

should be applicable to the spreading of films upon solids, and this is indeed the main purpose behind the present investigation. Solids have not been used in the experiments on account of the difficulty of determining their surface cohesion, that is their surface tension.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## SOME APPLICATIONS OF OXYGEN ELECTRODE, AIR ELECTRODE, AND OXIDATION POTENTIAL MEASUREMENTS TO ACIDIMETRY AND ALKALIMETRY

BY N. HOWELL FURMAN

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### Introduction

In this investigation an attempt has been made to extend the general principles of electrometric analysis, which have been pointed out by Böttger,<sup>1</sup> Hildebrand,<sup>2</sup> and others,<sup>3</sup> to the problem of the determination of alkali or acid in the presence of strong oxidizing agents. Immediate practical importance centers, of course, in those cases in which the oxidizing agent is highly colored.<sup>4</sup> In such cases, apparently the only general method available is that of conductance titration. Küster and Grüters<sup>5</sup> found that the conductance method gave excellent results in the determination of free alkali or acid in the presence of permanganate ion, or of acid in the presence of dichromate ion; the method failed, however, in the determination of free alkali in the presence of chromates.

The author has found that the electrometric method affords a quite general solution to this problem. As the neutral point is passed, sharp inflections are obtained in the titration curves, which are constructed by plotting as abscissas the number of cubic centimeters of reagent used, and as ordinates the electromotive force readings of some one of the following cells.

(A) Platinized platinum	Oxygen air	Acid or alkaline solution of oxidizing agent	Normal calomel electrode
(B) Platinized platinum			
(C) Platinized platinum			
(D) Smooth platinum			

<sup>1</sup> Böttger, *Z. physik. Chem.*, **24**, 253 (1897).

<sup>2</sup> Hildebrand, *THIS JOURNAL*, **35**, 847 (1913).

<sup>3</sup> For an extended bibliography, see W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1920, pp. 214, 219, 239, *et seq.*

<sup>4</sup> Mr. C. D. Marlatt of the Martin Dennis Co., Newark, N. J., pointed out to the author the importance of the measurement and control of the alkalinity of chromate solutions, together with some of the difficulties which he had encountered. (Private communication.)

<sup>5</sup> Küster and Grüters, *Z. anorg. Chem.*, **35**, 454 (1903).

It was found that Cells A and B gave satisfactory titration curves in both the presence and absence of oxidizing agents, there being no essential difference in general nature between the curves obtained with the aid of the oxygen electrode and those which were dependent upon the air electrode.

Cell C gave uniformly good results only when an oxidizing agent was present. The results with Cell D were erratic at times, even when an oxidizing agent was present. Somewhat more satisfactory results were obtained when platinized gold was substituted for the platinum electrode.

**The Oxygen Electrode.**—Numerous investigations<sup>6-13</sup> have proved conclusively that the oxygen electrode does not assume a final definite potential value in any given solution, presumably because we are dealing with an irreversible process which involves oxide formation. This behavior influences the electromotive force of any cell into whose construction the oxygen electrode may enter. Thus the final approximate value toward which the electromotive force of the oxy-hydrogen cell approaches generally lies between 1.08 and 1.14 volts. From three independent values of the free energy of formation of water Lewis and Randall<sup>14</sup> derive a weighted mean value of 1.227 volts for the oxy-hydrogen cell at 25°. The discrepancy between the found and calculated values is entirely due to the oxygen electrode.

Although the potential of the oxygen electrode is variable, the magnitude of the variation is only of the order of 5-10 millivolts per hour (in acid solution) after the electrode has become approximately saturated with the gas.<sup>15</sup> This drift in the electromotive force does not in any way obscure the course of an ordinary titration curve which may be constructed in a few minutes' time.

**Theoretical Considerations.**<sup>16</sup>—Every substance which we ordinarily regard as an oxidizing agent may be thought of as possessing a certain tendency to give up oxygen directly, or to cause the liberation of oxygen from

<sup>6-13</sup> The following list includes a large number of the principal investigations.

<sup>6</sup> Crotogno, *Z. anorg. Chem.*, **24**, 258 (1900).

<sup>7</sup> Bose, *Z. physik. Chem.*, **34**, 730 (1900); includes a bibliography.

<sup>8</sup> Wilsmore, *ibid.*, **35**, 291 (1900).

<sup>9</sup> Czepinski, *Z. anorg. Chem.*, **30**, 1 (1902).

<sup>10</sup> Westhaver, *Z. physik. Chem.*, **51**, 83 (1905).

<sup>11</sup> Lewis, *THIS JOURNAL*, **28**, 158 (1906).

<sup>12</sup> Schoch, *J. Phys. Chem.*, **14**, 665 (1910). "The Potential of the Oxygen Electrode: A Report of Progress."

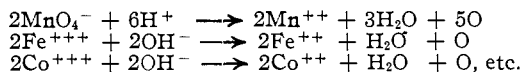
<sup>13</sup> Foerster, *Z. physik. Chem.*, **69**, 336 (1910).

<sup>14</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 1985 (1914).

<sup>15</sup> This value is based upon the author's experience and is in harmony with that of Crotogno, Ref. 6, Wilsmore, Ref. 8, and others.

<sup>16</sup> For a very complete treatment of the considerations involved, together with copious references to the literature, see F. Foerster, "Elektrochemie Wässeriger Lösungen," 2nd Edition, J. A. Barth, Leipzig, 1915, pp. 164-185.

water. This tendency may be indicated by partial equations as, for example



Cobaltic ions may even cause visible evolution of oxygen at a platinized surface.

For any given solution of an oxidizing agent which is in contact with a platinum electrode there will result a balance between the tendency of the substance to evolve oxygen and the opposing pressure of the oxygen which is dissolved in the electrode.<sup>17</sup> We may regard this process from the standpoint of the oxygen ion. Oxygen dissolved in the electrode tends to ionize in proportion to its partial pressure (concentration), the electrode becoming positively charged.  $\frac{1}{2}\text{O}_2 \rightleftharpoons \text{O}^-$ . At constant temperature  $\frac{[\text{O}^-]}{[\frac{1}{2}\text{O}_2]} = K_1$ .

This tendency is opposed by the osmotic pressure of the oxygen ions of the solution, which is constant at any given temperature. For any given solution at constant temperature the concentration of oxygen ions is defined by the relation  $[\text{O}^-] = \frac{k K_w}{[\text{H}^+]^2}$  (since  $[\text{H}^+][\text{OH}^-] = K_w$  and  $\text{O}^- +$

$\text{H}^+ \rightleftharpoons \text{OH}^-$ , and hence at equilibrium  $\frac{[\text{O}^-][\text{H}^+]}{[\text{OH}^-]} = k$ ). The intensity of the potential difference at the contact of electrode and solution will depend upon the relative magnitudes of the opposed tendencies.

If we substitute an oxygen or air electrode for the simple platinum electrode we oppose a fairly definite solution pressure to the osmotic pressure of the oxygen ion. The electromotive force which is developed by a cell composed of such an electrode together with a normal calomel electrode will be a function of the oxygen-ion concentration of the solution. The concentration of oxygen ions will be dependent both upon hydrogen-ion concentration and that of oxidizing agent. If we keep the latter concentration constant we should expect a sharp inflection in the electromotive force-hydrogen-ion concentration curve as we pass the neutral point. Such an inflection is experimentally realized in all of the cases which the author has been able to test.

The range of the electromotive-force change in the neighborhood of the neutral point will depend both upon the specific nature and concentration of the oxidizing agent.<sup>18</sup> (See Fig. 8.)

### Experimental

**Materials and Apparatus.**—Normal calomel electrodes and Weston (saturated

<sup>17</sup> The tendency of the electrode toward oxide formation will also be a complicating factor in this case as well as in that of the oxygen electrode proper.

<sup>18</sup> For a discussion of the effect of acidity upon oxidizing potential see Crotogno, Ref. 6.

type) standard cells were constructed from carefully purified materials.<sup>19</sup> Through the courtesy of Dr. G. A. Hulett and Mr. H. C. Howard it was possible for the author to compare his standard cells with others of accurately known electromotive force. All readings from which titration curves were constructed could thus be made with more than sufficient accuracy.

The calomel electrode vessels were essentially of the familiar Ostwald type, with a stopcock and reservoir sealed to the connecting side tube. When the electrode was in use the stopcock was so adjusted that potassium chloride solution flowed into the titration vessel at a rate of about 0.5 cc. per hour.

Several oxygen and air electrodes were used in the course of the investigation. They were of the type commonly used in hydrogen-electrode titrations and were constructed according to Hildebrand's description. The electrodes were supplied either from a cylinder of electrolytic oxygen, or with oxygen which was generated by the electrolysis of 10% sodium hydroxide solution with a nickel anode. In both cases the gas was passed through acidified permanganate and conc. sodium hydroxide solutions. When air was used instead of oxygen the permanganate washing was omitted.

Preliminary experiments were made with an apparatus which did not differ in any essential respect from that described by Hildebrand. All of the titration curves which are recorded in this paper were made with the aid of a potentiometer set of medium precision,<sup>20</sup> and with accurately known electromotive-force standards. A small stirrer motor-driven at a rate of about 200-300 r.p.m. was used in every titration.

Solutions of oxidizing agents, acids and alkalis were prepared from materials of tested purity without further special purification.<sup>21</sup> These solutions were carefully standardized by well-established analytical methods. By means of tested samples of Mohr's salt, sodium oxalate, and oxalic acid the standardizations of solutions of oxidizing agents and alkalis were compared and the whole series of normalities was found to be consistent. The normality values which were used were averages of at least three concordant determinations.

**Range of Variation of Electromotive Force Readings Before and After Titrations.**—It was found that the readings of the oxygen (or air) electrode-*N*-calomel electrode cell were much more nearly constant in acid than in alkaline solutions. During the first hour before or after titrations there was a drift of from 5 to 10 millivolts (in one case 15) in acid solution, and one of 30 to 60 millivolts in alkaline media. In both cases the over-all voltage of the cell generally, although not always, tended to increase. Some typical sets of readings are given in Table I.

Usually after 15 to 20 minutes the readings are steady enough to allow ordinary analytical determinations to be made. If the electrode is kept saturated with oxygen (or air) the titration may be commenced almost

<sup>19</sup> Calomel and mercurous sulfate were prepared by the "chemical method" from mercury redistilled by the method of Hulett [*Phys. Rev.*, **23**, 307 (1911)]. Cadmium sulfate was purified as specified by Wolf and Waters [*Bur. Standards Sci. Paper*, **70**, (1907)]. Potassium chloride was precipitated from its concentrated solution by a stream of pure hydrogen chloride. After washing, the salt was fused in platinum.

<sup>20</sup> A Students Type potentiometer, and galvanometer of current sensitivity 2 mm. per micro-ampere.

<sup>21</sup> The author had occasion to test the materials in connection with work of instruction in quantitative analysis.

immediately. During the titrations the readings were almost as steady as those during ordinary hydrogen-electrode titrations.

TABLE I  
DRIFT OF ELECTROMOTIVE FORCE READINGS

Time Min.	Acid solution		Alkaline solution	
	Before a titration Volt	After a titration Volt	Before a titration Volt	After a titration Volt
0	+0.499 <sup>a</sup>	+0.646	-0.009	-0.009
5	+0.505	.....	.....	-0.004
15	+0.506	+0.648	+0.048	.....
20	+0.507	+0.649	+0.050	+0.011
30	+0.508	+0.649	+0.050	+0.016
70	+0.509	+0.652	+0.064	+0.031

<sup>a</sup> A positive value is assigned to readings in which the flow of positive current external to the cell was from oxygen electrode to calomel electrode.

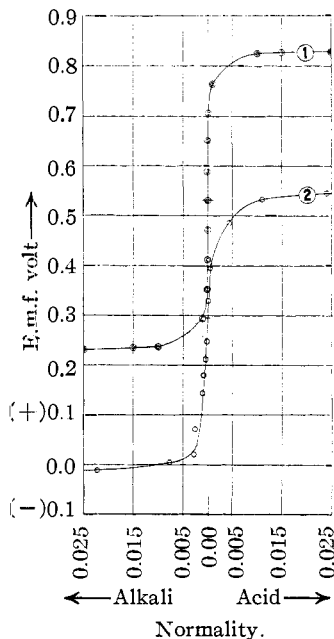


Fig. 1.—Observed and calculated variations of e.m.f. of oxygen-*N*-calomel cell. Curve 1 was calculated on the basis of 1.227 volts as the e.m.f. of the oxy-hydrogen cell at 25°. Curve 2 is based on observed values at 25°.

**Actual Behavior of the Oxygen Electrode.**—In Fig. 1 are plotted curves which compare the actual electromotive-force variation of the oxygen-*N*-

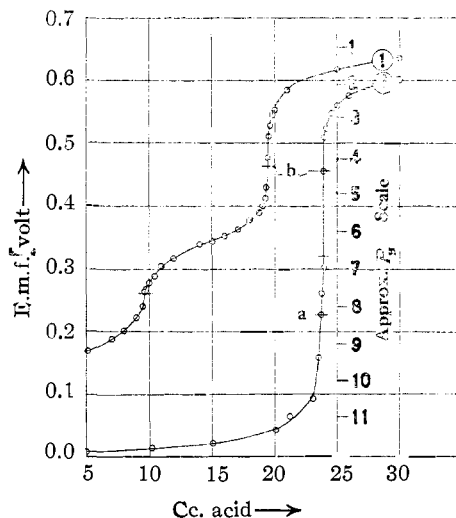


Fig. 2.—Oxygen electrode titrations. Curve 1: titration of 20 cc. of 0.5000 *N* sodium carbonate with 0.5176 *N* sulfuric acid. Calc.: 19.32 cc. Found: 19.37 cc. Curve 2: 25 cc. of 0.4952 *N* sodium hydroxide titrated with 0.5176 *N* sulfuric acid. Calc.: 23.92 cc. Found: 23.85 cc.

Points *a* are actual phenolphthalein changes, while Points *b* represent methyl orange end-points.

calomel electrode cell with the hypothetical variation, as the concentration of hydrogen ion is varied. Curve 2 is based upon a number of observations, but is at best only an approximation. Some idea of the range of variation which is to be expected may be gained from the fact that in 6 successive titrations of sodium hydroxide with sulfuric acid (or *vice versa*) the position of the point of inflection was at 0.320, 0.275, 0.295, 0.318, 0.280 and 0.330 volt, respectively.

### Comparison of Hydrogen and Oxygen Electrode Titrations

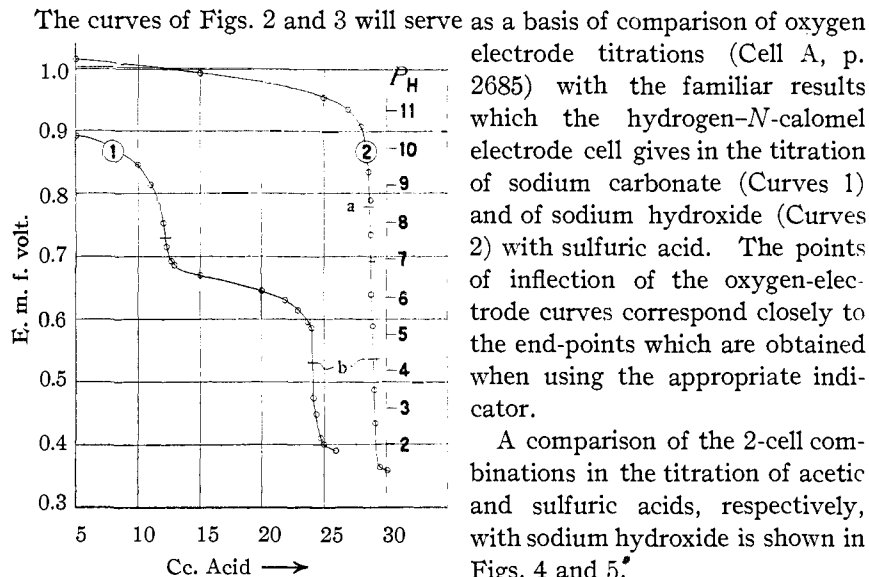


Fig. 3.—Hydrogen-electrode titrations. Curve 1: titration of 25 cc. of 0.5000 *N* sodium carbonate with 0.5176 *N* sulfuric acid. Calc.: 24.15 cc. Found: 24.20 cc. Curve 2: 30 cc. of 0.4952 *N* sodium hydroxide titrated with 0.5176 *N* sulfuric acid. Calc.: 28.70 cc. Found: 28.65 cc. Points *a* are actual phenolphthalein changes, while Points *b* represent methyl orange end-points.

evident, however, that qualitatively at least the results obtained with the oxygen electrode are of the same general nature as those which are dependent upon the hydrogen electrode.

Accurate results were obtained in a number of determinations using reagents of either 0.5 or 0.1 *N* concentration; both oxygen and air, and simple platinized electrodes were used successfully.

A comparison of the 2-cell combinations in the titration of acetic and sulfuric acids, respectively, with sodium hydroxide is shown in Figs. 4 and 5.

The scale which is affixed to Figs. 2 and 4 is at best only an approximate indication of the hydrogen-ion concentration. It is based upon the actual behavior of the oxygen electrode. Its position may be shifted considerably by changing the nature of the electrode material, etc. It seems quite

### Comparison of Oxygen, Air and Platinized Electrodes

Titrations made with all of these electrodes are similar in general nature. The behavior of the platinized-foil electrode will depend upon its previous history, and may occasionally be very erratic. Usually such a foil will act like a saturated oxygen electrode.

We should expect that the air electrode would develop a potential value about 0.008 volt less positive than that of the oxygen electrode under analogous conditions.<sup>22</sup> Experimentally the difference is ordinarily from 10 to 15 times as great as the calculated value.<sup>23</sup>

The air electrode has been found to be much more sensitive to the influence of traces of foreign substances than the oxygen electrode.

### Determination of Free Alkali in the Presence of Chromate

It is possible to obtain a moderately accurate determination of the amounts of free alkali which are present in *dilute* solutions of chromates by using phenolphthalein as indicator. The facts involved were established by Richter who proposed the use of potassium dichromate as a primary standard in acidimetry.<sup>24</sup> Obviously the end-point will be influenced by the presence of carbonate in the alkali. A second source of error is the hydrolysis of chromates, which varies with the degree of dilution. Kolthoff and Vogelenzang have recently investigated the acidimetric titration of dichromates and have found that potassium dichromate is not to be recommended as a primary standard in acidimetry.<sup>25</sup> They state that it is possible to obtain results which are accurate to within 0.1 to 0.3% in any of the following ways: (a) by using thymolphthalein as indicator; phenolphthalein may be successfully employed only (b) after repressing the hydrolysis of the chromate by saturating the solution with sodium chloride,

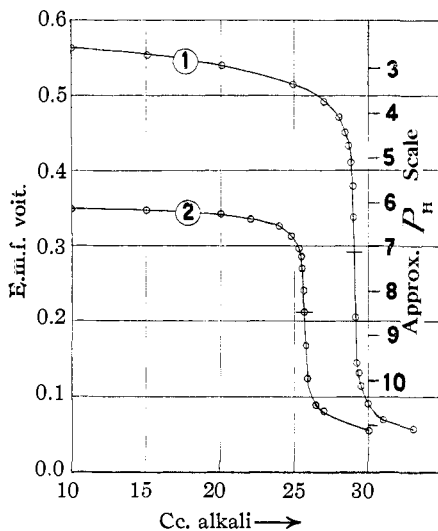


Fig. 4.—Oxygen-electrode titrations. Curve 1: 30 cc. of 0.0996 *N* sulfuric acid titrated with 0.1028 *N* alkali. Calc.: 29.07 cc. Found: 29.10 cc. Curve 2: titration of 25 cc. of 0.5050 *N* acetic acid with 0.4937 *N* sodium hydroxide. Calc.: 25.57 cc. Found: 25.63 cc.

<sup>22</sup> For basis of calculation see Crotogno, Ref. 6.

<sup>23</sup> For details of the investigation of the oxygen-air cell see Smale, *Z. physik. Chem.*, **14**, 600 (1894). Hooper, *Z. anorg. Chem.*, **20**, 423 (1899).

<sup>24</sup> Richter, *Z. anal. Chem.*, **21**, 205 (1892).

<sup>25</sup> Kolthoff and Vogelenzang, *Rec. trav. chim.*, **40**, 681 (1921).

or (c) after the addition of a suitable quantity of barium chloride (this addition must be made when the end-point has almost been reached; otherwise an error as great as 0.8% may result). The addition of barium chloride is useful since it practically eliminates the time factor which is introduced by the slow rate of reaction between dichromate and alkali.

These investigators have also found by a colorimetric method that the hydrogen-ion concentration of potassium chromate solutions varies with dilution; for molar concentrations, 0.500, 0.100, 0.050 and 0.010, Sørensen values ( $P_H$ ) 8.92, 8.79, 8.73 and 8.58 have been obtained. Accurate results have been obtained in the present work by electrometric titration

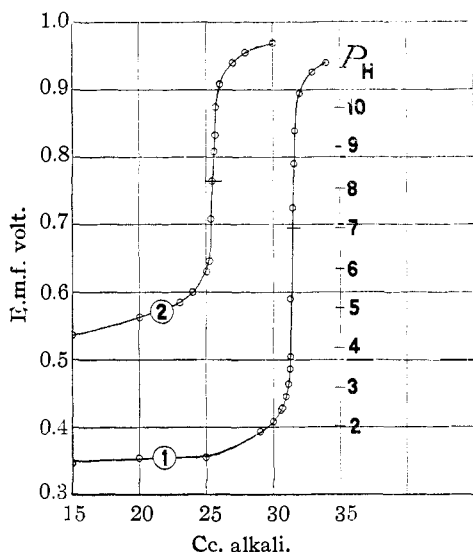


Fig. 5.—Hydrogen-electrode titrations. Curve 1: 30 cc. of 0.5176 *N* sulfuric acid titrated with 0.4952 *N* alkali. Calc.: 31.35 cc. Found: 31.40 cc. Curve 2: titration of 25 cc. of 0.5050 *N* acetic acid with 0.4937 *N* sodium hydroxide. Calc.: 25.57 cc. Found: 25.45 cc.

using an oxygen, an air, or a platinized electrode, provided that the alkali is practically free from carbonate. Upon electrometric titration of these solutions the position of the first inflection (*a*, *a'* Fig. 6) was found to correspond closely to the calculated value for free alkali, which of course was based upon a comparison of acid and alkali using phenolphthalein as indicator. (As the points of inflection *a*, *a'* (Fig. 6) occur at approximately the voltage or Sørensen value of the phenolphthalein change this indicator is appropriate (see p. 2688). If methyl orange were used in the comparison, the results for free alkali would be in error to an extent roughly proportional to the amount of carbonate present in each case.)

All of the points of inflection (end-points) which are recorded in this paper were determined by the position of the maximum value of rate of change of electromotive force with addition of reagent, ( $dE/dV$ ). If we plot values of  $dE/dV$  as ordinates against cubic centimeters of reagent as abscissas we obtain maxima at the points of inflection.<sup>26</sup>

<sup>26</sup> See *a*, *a'*, *b*, *b'* (Fig. 6.). This method was described and used by Hostetter and Roberts, *THIS JOURNAL*, **41**, 1341 (1919).

using an oxygen, an air, or a platinized electrode, provided that the alkali is practically free from carbonate.

A series of solutions which contained known amounts of free alkali was prepared by adding in each case a known excess of alkali to an aliquot portion of carefully standardized potassium dichromate solution. Upon electrometric titration of these solutions the position of the first inflection (*a*, *a'* Fig. 6) was found to correspond closely to the calculated value for free alkali, which of course was based upon a comparison of acid and alkali using phenolphthalein as indicator. (As the points of inflection *a*, *a'* (Fig. 6) occur at approximately the voltage or Sørensen value of the phenolphthalein change this indicator is appropriate (see p. 2688). If methyl orange were used in the comparison, the results for free alkali would be in error to an extent roughly proportional to the amount of carbonate present in each case.)



The sharpness of the inflection depends both upon the degree of dilution and upon the amount of carbonate which is present. Points  $b$ ,  $b'$  (Fig. 6), which correspond to the completed conversion of chromate to dichromate are affected only by the degree of dilution. The greater lack of sharpness of the inflection  $a'$  as compared with  $a$  is due to the presence of an appreciable amount of carbonate in the 0.1043  $N$  alkali, whereas the solution involved in Curve 1 (Fig. 6) was practically free from carbonate.

A summary of results which were obtained in this direct manner is given in Table II.

TABLE II  
DIRECT ELECTROMETRIC DETERMINATION OF FREE ALKALI IN THE PRESENCE OF CHROMATE

Results 1 to 6 are calculated to an exact 0.1  $N$  basis; 7 and 8 to 0.5  $N$  basis

Expt.	1	2	3	4	5
	NaOH calc. to neutralize $K_2Cr_2O_7$ taken Cc.	Total NaOH taken Cc.	Free NaOH calc. Cc.	Free NaOH found Cc.	Error Cc.
1	16.67	26.18	9.51	9.64	0.13
2	16.82	26.18	9.36	9.42	0.06
3	8.44	26.18	17.74	17.76	0.02
4	16.82	26.74	9.92	10.03	0.11
5	16.82	26.74	9.92	9.91	-0.01
6	16.82	29.68	12.86	12.85	-0.01
7	16.86	24.69	7.83	7.84	0.01
8	16.86	24.69	7.83	7.79	-0.04

Expts. 1, 2, 3 and 6 were made with the oxygen electrode, Expts. 4, 5 and 7 with an air electrode, and Expt. 8 with a simple platinized foil.

The alkali solutions which were used in the above determinations were standardized against the sulfuric acid solutions using phenolphthalein as indicator. If methyl orange is used in the standardization the calculated values for free alkali will differ from these given (Col. 3, Table II) by amounts which are closely proportional to the amounts of carbonate in the alkali.

The direct method of determining free alkali is thus limited to use in cases where the chromate solutions are known to be practically free from carbonate.

*The following indirect method is a much more generally useful mode of procedure.* We first find the total acid requirement (A) of a given portion of the solution by an electrometric determination of the inflection point which corresponds to the neutralization of free alkali and the completed conversion of chromate into dichromate (Points  $b$  or  $b'$ , Fig. 6). Only a few readings need be taken until the voltage value has reached 0.4. The amount of dichromate is then determined by any convenient method. The author used the excellent electrometric method of Forbes and

Bartlett.<sup>27</sup> Having thus found the volume of freshly standardized ferrous sulfate solution which is equivalent to the dichromate present, the volume of standard acid (B) which is equivalent to the dichromate is calculated.

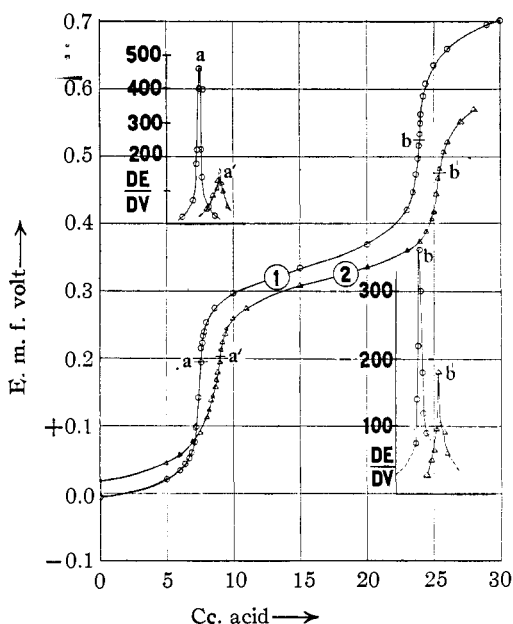


Fig. 6.—Curve 1: titration of 25 cc. of 1.011 *N* dichromate (oxidimetric) plus 25 cc. 0.4937 *N* sodium hydroxide with 0.5176 *N* sulfuric acid. Curve 2: titration of 50 cc. 0.1009 *N* (oxidimetric) dichromate plus 25 cc. of 0.1043 *N* sodium hydroxide with 0.1065 *N* sulfuric acid. Points *a, a'* correspond to the neutralization of free alkali.

(Cc. of *N* dichromate (oxidimetric) divided by 3 equals cc. of *N* dichromate (acidimetric).) Subtraction (A - B) gives the volume of standard acid which is equivalent to the free alkali present. Results which were obtained in this manner are given in Table III.

It is perhaps worth noting that in 20 successive determinations of the total acid requirement of such solutions 12 were within 0.06 cc. of the amount present, 5 were less than 0.10 cc. in error, and the others were 0.11, 0.12, and 0.18 cc. in error. These figures are for both 0.1 and 0.5 *N* solutions. The greatest error in case of the latter solutions was 0.12 cc.

The amount of acid which is equivalent to the dichromate can be determined with great exactness, since any error in the dichromate estimation

TABLE III  
INDIRECT DETERMINATION OF FREE ALKALI IN PRESENCE OF CHROMATE

Expt.	All results calculated to an exactly 0.1 <i>N</i> basis							
	1	2	3	4	5	6	7	8
	Total alkali taken	Total acid (A) used	Error (2-1)	Acid equiv. to $K_2Cr_2O_7$ calc.	Free alkali calc.	Free alkali found	Error (6-5)	Acid (B) equiv. to $FeSO_4$ found
	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
1	27.21	27.15	-0.06	16.82	10.39	10.33	-0.06	16.82
2	26.98	26.99	0.01	16.82	10.16	10.16	±0.00	16.80
3	27.26	27.30	0.04	16.82	10.44	10.50	0.06	16.83
4	27.26	27.32	0.06	8.44	18.82	18.90	0.08	08.42
5	20.61	30.67	0.06	8.44	22.17	22.22	0.05	08.45
$Na_2CO_3$	10.00							

<sup>27</sup> Forbes and Bartlett, THIS JOURNAL, 35, 1527 (1913).

is divided by 3 in calculating the amount of acid which is equivalent to it.

### Electrometric Determination of Excess of Acid in Presence of Dichromate. Titration of Dichromate with Alkali

The determination of the amount of acid which has been added to a dichromate solution may be made with a high degree of accuracy by the electrometric method. If the titration is carried beyond the neutralization of excess acid (Point *b*, Fig. 7) a second inflection is found at the point where the conversion of dichromate into chromate is complete (*a*, Fig. 7). A similar inflection is found when dichromate solutions are titrated with alkali (Points *a'*, Fig. 7). The position of these points (*a*, *a'*) is affected by the presence of carbonate in the alkali which is used in the titration. The results are quite good if phenolphthalein is used as indicator in comparing the alkali with standard acid. The alkali solution should of course be as nearly free from carbonate as possible.

Some representative results are to be found in Table IV.

From the nature of these results it seems quite evident that potassium dichromate could be used as a primary standard if the titration is carried out electrometrically, provided that the alkali solutions are entirely free from carbonate, and that undue dilution is avoided.

In 12 determinations the position of the inflections *a*, *a'* (Figs. 6 and 7), considering only those results which were obtained with the oxygen electrode, was between 0.175 and 0.260 volt which is very close to the Sørensen range 8-9 to which the author has assigned a voltage range of 0.188-0.242 volt (see scale, Figs. 2 and 4). The presence of carbonates in the solution and the uncertain behavior of the oxygen electrode make it futile to ascribe more than a qualitative significance to this rough agreement with the results of Kolthoff and Vogelenzang<sup>26</sup> for the value of the hydrogen-ion concentration of chromate solutions, namely,  $P_H$  8.58-8.79 for solutions between 0.01 and 0.1 *M*. The presence of sodium sulfate resulting from

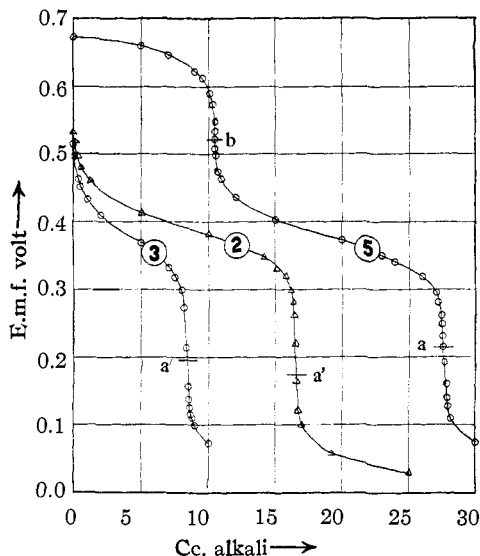


Fig. 7.—Curve 5 shows the determination of acid in the presence of  $K_2Cr_2O_7$ . Curves 2 and 3 represent the titration of dichromate solutions with alkali. In Table IV under the same numbers will be found data showing the accuracy of these determinations.

TABLE IV  
DETERMINATION OF ACID IN PRESENCE OF DICHROMATE. NEUTRALIZATION OF POTASSIUM DICHROMATE WITH ALKALI

Results 1, 2, 3 are calculated to 0.1 *N*; 4-7 to 0.5 *N*

Expt.	Acid equal to $K_2Cr_2O_7$ taken Cc.	Acid taken Cc.	Acid found Cc.	Error (3-2) Cc.	Alkali to neutralize $K_2Cr_2O_7$ found Cc.	Error (5-1) Cc.
1	16.82	25.15	25.21	0.06	16.88	0.06
2	16.82	...	...	..	16.86	0.04
3	8.44	...	...	..	8.46	0.02
4	16.86	25.89	25.90	0.01	17.02	0.16
5	16.86	10.36	10.37	0.01	16.89	0.03
6	16.86	25.89	25.93	0.04	16.86	0.00
7	33.72	..	...	..	33.80	0.08

Expts. 1, 5 and 6 were made with a simple platinized electrode, Expts. 2 and 3 with an oxygen, and 4 and 7 with an air electrode.

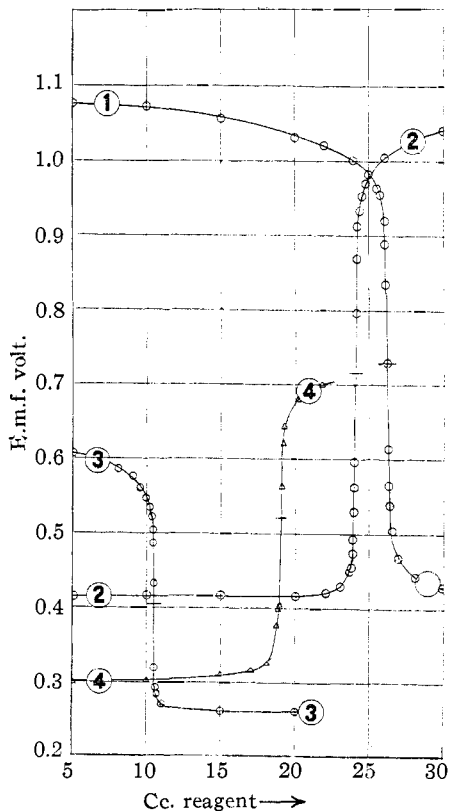


Fig. 8.—Determination of acid or alkali in the presence of potassium permanganate (Curves 1 and 2), or in the presence of potassium ferricyanide (Curves 3 and 4).

the neutralization of the alkali would also influence the degree of hydrolysis of the solutions in question.

#### Determination of Alkali or Acid in the Presence of Potassium Permanganate or Ferricyanide

Free alkali or acid may be readily determined in the presence of either of these oxidizing agents. Satisfactory results are obtained with either the oxygen, air or simple platinized electrodes. The general technique which was employed was entirely similar to that which has been described. The solutions of permanganate and alkali were titrated immediately after the addition of the alkali. In Fig. 8 are some typical curves which will serve to illustrate the general nature of the results. In the determinations the concentrations of the solutions were: sulfuric acid; 0.5176 *N*; sodium hydroxide, 0.4952 *N*; potassium permanganate, approx. 0.1 *N*; potassium ferricyanide, approx. 0.5 *N*.

Curve 1. Titration of 25 cc. of acid and 25 cc. of permanganate. Calc.: 26.13. Found, 26.15 cc. of alkali. Curve 2. Titration of 50 cc. of potassium permanganate and 25 cc. of alkali. Calc.: 23.92. Found, 24.00 cc. of acid. Curve 3. 25 cc. of ferricyanide and 10 cc. of acid titrated with alkali. Calc.: 10.45. Found, 10.48 cc. Curve 4. Titration of 25 cc. of ferricyanide and 25.1 cc. of alkali. Calc.: 24.01. Found: 24.07 cc. of acid.

If we are dealing with an acidified solution of permanganate a quite accurate determination of the end-point may be made by using an ordinary oxidation-potential cell (D, p. 2685). The end-point is marked by a sudden violent deflection of the galvanometer. This mode of procedure was not studied in detail.

### Discussion of Results

It seems that sufficient evidence has been presented to prove that the applications of the electrometric method which have been proposed in this paper are in general suitable for the determination of either acid or alkali in the presence of an oxidizing agent. Qualitative observations have been made in a number of cases other than those which have been described. When we determine free alkali in the presence of potassium bromate, for example, there is a sharp break in the titration curve at the end-point. As soon as a slight excess of free acid is present there is a large additional rise in the electromotive force, which is due to the development of the potential of the bromine electrode. Each oxidizing agent may then present special characteristics which will modify the voltage range at or near the end-point.

In the case of chromate solutions, the results which have been described indicate clearly the possibility of electrometric control of large scale neutralizations, as well as of analytical determinations of total alkalinity or acidity.

### Summary

1. A brief study of some analytical applications of the oxygen electrode has been made. The results are in general analogous to those which are obtained with the hydrogen electrode.
2. The oxygen electrode gives accurate results in the determination of total alkalinity or acidity. By employing an empirical scale, the e.m.f. readings of the oxygen-*N*-calomel cell will serve to give a qualitative indication of "relative acidity" (hydrogen-ion concentration).
3. In the presence of oxidizing agents an oxygen, an air, or a simple platinized electrode was found to give satisfactory results in the determination of total alkalinity or acidity. The facts which are involved have been established mainly by a study of alkaline chromate, or acidified dichromate solutions.