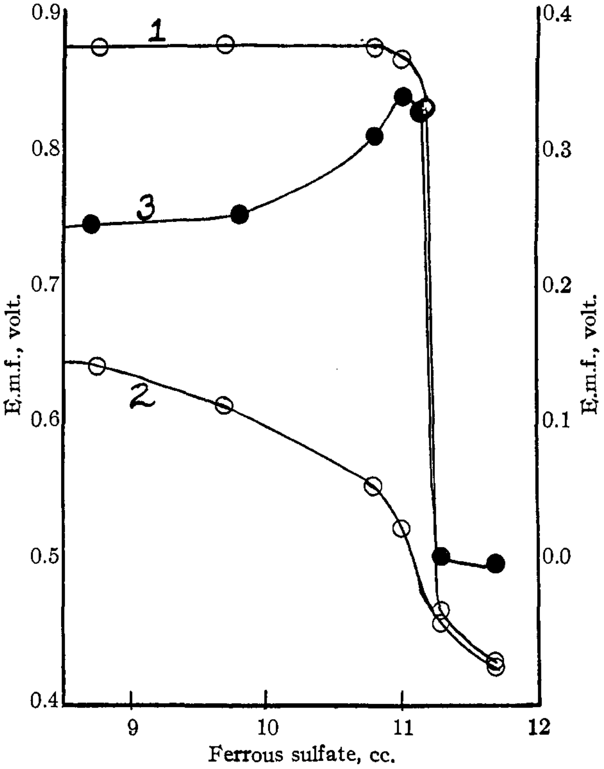

Fig. 2.—Titration of 0.1 *N* bichromate with ferrous sulfate. Ordinates for (1) and (2) at left. (1) Curve for Pt-N calomel, (2) for W-N calomel and (3) for Pt-W system, showing the sharp break at the end-point (ordinates of (3) at right of figure).

In the interactions between substances that are sufficiently far removed in the oxidation potential scale, there is a very close superficial analogy between the end-point indication in the present method and the excellent indication that is given by the method of Foulk and Bawden.[6] In the latter method, however, the high galvanometer readings are not always on the oxidizing side of the end-point.

[5] Willard and Fenwick, THIS JOURNAL, **44**, 2508 (1922).

[6] Foulk and Bawden, *ibid.*, **48**, 2045 (1926).

The authors intend to study the application of the "Galvanometric" method to other reactions than those studied.

Summary

This paper describes a simple, direct reading and inexpensive system for determining end-points of oxidation-reduction reactions. The method depends upon the sudden change at the end-point in the potential difference between a platinum and a tungsten electrode which are immersed in the solution.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THEORY OF THE SORET EFFECT

BY E. D. EASTMAN

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In a previous paper[1] a thermodynamic theory of the reversible Soret effect was given. It was there shown that the effect is related in magnitude to the heat of transfer of the constituents of the solutions in which it is manifested. Consideration of the nature of the latter quantity leads to a number of conclusions concerning general questions not yet experimentally settled. These inferences, and the views on which they are based, render intelligible many obscure features in this very uncertain field and offer guidance to further progress in it. They will, therefore, be outlined in this paper.

Definitions and Thermodynamic Relations

When a portion of one of the constituents of a solution is transferred by diffusion, or in the case of ions by an applied electric field, from one region to another within the solution, there is in general an accompanying absorption of heat from the surroundings of one region and evolution in those of the other. The quantity of heat absorbed from the surroundings of the region (of infinite extent) from which one mole of constituent A is transferred will be denoted by Q_A^*.[2] The entropy lost by the surroundings of the region from which the transfer is made is then $Q_A^*/T = S_A^*$. These quantities will be referred to as the heat and entropy of transfer, respectively. Their nature will be discussed in detail later.

In the former paper it was shown that in a binary solution placed in a temperature gradient the equilibrium compositions due to reversible effects are governed by the equation

$$(\partial \overline{F}_A/\partial N_A)_T \, \mathrm{d}N_A = -S_A^* \, \mathrm{d}T \tag{1a}$$

or

$$(\partial \overline{F}_A/\partial \ln N_A)_T \, \mathrm{d} \ln N_A = -S_A^* \, \mathrm{d}T \tag{1b}$$

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[1] Eastman, THIS JOURNAL, **48**, 1482 (1926).

[2] In the previous paper, ref. 1, $\overline{Q}_A$ was used as the symbol for the heat of transfer. To avoid confusion with the partial molal quantities in the case of entropy it seems better to adopt the symbols above.