six elements dysprosium, holmium, erbium, thulium, ytterbium and lutecium come in order of atomic number into Group III A, Series 10. These metals are typically tervalent and each of them could be placed in this position. If the reasons given above be accepted, these six elements must all go into this position. Between lutecium (71) and tantalum (73) in Series 10, there is still a vacant place in group IV A into which hafnium (72) naturally goes. The scheme presented places the whole of the elements of the rare earth group into Mendeléeff's periodic system without destroying its symmetry or impairing its utility in the slightest. It is difficult to submit the scheme to a rigorous test because many essential data are lacking; but a broad line taken through the existing chemical and physical data confirms, in general, the present arrangement.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

SIMPLE BIMETALLIC ELECTRODE SYSTEMS FOR POTENTIOMETRIC TITRATIONS. I. THE APPLICATION OF THE PLATINUM-GOLD AMALGAM SYSTEM TO CERTAIN OXIDATION-REDUCTION TITRATIONS

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Introduction

Hostetter and Roberts[1] suggested the possibility of substituting a palladium wire for the calomel half-cell that is generally used as a reference electrode in potentiometric titrations. Willard and Fenwick[2] have studied a large number of possible systems that consist of two dissimilar metallic electrodes. They did not, however, study amalgamated electrodes.

This investigation grew out of a study of certain platinum electrodes that were unintentionally "poisoned" with mercury. These electrodes behaved temporarily like mercury electrodes. It has not thus far been found possible to prepare amalgamated platinum electrodes that serve over long periods of time as mercury electrodes.

Amalgamated gold electrodes were found to behave like calomel electrodes in solutions that contained chloride and like mercurous sulfate electrodes in solutions that contained sulfate. During the course of most oxidation-reduction titrations the concentration of chloride or sulfate varies. Nevertheless, an amalgamated gold electrode will serve as a satisfactory reference electrode for such titrations. The reducing action of the minute quantity of mercury or gold that is in contact with

[1] Hostetter and Roberts, THIS JOURNAL, 41, 1343 (1919).

[2] Willard and Fenwick, *ibid.*, 44, 2504 (1922).

the solution does not occasion any systematic error when the reagents are as dilute as 0.05 *N*.

Experimental

Electrodes.—The gold amalgam electrodes were of the construction indicated in Fig. 1. The Bakelite block, e (6 × 3 × 0.5 cm. drilled with 6 holes of 0.45 cm. diameter), was found to be a very convenient support that permitted ready interchange of electrodes. Gold of C. P. grade from two sources (foil 0.23 mm. thick from the United States Mint and wire of 0.33 mm. diameter (28 gage B. and S.) from Baker and Co., Inc., Newark, N. J.) was used. A momentary immersion of the exposed gold tip in pure mercury effected the amalgamation. It was not found advisable to put a drop of mercury within the tube because of leakage of mercury through the gold. Molten paraffin was poured into the glass tubes (see Fig. 1) as a safeguard against leakage. (A number of electrodes served satisfactorily for long periods without the paraffin seal.) The amalgamated tip is immersed in dilute hydrochloric acid when the electrode is not in use. Electrodes that dry in air become sluggish. They may be reactivated by wiping the amalgamated tip and dipping it anew in mercury.

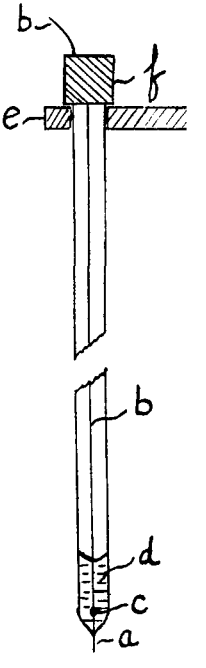

Fig. 1.—Amalgamated gold electrode. (a) Amalgamated tip of a gold wire that is sealed through the glass. Soft glass was used and care was taken not to fuse the gold. (b) Copper wire fused to gold at point (c). The upper end of (b) is wrapped around the glass tube and is held in position by rubber tubing (f). The shaded portion (d) represents paraffin.

It was found by heating portions of the tips of a number of electrodes that the initial percentage of mercury was between 15 and 20. It was anticipated that the reducing action of the mercury might be objectionable. McCay and Anderson[3] have shown that ferric iron, chromic acid, vanadic acid and other oxidizing agents are reduced quantitatively to lower states of oxidation when shaken with a large excess of mercury in the presence of a suitable amount of chloride. The tips of the electrodes that dipped into the solutions contained at most 2 mg. of mercury—a quantity capable of reducing only 10^{-5} g. equivalent, or 0.01 cc. of *N* solution. Only a small part of the 2 mg. or less of mercury is actually in contact with the solution. After a large number of titrations mercury is still visible in the electrodes.

There was a relatively large unintentional variation in the total time of titration. In a few instances that were noted as long as twenty minutes elapsed between the time that the solution was first stirred in contact with the electrodes and the start of the titration with ferrous sulfate. In a number of other instances interruptions occurred after a titration had proceeded a short distance. It was not necessary to reject any determinations that were interrupted nor was any definite trend due to this cause noted.

Thus far no tests have been made of the effectiveness of the Pt-Hg(Au) system with reagents more dilute than 0.05 *N*.

[3] McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921); **44**, 1018 (1922).

Apparatus.—A Leeds and Northrup Co. students' type potentiometer and a portable galvanometer (type 2320 d) of 0.5 micro-ampere sensitivity were used.[4] All volumetric apparatus had been carefully calibrated.

Procedure.—Tenth or 0.05 *N* solutions of oxidizing and reducing agents were standardized potentiometrically. Anhydrous sodium oxalate of known purity was the primary standard. Bichromate and permanganate solutions were compared by as nearly as possible simultaneous potentiometric titrations of portions of a solution of Mohr's salt.

Titrations with the usual system[5] were interspersed with those made with the Pt-Hg(Au) combination. No attempt was made to free the solutions from dissolved air by working in an inert atmosphere. This may affect the accuracy of the results with the 0.05 *N* solutions but should not affect the precision of the comparison of the two electrode systems because both sets of titrations were made under as nearly as possible identical conditions.

The Bichromate-Ferrous Iron Reaction.—The average of at least three concordant determinations by the usual potentiometric method was assumed to be correct. The volume was 100 cc. at the start of each titration. The general conditions that were employed will be evident from Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *N* POTASSIUM BICHROMATE WITH FERROUS SULFATE

	1	2	3	4	5	6
I. Cc. of $FeSO_4$ (Pt-N. C. E.)	10.00	10.00	25.01	25.01	25.01	25.01
II. Cc. of $FeSO_4$ (Pt-Hg(Au))	10.04	10.04	24.98	25.00	24.98	24.96
Difference (II–I)	+0.04	+0.04	−0.03	−0.01	−0.03	−0.05
Acid present, cc. { 12 *N* HCl	15	15	15	15	...	...
Acid present, cc. { 6 *N* H_2SO_4	...	...	...	...	25	25

The reverse titration was then studied, varying the experimental conditions in a similar manner. The differences in quantities of bichromate that were found by using the two systems were: +0.07, +0.02, +0.03, −0.04, +0.02, −0.03, −0.05 and +0.02 cc. of 0.1 *N* potassium bichromate.

Further comparisons of the two systems were made with 0.05 *N* solutions; differences found: cc. of 0.05 *N* $FeSO_4$: +0.01, +0.02, −0.03, −0.02, +0.01 and −0.05; and in the reverse titration the differences were cc. of 0.05 *N* $K_2Cr_2O_7$: −0.07, −0.04, +0.02, −0.06, −0.02, +0.04 and +0.01.

The values in Table I, and the paragraphs that follow it, have been

[4] For further details of the apparatus, see Furman, *J. Chem. Education*, **3**, 936 (1926).

[5] Hereafter designated as Pt-N. C. E. When necessary a salt bridge of *N* potassium sulfate solution was interposed between the normal calomel electrode and the titration beaker.

calculated to cc. of exactly 0.1 or 0.05 *N* solution. The actual normalities of the bichromate solutions were 0.1000 and 0.05098. The substitution of the amalgamated gold electrode for the *N* calomel electrode does not cause any systematic error. The average deviation of the values from the mean is practically the same with both systems.

Graphs that are constructed from the titration data show some interesting features. When the solutions contain chloride, the curves (Pt-Hg(Au) system) are very similar to those that are obtained with the Pt-N.C.E. system. They are merely displaced upward on the e.m.f. axis (see Fig. 2) because the chloride concentration is usually greater than *N*.

In solutions that contain sulfuric acid and sulfates, the curves resemble closely those obtained with Pt-*N* potassium sulfate-*N* mercurous sulfate system. When the surface of the electrode becomes depleted of mercury by long use, the curves representing the titration of bichromate with ferrous sulfate show a pronounced sweep upward before the end-point. This is characteristic of the Pt-Au system.[6]

The Permanganate-Ferrous Iron Reaction.—The permanganate solutions were 0.0518 and 0.0510 *N*, respectively. The values found have been calculated to cc. of exactly 0.05 *N* solutions. A salt bridge of *N* potassium sulfate solution was interposed between the *N* calomel cell and the titration beaker.

In the titration of ferrous sulfate with permanganate the differences, expressed in cc. of 0.05 *N* potassium permanganate, were: +0.01, −0.03, −0.06, −0.05, −0.03 and ±0.00.

[6] A detailed study of the Pt-Au system is presented in the second paper of this series, THIS JOURNAL, **50**, 273 (1928).

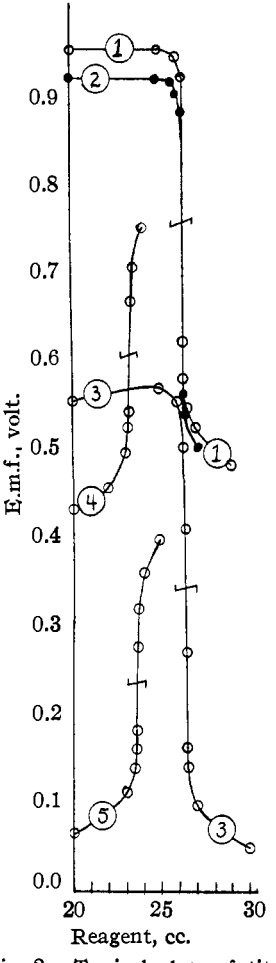

Fig. 2.—Typical plots of titration data. Curves 1, 2 and 3 represent the titration of 25cc. portions of 0.1000 *N* $K_2Cr_2O_7$ with an approximately 0.1 *N* ferrous sulfate solution, first with Pt-Hg(Au) system, second with Pt-N. C. E., both in HCl solution, and the third with the Pt-Hg(Au) system in H_2SO_4 solution. Curve (4) represents titration of 25 cc. of approximately 0.05 *N* $FeSO_4$ in HCl solution and (5) titration of 25 cc. of approximately 0.1 *N* $FeSO_4$ in H_2SO_4 solution with the Pt-Hg (Au) system. Bichromate was the oxidant in both cases.

The data for the reverse titration are presented in Table II.

TABLE II

TITRATION OF APPROXIMATELY 0.05 *N* PERMANGANATE WITH FERROUS SULFATE

	1	2	3	4	5
I. Cc. of $FeSO_4$ (Pt-N. C. E.)	25.50	25.50	25.50	10.20	10.20
II. Cc. of $FeSO_4$ (Pt-Hg(Au))	25.51	25.51	25.44	10.18	10.21
Difference (II−I)	+0.01	+0.01	−0.06	−0.02	+0.01

In each instance the initial volume was 50 cc., containing 25 cc. of 6 *N* H_2SO_4.

The potentiometric titration of permanganate with ferrous sulfate must be carried out under the conditions that were established by Müller and Möllering.[7] They found that the acid concentration must be sufficiently high and that the ferrous sulfate must be added rapidly until the end-point is closely approached. The permanganate color disappears a few drops before the end-point is reached. The work of Müller and Möllering explains this fact in terms of the reactions

$$Mn^{VII} + 3Fe^{II} = Mn^{IV} + 3Fe^{III}, \text{ and} \quad (1)$$
$$Mn^{IV} + 2Fe^{II} = Mn^{II} + 2Fe^{III} \quad (2)$$

that occur simultaneously. The author's experience is entirely in accord with these views. It was found, for example, that slow addition of ferrous sulfate to 25 cc. of 0.05 *N* permanganate in a volume of 100 cc. containing 25 cc. of 6 *N* sulfuric acid caused a very considerable separation of manganese dioxide (Equation 1). All determinations in which there was any visible precipitation of manganese dioxide were inaccurate.

The Vanadic Acid-Ferrous Sulfate Reaction.—The normality of the vanadic acid solution was established by titration with ferrous sulfate that had been titrated potentiometrically with standard permanganate solution. Found: vanadic acid 0.05596 *N* (average) by the potentiometric method, and 0.05597 *N* (average) when diphenylamine was used as indicator.[8,9]

TABLE III

TITRATION OF 0.05597 *N* VANADIC ACID WITH 0.0488 *N* FERROUS SULFATE

	1	2	3	4	5
Cc. of vanadic acid	25	25	25	25	10
$FeSO_4$ calcd., cc.	28.67	28.67	28.67	28.67	11.46
$FeSO_4$ found, cc.	28.62	28.68	28.70	28.66	11.50
Error, cc.	−0.05	+0.01	+0.03	−0.01	+0.04

In nos. 1–2, 15 cc. of concd. HCl (sp. gr. 1.2), and in nos. 3–5, 25 cc. of 6 *N* sulfuric acid were present. The initial volume was 50 cc. in each determination.

The graphs of the titration data present no unusual features.

[7] Müller and Möllering, *Z. anorg. allgem. Chem.*, **141**, 111 (1924).
[8] Someya, *ibid.*, **139**, 237 (1924); **152**, 391 (1926).
[9] Furman, *Science*, **59**, 560 (1924); *Ind. Eng. Chem.*, **17**, 314 (1925).

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*.

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[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.

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