

been investigated. In presence of sufficient hydrofluoric acid in proportion to sulfuric or hydrochloric acid, diphenylamine is an excellent indicator for this titration. The presence of diphenylamine does not prevent an accurate determination of the total iron in the solution by a reduction titration with titanous chloride and thiocyanate indicator, following the oxidation titration, provided the hydrofluoric acid necessary in the first titration is inactivated by addition of excess boric acid prior to the second.

Potentiometric titration curves show that the pronounced effect of hydrofluoric (also phosphoric) acid in increasing the sharpness of the diphenylamine end-point in iron titrations is due to a lowering of the oxidation potential in a solution containing both ferrous and ferric ions, which is high enough under the usual conditions of the titration to cause the indicator color to develop prior to complete oxidation of the iron. The effect of these reagents upon the thiocyanate end-point in the reduction titration and upon the color of solutions containing ferric salts indicates that the underlying cause is the slight dissociation of ferric fluoride (or phosphate).

Based upon these observations, an improved procedure for the determination of ferrous and ferric oxides in silicates is described. Manganese does not interfere in the dichromate titration with diphenylamine in the presence of hydrofluoric acid, but it is shown that in the presence of organic matter results for ferrous oxide may be expected to be high in proportion to the amount of ferrous oxide actually present.

WOOSTER, OHIO

---

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 271]

## THE REDUCTION POTENTIAL OF THE CERIC-CEROUS ELECTRODE

By ADOLF H. KUNZ<sup>1</sup>

RECEIVED NOVEMBER 6, 1930

PUBLISHED JANUARY 12, 1931

### Introduction

The only work upon the reduction potential of the ceric-cerous electrode recorded in the literature is the early research of Bauer and Glaessner,<sup>2</sup> which involved several factors that diminished its accuracy and reliability. Thus the measurements were made at room temperature, no statement being made about its constancy, and a saturated solution of potassium chloride was used to eliminate liquid potentials. In view of these imperfections and of the recent interest in the use of ceric sulfate solutions for analytical work,<sup>3,4</sup> it seemed advisable to make a thorough study of the

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> Bauer and Glaessner, *Z. Elektrochem.*, 9, 534 (1903).

<sup>3</sup> Willard and Young, *THIS JOURNAL*, 50, 1322 (1928), *et seq.*

<sup>4</sup> Furman, *ibid.*, 50, 755 (1928), *et seq.*

ceric-cerous potential under a wider range of carefully controlled conditions.

The cell studied may be represented as follows

$\text{Pt} + \text{H}_2, \text{H}_2\text{SO}_4 (0.5 \text{ or } 1.0 f), \text{H}_2\text{SO}_4 (0.5 \text{ or } 1.0 f) + \text{Ce}_2(\text{SO}_4)_3 (c_1) + \text{Ce}(\text{SO}_4)_2 (c_2), \text{Pt}$

There are in this cell three sources of potential: the potential of the hydrogen electrode against sulfuric acid, the potential of the ceric-cerous electrode, and the liquid potential. By making the concentration of the sulfuric acid in both half-cells the same and making the concentration of the sulfates of cerium small, the liquid potential was made negligible.

The author wishes to express appreciation for the suggestions and interest of Professor A. A. Noyes during the progress of the research and for his assistance in preparing this paper for publication.

### Apparatus and Materials

The apparatus was essentially that used by Popoff and Kunz<sup>5</sup> in studying the ferric-ferrous electrode. An all-glass electrode vessel was used as before, but the chambers were made smaller to facilitate a more rapid saturation of the acid with hydrogen in the hydrogen half-cell. Instead of a rotary stirrer in the cerium half-cell, the solution was stirred by blowing in an inert gas.

The cell was placed in a thermostat at 25.00° maintained constant within 0.01°. A Leeds and Northrup Type K potentiometer was used.

The hydrogen for the hydrogen electrode was generated by electrolyzing a 5% solution of sodium hydroxide between a nickel and a platinum electrode. The gas was passed through a purifying train and a saturator before entering the cell.

All chemicals with the exception of the cerium salts were of the best grade obtainable and were used without further purification. The water had been redistilled.

The cerium salt was prepared from a commercial cerium oxalate. An analysis by the bismuthate method of Metzger<sup>6</sup> of the ignited oxides obtained from this material showed them to contain less than 48%  $\text{CeO}_2$ . Assuming that all other rare earths and thorium, iron and calcium might be present, a number of methods were used in attempts to prepare the pure ceric oxide needed.

The best results were obtained by the basic ceric nitrate-bromate process.<sup>7</sup> The crude oxalate was partially ignited to  $\text{CeO}_2$ , and the residue was moistened with water and treated with nitric acid. The undecomposed oxalate helps reduce the ceric oxide to cerous nitrate. Oxalic acid was added until most of the material was reduced, and the reduction was completed with hydrogen peroxide.

After filtration and evaporation to small bulk to eliminate the large excess of nitric acid, the solution was diluted, potassium bromate was added, and the mixture was boiled until fumes of bromine were evolved. Marble was then added in large pieces, and the boiling was continued with the occasional addition of a little nitric acid. Even with this precaution the precipitate was not free from other rare earths. In the later attempts the basic salt was filtered off and digested for thirty minutes with very dilute nitric acid. Two applications of the entire process were required to produce an oxide which, when converted to the sulfate, would dissolve completely in water.

The purified basic salt was dissolved by nitric acid and oxalic acid and the solution

<sup>5</sup> Popoff and Kunz, *THIS JOURNAL*, 51, 382 (1929).

<sup>6</sup> Metzger, *ibid.*, 31, 523 (1909).

<sup>7</sup> James and Pratt, *ibid.*, 33, 1326 (1911).

filtered. Cerous oxalate was then precipitated and thorium was removed by digesting the precipitate with ammonium oxalate solution. The oxide prepared by ignition of this oxalate was very pale yellow.

A weighed portion of the oxide was heated to fuming with sulfuric acid for an hour. The sulfate went into solution in water slowly, but completely. An analysis of this solution made by titration with standard ferrous sulfate after oxidation with persulfate with silver ion as a catalyst as recommended by Willard and Young<sup>8</sup> showed the product to contain 99.89% of cerium dioxide. This is within the limits of the experimental precision obtained in the analyses.

**Preparation of Solutions.**—A large quantity of the purified ceric oxide was converted to the sulfate by heating it with concentrated sulfuric acid. The solution was diluted to a volume in which the total cerium content was about 0.07 formal and the sulfuric acid about 0.75 formal. The total cerium content per gram of solution was then determined by standard ferrous sulfate after oxidation by persulfate. Similarly, the ceric content was determined by direct titration with standard ferrous sulfate. All titrations were made electrometrically. The close agreement observed between the ceric and the total cerium concentrations indicated that there is very little auto-reduction of the ceric sulfate solutions. Analyses of ceric sulfate solutions in sulfuric acid concentrations used in this study over a period of several months bear out the observations of Willard and Young and of Furman that ceric sulfate solutions are remarkably stable. The total sulfate concentration per gram of solution was then determined gravimetrically after dilution by weight. From these values the amount of water (or of more concentrated sulfuric acid) required to make the formality of the sulfuric acid exactly 0.5 (or any other value) was calculated.

Cerous sulfate solution was prepared by reducing ceric sulfate solution with hydrogen peroxide, crystallizing out the salt by concentration, and washing it free from peroxide. This salt was then dissolved in sulfuric acid, and the solution was diluted to the extent required.

**The Electromotive Forces and Electrode Potentials.**—The electromotive force  $E$  of the cells can be expressed as follows

$$E = E_0 - 0.0591 \log \frac{P_H (Ce^{IV}) \alpha^{IV}}{a_{H^+} (Ce^{III}) \alpha^{III}}$$

The data are given in Table I. Here the "observed" electromotive force represents the electromotive force of the cells as measured at 25°, and the "corrected" electromotive force represents this value corrected to a hydrogen pressure of one atmosphere and to a value of the ratio  $(Ce^{IV})/(Ce^{III})$  equal to unity. The only other variable within any series of experiments in which the acid concentration is constant should then be the activation ratio  $\alpha^{IV}/\alpha^{III}$ ; and except in so far as this ratio varies there should be no difference between the values of the corrected electromotive forces of the different cells.

Table I shows that, so long as the sulfuric acid concentration is constant, the electromotive force is changed only slightly (at most by 0.7 mv.) either by varying the total concentration of the two cerium salts (even 15-fold) or by varying the ratio of the concentrations of the ceric and cerous salts (even 13-fold). This shows that the activities of the ceric and cerous

<sup>8</sup> Willard and Young, *THIS JOURNAL*, 50, 1379 (1928).

TABLE I  
ELECTROMOTIVE FORCES AT 25° OF CELLS

Series no.	Cell no.	H <sub>2</sub> , { H <sub>2</sub> SO <sub>4</sub> $\begin{matrix} 0.5 \text{ or} \\ 1.0 f \end{matrix}$ }, { Ce <sup>IV</sup> + H <sub>2</sub> SO <sub>4</sub> $\begin{matrix} 0.5 \text{ or} \\ 1.0 f \end{matrix}$ }, Pt			Electromotive force	
		H <sub>2</sub> SO <sub>4</sub> , <i>f</i>	(Ce <sup>IV</sup> ) <sup>a</sup> + (Ce <sup>III</sup> )	(Ce <sup>IV</sup> )/(Ce <sup>III</sup> )	Observed	Corrected
I	1	0.5	20.74	1.000	1.4610	1.4617
	2		11.638		1.4602	1.4609
	3		9.472		1.4600	1.4607
	4		8.832		1.4600	1.4607
	5		6.234		1.4600	1.4607
	6		6.094		1.4600	1.4607
	7		6.072		1.4601	1.4608
	8		4.736		1.4598	1.4605
	9		3.778		1.4598	1.4605
	10		3.044		1.4597	1.4604
	11		1.384		1.4596	1.4603
II	1	0.5	4.000	0.1351	1.4088	1.4610
	2			0.5248	1.4436	1.4609
	3			1.260	1.4659	1.4607
	4			3.503	1.4923	1.4608
	5			11.16	1.5221	1.4608
	6			18.16	1.5351	1.4609
III	1	1.0	15.808	1.000	1.4430	1.4437
	2		15.456		1.4431	1.4438
	3		8.450		1.4428	1.4435
	4		4.802		1.4428	1.4435
	5		2.832		1.4428	1.4435
	6		1.162		1.4426	1.4433
	7		1.988		1.4426	1.4433
IV	1	1.0	4.000	10.903	1.5042	1.4435
	2			2.041	1.4612	1.4436
	3			0.3336	1.4145	1.4434
	4			.1402	1.3921	1.4433

<sup>a</sup> Concentration expressed in millimoles per 1000 g. of solution.

ions Ce<sup>4+</sup> and Ce<sup>3+</sup> are always proportional to the concentrations of the respective salts. This result doubtless arises from the fact that sulfuric acid and sulfate ion are present at a substantially constant concentration very much greater than that of the cerium salt.

Inasmuch as the total molal concentration of the cerium salts is at most only 2% of that of the hydrogen ion of the sulfuric acid, the liquid potential must be so small as to be negligible, and the corrected electromotive forces (with sign reversed), namely, the values -1.461 and -1.443, represent almost exactly the electrode potential of the cerous-ceric combinations in the presence of 0.5 *f* and of 1 *f* sulfuric acid, respectively, referred to the electrode potential (taken as zero) of hydrogen against these two concentrations of acids, respectively.

Since there seem to exist no electromotive force measurements which

enable the electrode potential of hydrogen against 0.5 and 1.0 *f* sulfuric acid to be referred to the usual standard of electrode potentials, that of H<sub>2</sub> (1 atm.), H<sup>+</sup> (1 *m*) taken as zero, the ceric-cerous potentials cannot at present be expressed accurately with reference to this standard. However, the activity of hydrogen ion in 1.0 *f* sulfuric acid is probably not greatly different from 1 molal in view of the facts that its concentration (owing to the probably complete ionization of the acid into H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup> and its relatively small ionization, perhaps 5 to 10%, into 2H<sup>+</sup> + SO<sub>4</sub><sup>=</sup>) is somewhat greater than 1 molal and its activity coefficient is somewhat less than unity (0.823 if like that of 1 *m* HCl). The value -1.44 volts therefore represents (almost certainly within 0.01 volt) the molal reduction potential of ceric and cerous sulfate in 1.0 formal sulfuric acid.

### Summary

In this article have been described measurements at 25° of the electromotive force of cells consisting of a hydrogen gas electrode in 0.5 or 1.0 formal sulfuric acid and of a platinum electrode in solutions in the same acid of cerous and ceric sulfates at various small concentrations.

The electromotive force, corrected by the usual logarithmic formula to correspond to a hydrogen gas pressure of one atmosphere and to a ratio of the cerous to ceric salt equal to unity, was found to be 1.461 volts with the 0.5 *f* sulfuric acid, and 1.443 volts with the 1.0 *f* sulfuric acid. These values were found to change only very slightly with large variations of the ratio of the concentrations of the two cerium salts, or of their total concentrations, which, however, was always kept so small as to make the ratio of cerium to hydrogen ion very small and the liquid potential of the cells insignificant.

These values cannot be exactly expressed at present on the molal hydrogen electrode standard, since the potential of hydrogen against 0.5 or 1.0 *f* sulfuric acid is not well known; but the value -1.44 volts is probably exact within ±0.01 volt for the reduction potential on that standard of cerous and ceric sulfates in 1.0 formal sulfuric acid in terms of the total concentrations of trivalent and quadrivalent cerium (not of their ions). It is noteworthy that this reduction potential for the ceric-cerous potential is nearly the same as the potential (-1.48 volts) derived<sup>9</sup> for the molal potential of Mn<sup>++</sup>, MnO<sub>4</sub><sup>-</sup> + 8H<sup>+</sup>.

PASADENA, CALIFORNIA

<sup>9</sup> From the data of Brown and Tefft, *THIS JOURNAL*, 48, 1128 (1926), and of Tower, *Z. physik. Chem.*, 32, 568 (1900), as computed by Gerke, "International Critical Tables," 1929, Vol. VI, p. 332.