taneous decomposition of hydrogen peroxide itself. The platinum, after precipitation by the light, was in the form of large, mossy clusters.

To show more conclusively that the ultra-violet light is capable of destroying the catalytic activity of colloidal platinum in a short period of time, the following experiment was performed:

Five cc. of colloidal platinum solution were placed in a dish of such a size that the depth of the liquid was not more than 3 mm. This solution was exposed to the ultra-violet light for one hour. On testing the catalytic activity of this platinum solution, only 0.5 cc. of water was displaced. This was undoubtedly due to the spontaneous decomposition of the hydrogen peroxide solution.

### EXPERIMENT NO. 4.

| Time of exposure to ultra-violet light. | Amount water displaced |
|---|---|
| 1 hour | 6.5 cc. |
| 2 hours | 6.0 cc. |
| 3 hours | 3.2 cc. |
| 4 hours | 2.6 cc. |
| 5 hours | 1.1 cc. |
| 6 hours | 1.2 cc. |
| Colloidal platinum unexposed to light at first | 5.0 cc. |
| Colloidal platinum unexposed to light after standing 5 1/2 hours | 3.5 cc. |

In all cases, with one exception, the colloidal platinum solution was stimulated to greater activity by a short exposure to the light. This fact is shown by the increased decomposition of the hydrogen peroxide solution after 1 hour of exposure to the light. This is in harmony with observations by Mr. Bovie in his work.

We believe that the above experiments clearly demonstrate the fact that ultra-violet light destroys the catalytic activity of colloidal platinum.

# THE INCREASE IN THE OXIDIZING POTENTIAL OF DICHROMATE ION ON PLATINUM CAUSED BY CERTAIN REDUCING AGENTS. AN IMPROVED METHOD FOR THE ELECTROMETRIC TITRATION OF FERROUS SALTS.

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During a research begun last year on the reduction of chromic acid at a platinum cathode, the electrolyzed solutions were titrated with ferrous salts. The end point, as determined by potassium ferricyanide, proving useless in concentrated solutions, owing to the intense color of the chromic salts, recourse was had to the electrometric determination of the end point, as proposed by Crotogino,[1] by Ostwald, Luther, and Drucker,[2]

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[1] *Z. anorg. Chem.*, 24, 225 (1900).

[2] *Physiko-chemische Messungen*, p. 454.

and very recently by Hildebrand.[1] A rotating electrode of platinum was placed in the solution, and connected through a potentiometer to a normal calomel electrode whose syphon completed the electrolytic circuit. On adding a ferrous solution it was expected that the oxidizing potential of the dichromate electrode, and, therefore, of the cell, would fall slowly until the dichromate was nearly exhausted, then with considerable abruptness, the mid-point of this sharp decline marking the true end point. Greatly to our surprise, however, the oxidizing potential of the dichromate steadily increased with each addition of ferrous solution followed by stirring and waiting, until a final drop established an actual excess of ferrous ion. Then a striking and permanent decrease in the electromotive force of the cell immediately followed. An examination of the literature revealed only one observation, in any way similar, by Mazzuchelli,[2] who measured the potentials of mixed chromic and chromous ions on tin electrodes. On adding chromous ion there first resulted an increase in oxidizing potential, which, however, soon righted itself, and which, therefore, appeared only worthy of passing mention. The magnitude and permanency of the effect in the case of dichromate invited further study.

In order to limit, so far as possible, the number of highly variable quantities, the chromic and the ferric salts were each taken 0.05 molar normal at the start, and the sulfuric acid three times equivalent normal. The substances used were all Merck's highest purity reagents. Two cells were usually observed simultaneously under parallel conditions. These were made from wide mouthed bottles of 250 cc. capacity, provided with rubber stoppers pierced with holes, through which respectively passed an efficient centrifugal stirrer, a rotating electrode of platinum foil, a tube for the delivery of an indifferent gas, and a capillary leading toward a normal calomel electrode. The platinum electrode was bent so that the horizontal cross-section was in the shape of the letter S. The capillary emptied first into a test tube of 10 cc. capacity filled with the solution above described; this in turn was connected by another capillary to a similar tube containing a very concentrated solution of 76% potassium chloride and 24% potassium nitrate to minimize diffusion potentials.[3] This finally was connected by another capillary to a very large normal calomel electrode made up in a bottle of 150 cc. capacity, and provided with a piston for the ejectment of small quantities of solution. The introduction of dichromate into the calomel electrode was thus avoided, but the latter was none the less frequently checked against a standard kept carefully from any possibility of contamination. A stream of carbon

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[1] This Journal, **35**, 869 (1913).

[2] *Zentralbl.*, **79**, II, 294 (1905).

[3] Bjerrum, *Z. physik. Chem.*, **53**, 438 (1905).

dioxide was run continuously through the solution under investigation and all reagents were swept out with the same gas. Observations showed that the anomalous rise in potential took place in the presence of air, so it was considered best to eliminate this influence as far as possible.

Two pairs of electrodes were employed. Each electrode was from 2 to 2.5 cm. square. One pair was of bright platinum, the other pair of gray platinum, prepared according to the directions of Bancroft.[1] These were platinized, washed and boiled for some time with concentrated sulfuric acid, then washed and heated white hot in a Bunsen flame. At first they gave nearly equal potentials under identical conditions; later they diverged several centivolts, as did also the bright electrodes. No attempt was made to keep them all the same, as the absolute potential of the dichromate electrode was not the primary object of the investigation. No difference in the average behavior of the bright and gray electrodes, respectively, was established.

The potentials of the cells composed of the dichromate electrode and the calomel electrode were measured by the compensation method. The details of the potentiometer will be given at the end of the paper. To find the potential of the dichromate electrode, a value commonly assigned to the single potential of the calomel electrode, +0.560 volt, was added to the total potential of each cell. Here also, as absolute potentials were not the main object, the small and constant value of the diffusion potentials was not considered.

The following data are entirely typical of a long series of observations, but only a small part of these are given in this paper in order to avoid unnecessary repetition. None of the omitted results could lead to other conclusions than those which follow:

I. Starting with dichromate in slight excess, each successive drop of ferrous solution raises the potential until the end point is reached. A momentary decrease, often observed, especially near the end point, disappears after thorough mixing. The first of several equal additions produces the greatest effect.

| | | | | | |
|---|---|---|---|---|---|
| Drops 0.1 *N* $(NH_4)_2Fe(SO_4)_2$... | 0 | 1 | 2 | 3 | 4 |
| Potentiometer reading........ | 75.7 | 81.2 | 83.0 | 84.3 | 61.8 |

II. After excess of dichromate is established, the potential always rises for some time; but this ultimately reaches a maximum upon which the rise noted on adding the ferrous salt is superposed.

| | | | | | |
|---|---|---|---|---|---|
| Minutes elapsed.............. | 0 | 15 | 33 | 43 | 44 |
| Potentiometer reading........ | 53.5 | 57.9 | 59.3 | 59.4 | 65.1 |
| Drops $(NH_4)_2Fe(SO_4)_2$, 0.1 *N*.. | .. | .. | .. | .. | 10 |

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[1] *Z. physik. Chem.*, 10, 387 (1892).

In all the following observations no reducing agent was added until the maximum potential obtainable with dichromate alone was established, usually after the cell had stood over night.

III. The maximum increase on adding ferrous salt cannot be predicted for a given solution and a given electrode. But it is usually large if the electrode has been previously soaked in a solution containing excess of dichromate, and small if the electrode has been soaked in ferrous solution. This would be expected if the action of ferrous salt on the electrode is the cause of the phenomenon.

Electrode immersed over night in excess of dichromate.

| Drops 0.1 *N* $(NH_4)_2Fe(SO_4)_2$... | 0 | 40 | 60 | 70 | Excess |
|---|---|---|---|---|---|
| E. M. F. in volts............ | 1.335 | 1.446 | 1.460 | 1.476 | 1.074 |

Electrode immersed over night in excess of ferrous salt.

| Drops 0.1 *N* $(NH_4)_2Fe(SO_4)_2$... | 0 | 10 | 40 | 50 | 60 | Excess |
|---|---|---|---|---|---|---|
| E. M. F. in volts............ | 1.220 | 1.238 | 1.267 | 1.276 | 1.276 | 0.956 |

In another case the electromotive force changed from 1.461 volts to 1.506 volts. The value of the electromotive force after excess of ferrous salt has been added is, of course, fixed by the expression[1]

$$\text{E. M. F.} = 0.988 + \frac{RT}{F} \ln \frac{(Fe^{+++})}{(Fe^{++})}$$

which varies greatly near the end point with small changes in the amount of ferrous salt.

IV. The magnitude in the increase produced by ferrous salt does not depend on the magnitude of the potential attained by the platinum in dichromate before adding the ferrous salt. But of necessity the greatest effects were noted when the initial potential was well below 1.515 volts, the maximum value attained in our experimentation. The following three experiments were made under apparently parallel conditions:

| | | | |
|---|---|---|---|
| Initial potential.................. | 1.357 | 1.215 | 1.461 |
| Maximum potential............... | 1.503 | 1.280 | 1.506 |
| Increase in potential.............. | 0.146 | 0.065 | 0.045 |

V. After the potential has been raised so far as possible by the addition of ferrous salt, and the end point is near, a further increase may be produced by adding more dichromate and then more ferrous salt. Thus, in one experiment, successive maxima of 1.276, 1.280 and 1.306 volts were attained without the end point having been passed. The highest value recorded, 1.515 volts, was obtained in this way.

VI. The increase in potential produced as above, by excess of ferrous salt, varies considerably in permanency.

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[1] Peters, *Z. physik. Chem.*, **26**, 206 (1898).

| Minutes elapsed. | Drops $(NH_4)_2Fe(SO_4)_2$. | E. M. F. |
|---|---|---|
| .. | .. | 1.245 |
| 10 | 60 | 1.328 |
| 14 | .. | 1.335 |
| 17 | .. | 1.340 |
| 23 | .. | 1.347 |
| 43 | .. | 1.341 |
| 110 | .. | 1.336 |
| 116 | .. | 1.325 |
| 133 | .. | 1.310 |
| 153 | .. | 1.301 |

With another electrode, the permanency was much less.

| Minutes elapsed. | Drops $(NH_4)_2Fe(SO_4)_2$. | E. M. F. |
|---|---|---|
| .. | .. | 1.431 |
| .. | 10 | 1.475 |
| 11 | .. | 1.486 |
| 25 | .. | 1.471 |
| 35 | .. | 1.460 |
| 53 | .. | 1.416 |

VII. The introduction of chloride after raising the potential by ferrous salt causes a rapid decrease in the electromotive force.[1]

| Minutes elapsed. | Drops 0.1 *N* $(NH_4)_2Fe(SO_4)_2$. | Solid NaCl. | Potentiometer reading. |
|---|---|---|---|
| .. | .. | .. | 60.5 |
| 10 | 10± | .. | 66.7 |
| 20 | .. | .. | 66.8 |
| 21 | .. | 2± grams | 63.0 |
| 22 | .. | .. | 61.9 |
| 32 | .. | .. | 59.8 |
| 120 | .. | .. | 56.7 |

This would seem to be due to the evolution of chlorine gas or of chromyl chloride.

Experiments under the same conditions as above were next carried out with reducing agents other than ferrous salts. Arsenious acid solution was prepared by dissolving arsenious oxide practically free from chloride in sodium hydroxide and neutralizing with sulfuric acid. The initial electrolyte contained chrome alum, arsenic acid, and the usual concentration of sulfuric acid. Equilibrium was attained with dichromate alone before adding the arsenious solution. In each case a decrease in potential was first noted, followed immediately by an increase above the initial value. The increases noted in parallel experiments ranged from 0.022 to 0.087 volt. With one exception, greater increases were noted after immersion in excess of dichromate than after treatment with excess of arsenite. The potentials reached on adding portions of arsenite began to fall off within a few seconds, and soon reached values lower than before

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[1] Compare the effect of chloride on the potential of nitric acid noted by Moore, THIS JOURNAL, 35, 333 (1913).

these additions, as would be expected from the logarithmic formula. This tendency to fall off may explain the fact that these increments were smaller than with ferrous salt.

Chromous sulfate was made by boiling chrome alum with excess of amalgamated zinc and sulfuric acid until a bright blue solution resulted. The original solution in the cells contained chrome alum and sulfuric acid as well as excess of dichromate, and the usual method was followed. Twenty-two experiments were performed. On adding the chromous solution, a sharp decrease in electromotive force was always noted, then an increase of from six to thirty millivolts above the original value, except in one case where this was barely attained. The smallest values were here noted with gray platinum electrodes. Chromous chloride never produced an increase in potential, due apparently to the previously described effect of chlorides.

After several unsuccessful attempts to prepare stannous sulfate,[1] a series of experiments was carried out with stannous chloride; by adding this rapidly under the usual conditions, increments up to 0.086 volt were obtained, which soon vanished, evidently because of the presence of chlorides.

Tenth normal potassium ferrocyanide was added to an electrolyte containing sulfuric acid, chrome alum, and potassium ferricyanide. Very large and permanent increments in potential immediately followed. Gray platinum electrodes were used. The most striking case is here given:

| Minutes elapsed. | Drops $K_4Fe(CN)_6$. | E. M. F. |
|---|---|---|
| .. | .. | 1.238 |
| 20 | .. | 1.241 |
| 30 | 4 | 1.435 |
| 90 | .. | 1.436 |
| 150 | .. | 1.447 |
| 240 | .. | 1.455 |
| 300 | .. | 1.445 |
| 3000 | .. | 1.426 |

It will be noted how much the action of this reagent resembles that of ferrous ion not involved in any complex.

Series of experiments similar to the above were carried out, adding respectively, sulfurous acid and hydrazine hydrochloride. These in each case at once depressed the potential of the platinum in dichromate, and though some recovery was always noted, the original potential was never reattained, much less exceeded. Hypophosphorous acid always slowly depressed the potential and no recovery was noted; its action on dichromate was shown, in a separate experiment, to be very slow. Oxalic acid seemed

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[1] Sn dissolved with much difficulty in $H_2SO_4$; and solution apparently owed any reducing power to $H_2SO_3$.

to behave similarly to hyphophosphorous acid, but its action was so feeble and slow that other influences may have been responsible for the results.

It may be of significance that all the reducing agents which produced increments in electromotive force can enter into reversible equilibrium with oxidizing agents under the conditions of the experiments, while all the others react irreversibly.

Other oxidizing solutions were now investigated in the same way as was the dichromate. Solutions containing potassium permanganate, manganous sulfate and large excess of sulfuric acid were tested under the usual conditions with potassium ferrocyanide and sulfurous acid successively. Mixtures of potassium ferrocyanide and potassium ferricyanide in equilibrium, also of arsenious and arsenic acids, were treated with a variety of reducing agents. In no case were increments in electromotive force noted, but rather decrements, more or less rapid according to the velocity of the reaction.[1] The phenomenon under discussion has, therefore, been noted with no other oxidizing reagent except dichromic acid.

What explanation can be offered of this phenomenon? The fact mentioned above that an electrode previously immersed in dichromate shows the greatest response to the reducing agent indicates that the rise in potential results from some action of the reducing agent on the surface of the electrode. It would be hard to conceive of the effect as localized in the solution.

According to views generally accepted, an oxidizing agent in solution is in equilibrium with a certain pressure of oxygen upon the electrode All concentrations being fixed, the single potential

$$\text{E. M. F.} = b + \frac{\text{RT}}{4\text{F}} \ln \frac{p(\text{O}_2)}{(\text{OH}^-)^4}.$$

Taking the potential of the hydrogen-oxygen cell at its theoretical value, 1.23 volts, and the single potential of the hydrogen electrode in normal hydroxyl ion as —0.53, referred to the calomel electrode as 0.560, $b$ = +0.70, all at 19°. The actual value of $b$ for oxygen on platinum, however, is 0.15 volt lower, an irregularity commonly ascribed to the presence of platinum oxides, whose composition determins the single potential observed.

The potential of dichromate ion on platinum is irreversible, as is shown by the fact that dichromate can be reduced at a platinum cathode, but not reoxidized at a platinum anode.

If now certain reducing agents assist a film of oxygen at given pressure on an electrode to impart to that electrode more nearly the theoretical pressure of positive electrons, then these reducing agents should raise

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[1] An experiment was carried out using permanganate and no manganous salt, to obviate the catalytic effect of Mn. No increase in potential was observed on adding ferrous salt.

the potential of a simple oxygen electrode. To test this point two electrodes of gray platinum in normal sulfuric acid were charged for a short time with oxygen until their single potentials were 1.116 and 0.956 volts, respectively. Each drop of ferrous sulfate now produced a decrease in potential; no rising tendency whatever could be detected. Therefore, the above hypothesis was abandoned.

A second possibility is that certain reducing agents reduce the hypothetical oxides of platinum on the surface of the electrode, thus eliminating their effect. According to this hypothesis, a substance, to raise the oxidizing potential, should reduce platinum oxides vigorously; but if its effect is to persist, the last traces of it at least should be oxidized very slowly by dichromate. Ferrous salt at considerable dilution poured over platinum oxide, made by precipitation with sodium hydroxide followed by washing, reduces it instantly. A similar experiment with sulfurous acid showed like results. The action of ferrous salt and sulfurous acid on dichromate is in each case very rapid. Nevertheless ferrous salts produce large increases and sulfurous acid decreases only. Another piece of evidence tending to discredit the second hypothesis is that low potentials are always observed on adding excess of dichromate to electrodes soaked over night in ferrous salt, and high potentials after long immersion in dichromate. Finally the question remains how the oxidizing potential is to be carried over to the platinum electrode[1] in the absence of platinum oxide.

A remaining possibility is that some reducing agents may catalyze a process by which dichromate establishes more nearly a reversible pressure of oxygen or of positive electrons on the electrode. No direct test of this hypothesis could be devised. The fact that only a limited number of combinations of oxidizing and reducing agents show the phenomenon does suggest catalysis. As the final products of the oxidation (chrome alum, ferric or stannic sulfate, etc.) were in all cases present at the start, they obviously do not contribute the catalytic effect. Evidently any catalysis which may take place is intimately connected with reduction. But the catalytic agent must do more than incite the oxidizing agent to yield up oxygen or positive electrons; it must, in some way, facilitate the action of these on the electrodes.

The remarkable increase, or at least constancy, in potential as certain reducing agents are added, in spite of the consequent decrease in dichromate concentration, may perhaps be explained thus: As the process goes on, greater and greater concentrations of ferrous salt remain unoxidized for a given time. Their increasing catalytic effect on the electrode may more than compensate for the decrease in oxidizing power of the di-

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[1] Peters, *Z. physik. Chem.*, 26, 197 (1898), has shown that ferrous salts react rapidly with oxygen on a platinum surface.

chromate due to concentration effect alone. From this point of view, the relatively high oxidizing potentials observed in exceedingly dilute dichromate solutions indicate that the values hitherto reported for more concentrated solutions are much too low.[1]

## The Electrometric Titration of Dichromate Ion with Ferrous Ion.

The observations recorded in this paper suggest an improvement in the electrometric method of titrating dichromate and ferrous salts which makes it both more rapid and more accurate than the method depending on the ferricyanide end point.

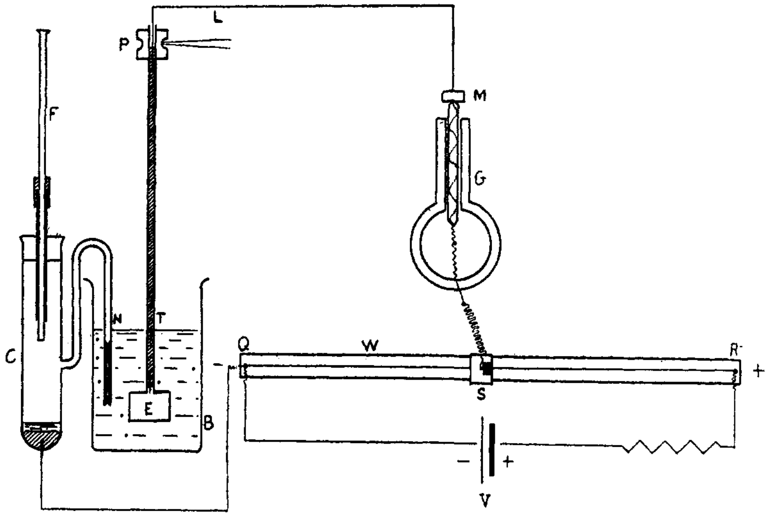

Diagram of Apparatus.

The solution to be titrated is placed in the beaker B. The acid in excess may be either hydrochloric or sulfuric. The electrode E of platinum foil is sealed into a glass tube, T, provided, if possible, with a pulley, P, and a belt to rotate it; this obviates stirring by hand. Connection is made between E and L by filling the tube with mercury. C is a calomel electrode containing mercury, mercurous sulfate and potassium chloride, not too dilute. A plunger, F, if added, will make it possible to sweep out the side neck N just before the end of a titration. QR is a thin wire of manganin or German silver stretched over a strip of wood, W; the con-

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[1] Bancroft (*Z. physik. Chem.*, 10, 387 (1892)) and Neuman (*Ibid.*, 14, 228 (1894)) report for 0.2 $N$ $H_2Cr_2O_7$ the single potential of 1.397 volts. Crotogino (*Z. anorg. Chem.*, 24, 245 (1900)) for the same strength of solution reports 1.337 volts which after three days rises to 1.477 volts. These latter values are calculated from the values the author gives for the potential of the cell measured with dichromate on one side and a normal calomel electrode on the other.

nection to the battery V should be made with a piece of the manganin wire of such length that the sliding contact is near R at the start of the titration. The connections with the galvanometer G require no comment. This is conveniently provided with a mirror, M, which reflects a beam of light from a lamp, focused upon it by a small lens. The beam of light moving over a strip of white paper shows the operator when current is flowing through the glavanometer, with a minimum of effort on his part. A very sensitive galvanometer is unnecessary and in fact undesirable unless shunted.

To titrate a dichromate solution with ferrous salt, the galvanometer is first brought to rest by moving the sliding contact S, then ferrous salt is run in and the contact is moved toward Q sufficiently to neutralize the anomalous increase in potential. If ferrous salt is to be titrated, a slight excess of dichromate is added, and the solution run back with a known solution of ferrous salt. Very soon a nearly constant maximum is reached, so that the operator can abandon the sliding contact and busy himself with the buret, only watching the spot of light until a last drop sends it off the scale. This last drop should be subtracted from the volume used. The two or three drops preceding the end point cause temporary disturbances in the galvanometer, but it will always come back to its original position until a drop in excess has been added. The improvement claimed in this method over those previously suggested lies in the constancy of the electromotive force right up to the end point, and the great simplicity of apparatus and method which can be employed in consequence.

No comparison of the end points as obtained by this method and by the ferricyanide method, respectively, appears in any article hitherto published. It is, therefore, not superfluous to record briefly a few experiments, using an apparatus identical with that described above, except that the beaker was covered with a perforated mica sheet and air was excluded by a current of carbon dioxide. The experiments could thus be performed with greater accuracy and deliberation. In each case the initial solution was 0.05 normal in ferric salt and chrome alum and 3 normal in sulfuric acid. The ferricyanide indicator was very dilute, a crystal the size of a pin head being dissolved in 25 cc. of water, and the tests were carried out on a porcelain tile as usual,[1] except that drops of a similar solution of acidified chrome alum were placed on the tile for purposes of comparison. Only one of the five experiments made is given below, as the results are entirely similar in all cases. Tenth normal solutions of ferrous ammonium sulfate and potassium dichromate were employed and the total volume was about 100 cc. The solution contained at the start only six drops excess of potassium dichromate.

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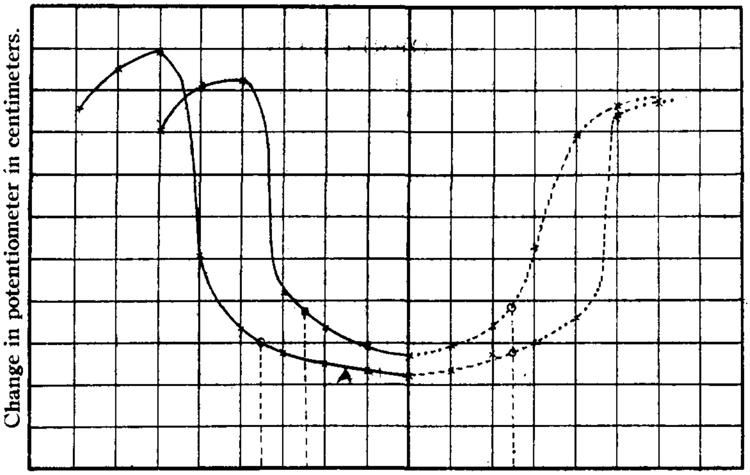
[1] Talbot, *Quantitative Analysis*, p. 106 (1908).

| Substance. | Drops. | Potentiometer reading. | Change. | Indicator. |
|---|---|---|---|---|
| .... | .. | 88.10 | .... | No color |
| $FeSO_4$ | 1 | 94.20 | +6.10 | No color |
| .... | 2 | 96.20 | +2.00 | No color. |
| .... | 3 | 71.75 | —24.45 | No color |
| .... | 4 | 63.10 | —8.65 | No color |
| .... | 5 | 60.50 | —2.60 | Faint blue, 30 sec. |
| .... | 6 | 59.10 | —1.40 | Good blue, 30 sec. |
| .... | 7 | 58.20 | —0.90 | Blue at once |
| .... | 8 | 57.40 | —0.80 | Blue at once |
| $K_2Cr_2O_7$ | 1 | 58.50 | +1.10 | Blue at once |
| .... | 2 | 59.70 | +1.20 | Faint blue, 20 sec. |
| .... | 3 | 61.20 | +1.50 | Faint blue, 30 sec. |
| .... | 4 | 64.45 | +3.25 | No color |
| .... | 5 | 88.70 | +24.25 | No color |
| .... | 6 | 90.40 | +1.70 | No color |

The accompanying diagram shows the titration curves of two samples. The data for the lower curve, A, are given in the table. Perpendiculars to the axis of abscissas cut the curve at the end points determind by the use of potassium ferricyanide. A single drop of reagent is estimated to contain a volume of 0.03 cc.



Equal portions of 0.00017 gms. $Fe''$. Equal portions of 0.00015 gms. $K_2Cr_2O_7$.
Titration Curves.

It will be noted that nearly two drops excess of 0.1 normal ferrous solution ($6 \times 10^{-6}$ or 0.0003 gram ferrous iron) in 100 cc. are required to develop a visible blue color within 30 seconds, and that in titrating ferrous salt with dichromate, no blue color is developed when 0.0003 gram ferrous iron is still present in 100 cc. This correction must be considered if dichromate is made up determinate and not standardized against pure iron.

## Summary.

Certain reducing agents increase the oxidizing potential of the dichromate ion on platinum by amounts up to two-tenths of a volt. No other oxidizing agent was found which would give a similar effect.

The potential continues to increase up to the very end point of the reaction and is highest when the dichromate concentration is least. A final drop of 0.1 normal reducing agent often depresses the potential by half a volt.

The duration of the effect varies with the reducing agent used from a few seconds to many hours. Chlorides are fatal to the permanency, owing apparently to a side reaction.

The phenomenon may be plausibly explained by assumptions of catalytic action.

An improved apparatus and method of titrating dichromate and ferrous salts, based on the phenomenon, is suggested.

When the end point of this reaction is determined with a ferricyanide indicator, 0.0003 gram excess of ferrous iron in each hundred cubic centimeters of solution is present when the blue color barely develops within thirty seconds.

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## A CORRECTION.

The paper in the July number of THIS JOURNAL on "Some Applications of the Hydrogen Electrode in Analysis, Research and Teaching," was made somewhat unintelligible by a rather natural mistake made after the proof was read. The writer had inserted the titles of the curves as subheadings in the manuscript as each curve was discussed. When the proof was read they were still in their proper places. However, when the cuts were inserted these sub-headings were removed to the cuts, which were, of course, placed frequently out of their immediate connection with the text. At the beginning of a number of paragraphs, therefore, the reader is at a loss to know to which curve the text refers. The following corrections should be made:

Page 853, paragraph 2, Fig. 3.
Page 857, paragraph 3, Fig. 4.
Page 861, paragraph 1, Fig. 7.
Page 862, paragraph 1, Fig. 8; paragraph 2, Fig. 9.
Page 863, paragraph 1, Fig 10.
Page 864, paragraph 1, Fig. 11.
Page 866, paragraph 1, Fig. 12; paragraph 4, Fig. 13.
Page 869, paragraph 2, Fig. 15.

The reference to the work of Blum, page 863, should be THIS JOURNAL, 34, 123 (1912).

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