Discussion

A number of incidental observations have been made upon the use of the amalgamated gold electrode in other oxidation-reduction reactions. The results were satisfactory in all instances. Six different electrodes, three of foil and three of gold wire, were used in the progress of the work. All served satisfactorily. The especial advantages of these electrodes are their simplicity and the fact that in solutions that contain chloride the voltage readings are very close to those that are obtained with the familiar Pt-N. C. E. system.

Preliminary observations have shown that the amalgamated gold electrode may be used in following neutralizations of hydrochloric or sulfuric acid; also that such electrodes serve as indicator electrodes for certain precipitation reactions, for instance, precipitation of halides with silver, or vice versa. It is planned to make a detailed study of some of these possible applications of gold amalgam as an indicator electrode.

Summary

A small amalgamated gold electrode has been shown to be a suitable reference electrode for several kinds of potentiometric oxidation-reduction titrations with reagents as dilute as 0.05 *N*.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

SIMPLE BIMETALLIC ELECTRODE SYSTEMS FOR POTENTIOMETRIC TITRATIONS. II. NOTES ON THE USE OF THE PLATINUM-GOLD ELECTRODE SYSTEM

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Introduction

A knowledge of the platinum-gold system was found to be desirable in connection with a study of the platinum-gold amalgam electrode system that has been described in the former communication.[1] The construction of electrodes, electrical apparatus, and mode of procedure were there described.

Experimental

Titration of Permanganate with Ferrous Sulfate.—The general form of the graph of the titration data is indicated in Fig. 1. There is always a sharp rise to a "peak" in e.m.f. just before the end-point. The position of this peak is extremely variable (see Table I). The drop in voltage at the end-point is unmistakable.

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[1] Furman, THIS JOURNAL, 50, 268 (1928).

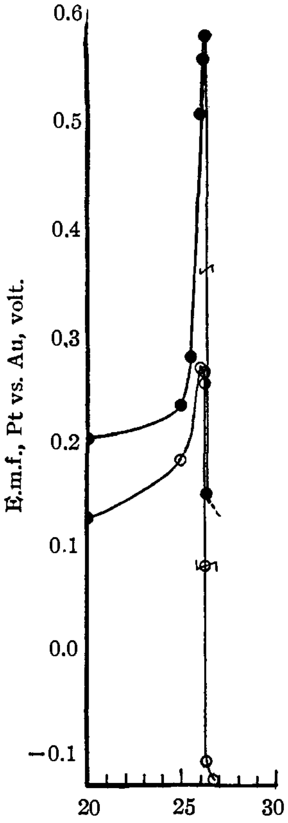

Fig. 1.—Characteristic curves, permanganate-ferrous sulfate reaction, followed by Pt-Au system, showing variability of peak of e.m.f.

Table I

Titration of Approximately 0.05 *N* Permanganate with Ferrous Sulfate

No.	$FeSO_4$ calcd., cc.	$FeSO_4$ found, cc.	Error, cc.	Difference in voltage, Pt vs. Au (a) Initial	(b) Maximum	(c) Break at end-point (1 or 2 drops)
1	26.32	26.30	−0.02	0.180	0.671	0.496 (1 drop) $FeSO_4$
2	26.32	26.28	− .04	.153	.622	.482 $FeSO_4$
3	26.32	26.26	− .06	.175	.330	.454 $FeSO_4$
4	26.32	26.33	+ .01	.150	.279	.386 { 0.186 1st drop .200 2nd drop
5	10.52	10.46	− .06	.169	.424	.482 { .305 1st drop .177 2nd drop
6	10.52	10.58	+ .06	.177	.392	.486 1 drop
7	10.52	10.53	+ .01	.186	.340	.455 1 drop

The initial volume was 50 cc. in each case, with 25 cc. of 6 *N* sulfuric acid present.

The precautions noted by Müller and Möllering[2] were carefully followed in order to avoid formation of any appreciable amount of manganese dioxide.

The Bichromate-Ferrous Iron Reaction.—The ferrous sulfate solutions were frequently restandardized by potentiometric titration with potassium bichromate. The results of the titrations using the Pt-Au electrode system are presented in Tables II–IV.

TABLE II

TITRATION OF APPROXIMATELY 0.05 *N* BICHROMATE WITH FERROUS SULFATE

	Ferrous sulfate			E.m.f. difference, Pt vs. Au		
No.	Calcd., cc.	Found, cc.	Error, cc.	(a) Initial	(b) Maximum	(c) Break per 1 drop of $FeSO_4$
1	26.16	26.11	−0.05	0.144	0.176	0.187
2	26.16	26.11	− .05	.246	.315	.200
3	26.16	26.13	− .03	.241	.332	.211
4	26.16	26.19	+ .03	.218	.427	.270
5	26.16	26.17	+ .01	.207	.368	.122

In determinations 1, 4 and 5, 5 cc. of concd. sulfuric acid (sp. gr. 1.84) and in nos. 2 and 3, 10 cc. of hydrochloric acid of sp. gr. 1.2 were present. The initial volume was 50 cc.

The determinations in Tables III and IV were made by Mr. H. H. Carspecken, to whom the author wishes to express his indebtedness.

TABLE III

TITRATION OF APPROXIMATELY 0.1 *N* FERROUS SULFATE WITH BICHROMATE

	Bichromate					
No.	Calcd., cc.	Found, cc.	Error, cc.	H_2SO_4 of sp. gr. 1.84, cc.	Initial volume, cc.	Voltage break per 1 drop of reagent
1	48.26	48.25	−0.01	10	100	0.091
2	9.66	9.65	− .01	2	40	.175
3	9.66	9.65	− .01	2	40	.169
4	24.13	24.18	+ .05	5	50	.050
5	24.13	24.15	+ .02	5	50	.108

TABLE IV

TITRATION OF APPROXIMATELY 0.1 *N* BICHROMATE WITH FERROUS SULFATE

	Ferrous sulfate			E.m.f. difference, Pt vs. Au		
No.	Calcd., cc.	Found, cc.	Error, cc.	(a) Initial voltage	(b) Maximum voltage	(c) Break per drop of reagent at end-point
1	51.84	51.80	−0.04	0.203	0.495	0.287
2	25.92	26.00	+ .08	.220	.560	.340
3	10.36	10.35	− .01	.300	.505	.315
4	10.36	10.35	− .01	.293	.503	.313

From 2–10 cc. of sulfuric acid (sp. gr. 1.84) was present. Initial volume 100 cc. in no. 1 and 50 cc. in nos. 2–4.

Discussion

The Pt-Au system appears to be capable of use in solutions that are as dilute as 0.05 *N*.

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[2] Müller and Möllering, *Z. anorg. allgem. Chem.*, 141, 111 (1924).

The general features of the graphs of the titration data are shown in Fig. 2. It will be noted that there is no pronounced peak in the curve for the titration of bichromate in hydrochloric acid solution. The very marked rise that is observed with sulfuric acid solutions appears to be a composite of the usual anomalous rise in potential at the Pt electrode[3] and the fall at the gold electrode. This was found to be true by following the changes at each electrode with the aid of an auxiliary reference electrode (see curves 3, 4 and 5, Fig. 2).

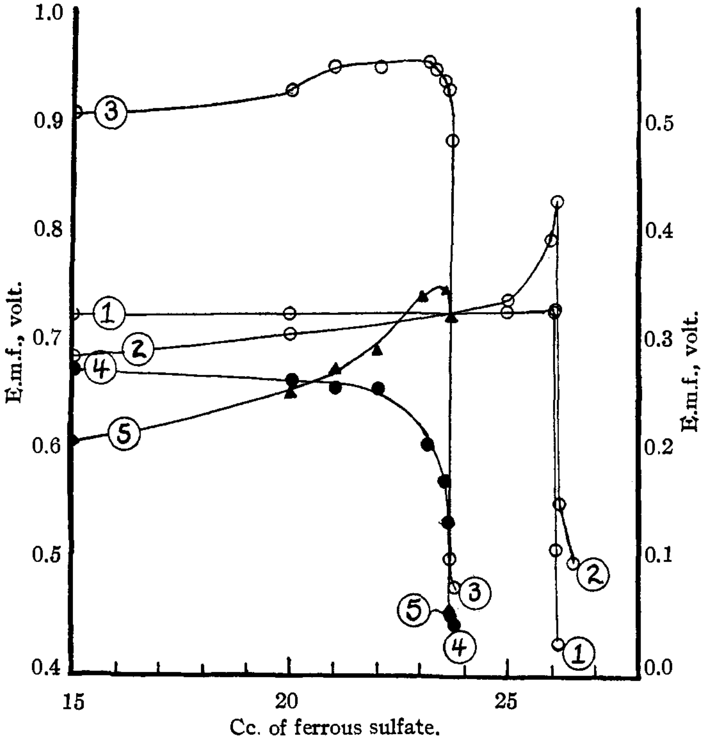

Fig. 2.—Titration of bichromate with ferrous sulfate (Pt-Au system). (Ordinates for 1, 2 and 5 at right; 3 and 4 at left.) Curve (1) 25 cc. of approximately 0.05 *N* bichromate titrated in hydrochloric acid solution. Curve (2) similar to (1) except that sulfuric acid was present. Curves (3, 4, 5) are from data of a single titration of 0.1 *N* bichromate with ferrous sulfate. (3) Pt-N. C. E. system. (4) Au-N. C. E. (5) Pt-Au system; (5) is a composite of (3) and (4).

The chief disadvantage of the Pt-Au system is the variable nature of the readings. The initial and maximum voltages show wide variations in magnitude for the same type of titration, so that it is difficult to judge

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[3] Forbes and Bartlett, This Journal, 35, 1527 (1913).

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.

PRINCETON, NEW JERSEY

[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.