[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 24]

# THE ELECTRODE POTENTIAL OF BISMUTH DETERMINED BY EQUILIBRIUM MEASUREMENTS

BY ERNEST H. SWIFT

Received November 22, 1922

## Outline of the Investigation

Several attempts[1] have been made to measure the potential of a bismuth electrode against solutions of bismuth salts; but the interpretation of the results has been impossible, owing to the lack of definite knowledge as to the activity of the bismuth ion in these solutions. The hydrolysis of the normal bismuth salts and the insolubility of the hydrolysis products have contributed to the uncertainty of the calculation.

Of the normal salts of bismuth the perchlorate has the advantage that it does not give insoluble hydrolysis products. Accordingly, attempts were made by Mr. R. C. Sticht in this Laboratory some years ago to measure the electromotive force of a bismuth electrode in a solution of bismuth perchlorate and perchloric acid against a hydrogen electrode in a perchloric acid solution of approximately the same strength; and also to check the electrode potential so obtained from the electromotive-force data by measuring the equilibrium of the reaction between metallic bismuth and copper and their perchlorates in aqueous solution.

These latter measurements were made only in a preliminary manner with analytical methods of doubtful accuracy; but it was shown that at equilibrium the concentration of each of the elements in the solution is great enough to be determined with reasonable accuracy.

While bismuth perchlorate solutions do not give insoluble hydrolysis products, it became evident early in the experimental work that hydrolysis does take place; for it was observed that it was possible to dissolve one atomic weight of bismuth in the form of oxide in one formula weight of perchloric acid, showing that the bismuth in such a solution could not exist mainly as the normal trivalent bismuth ion, and suggesting that a large proportion of it must exist as $BiO^+$ or $Bi(OH)_2{}^+$ ion. Accordingly, an investigation, the results of which are given in the preceding paper, was undertaken in this Laboratory by Dr. D. F. Smith to determine the state in which bismuth exists in perchloric acid solutions, and to derive from electromotive-force measurements a value of its molal electrode potential.

The purpose of the research to be here described was to derive independently the molal electrode-potential of bismuth by determining the equilibrium conditions of a reduction reaction in which it is involved. This

---

[1] Bernhard Neuman, *Z. physik. Chem.*, **14**, 193 (1894). Foerster and Schwabe. *Z. Elektrochem.*, **16**, 298 (1910).

method is based upon the principle that when a solution containing the ions of 2 metals M and M′ is in contact with each of these metals as solid phase, equilibrium is attained when the ion concentrations are such that the potentials of these 2 metals against the solutions are equal. Therefore the molal electrode-potential $E_{M'}$ of one of these metals being known and the ion concentrations (M) and (M′) in the equilibrium mixture having been determined, the molal electrode-potential $E_M$ of the other metal can be calculated by the general equation:

$$E_M - \frac{RT}{NF} ln\ (M) = E_{M'} - \frac{RT}{NF} ln\ (M').$$

Copper was chosen as the reference metal in this case, for the value of its molal electrode-potential has been accurately determined and this value indicated that a measurable equilibrium would be reached with bismuth salts. An analytical method was worked out by which salts in the solution could be determined without great difficulty.

Since the concentration of any basic bismuth ion produced by the hydrolysis will be a function of the hydrogen-ion concentration, a calculation of the equilibrium conditions requires a knowledge of its concentration as well as of those of the 2 metal ions present. The total perchlorate present was determined as a basis for its indirect calculation, since direct determination of the free acid present in the equilibrium mixtures was impracticable.

This research was carried on with the aid of a grant to Professor A. A. Noyes by the Carnegie Institution of Washington, for which the author wishes to express his indebtedness. The author also wishes to acknowledge his obligation to Professor Noyes for his advice and aid during the progress of this investigation and for his valuable assistance in preparing this paper for publication.

## The Method of Preparing the Equilibrium Mixtures

The equilibrium mixtures were prepared by sealing in glass bottles solutions of bismuth perchlorate and copper perchlorate with a large excess of copper and bismuth in a finely divided metallic state. The mixtures were then rotated in a thermostat at 25°, in such a manner that there was continuous mixing of the solid material with the solution, for periods varying from 5 to 65 days. To determine when equilibrium had been attained the equilibrium was approached from both sides, two mixtures of any one concentration being always started simultaneously, one containing a larger concentration of bismuth in solution than would be present at equilibrium, the other containing an excess of copper in the solution.

Before the bottles were sealed, a vigorous stream of purified carbon dioxide gas was passed through the bottles for 30 minutes, in order to free the solutions as far as possible from oxygen, and prevent it from causing the metals to dissolve during the rotation. However, this treatment was inadequate, as was shown by the fact that small amounts of both metals did dissolve during the rotation. For the purpose of analysis the bottles were removed from the thermostat, and their contents were immediately filtered by suction through tightly packed asbestos filters, which removed all the finely divided particles of the metals.

## Preparation of the Materials

The perchloric acid used was a C. P. product purchased in the open market, approximately 60% by weight and of specific gravity 1.54. The absence of chloride, chlorate, sulfate, and heavy metals was proved by qualitative tests. There was no residue upon evaporation of a 10cc. portion to dryness. The concentration of the acid was checked by precipitation of the perchlorate as the potassium salt, and by titration against a standard alkali solution.

The metallic bismuth was prepared from an imported C. P. bismuth oxychloride. This was once reprecipitated. A finely divided state of the metal was secured by precipitating it by electrolysis from a saturated solution of the bismuth oxychloride in 12 $N$ hydrochloric acid in contact with an excess of the solid. The precipitation was effected between platinum electrodes, a heavy platinum wire serving as the cathode in order to secure a high current-density, and a current of 4 to 6 amperes at 10 to 12 volts being used. The metal was deposited upon the cathode in an extremely finely divided form which fell off or was shaken off into a separate receiving vessel which prevented contact of this metal with any of the solid bismuth oxychloride. The metal so prepared was then collected and triturated in 2 $N$ perchloric acid and finally washed with a dilute solution of perchloric acid until the washings failed to give any test for chloride. The metal was kept under 0.1 $N$ perchloric acid.

Bismuth trioxide was prepared by igniting an imported basic bismuth nitrate, after qualitative tests had proved the absence of any impurities and after it had been once precipitated. A domestic brand of C. P. analyzed trioxide was tried, but found to be unsatisfactory owing to the presence of considerable quantities of iron and other metals.

Metallic copper was prepared by electrolytic precipitation between an anode of electrolytic copper foil and a cathode of heavy platinum wire in a solution of copper sulfate. By using a high current-density with approximately 12 volts the metal was deposited in a spongy, finely divided form. The precipitated metal was collected, triturated with 2 $N$ perchloric acid, and then washed with dil. perchloric acid until the washings gave no test for sulfate. The metal was kept under 0.1 $N$ perchloric acid.

All of the solutions were prepared by weight, rather than by volume.

The solutions of bismuth perchlorate were made by dissolving the bismuth oxide, prepared as described above, in an equivalent amount of the perchloric acid and then diluting to the desired concentration.

The copper perchlorate solutions were prepared by dissolving copper oxide in an equivalent amount of perchloric acid and then diluting to the desired concentrations. The copper oxide was made by weighing out metallic copper, prepared as described above, dissolving it in nitric acid, and igniting the nitrate to constant weight.

## Analytical Methods

Owing to the fact that in the equilibrium solutions the amount of copper is small in proportion to the amount of bismuth present, the problem of an analytical method of sufficient accuracy for this separation offered some difficulties. The more promising of the standard methods for the separation of bismuth and copper were applied to a standard solution of bismuth and copper in the approximate proportions present in the equilibrium solutions. Most of these were found not to give the desired accuracy. Precipitation of the bismuth as carbonate from an ammoniacal solution was unsatisfactory, as the amorphous flocculent precipitate, formed in alkaline solution, carried with it 10 to 15% of the copper present. To ascertain whether the more stable complex of copper with cyanide would prevent this, the bismuth was precipitated from a solution in which an excess of potassium cyanide was present; but the results were no more favorable. The same difficulty was encountered in trying to precipitate the bismuth as sulfide from a cyanide solution.

Rivot's method of precipitating the copper, after reduction, as cuprous thiocyanate is also unreliable, because of the solubility of the precipitate, where the quantity of copper is very small. Direct determination of the copper volumetrically by means of potassium iodide and sodium thiosulfate is impossible in the presence of bismuth, because of the interference of the color of the bismuth iodide with the end-point.

Moser[2] describes a method for the estimation of bismuth and its separation from copper which depends upon the relative solubilities of the phosphates of the 2 metals in dil. nitric acid. As this method would permit of the precipitation of the bismuth in an acid solution and in the form of a crystalline precipitate, whereby occlusion would be diminished, a series of experiments was carried out in order to determine the conditions most favorable for an accurate separation. These experiments indicated that with a hydrogen-ion concentration as high as 0.3–0.4 $N$ it is possible to secure practically complete precipitation of the bismuth; while with an acid concentration as low as 0.1 $N$ it was impossible to detect an appreciable amount of copper in the precipitate from solutions containing much bismuth and little copper. In cases where the hydrogen-ion concentration was somewhat less than 0.1 $N$, tests for copper, estimated to correspond to less than 0.1 mg., were obtained. In the actual analyses, in order to avoid introducing alkali or ammonium salts into the solution, 1 formal phosphoric acid was used as the precipitant. This was added from a buret drop by drop, the solution being kept hot and constantly agitated in order to prevent the precipitate from separating in a finely divided form that was difficult to filter. By the manner in which the precipitate settled out it was possible to tell when just an equivalent amount of the acid had been added. The precipitated normal bismuth phosphate $BiPO_4$ was collected in a Gooch crucible, washed until the filtrate no longer gave an acid reaction, and ignited to constant weight at 400–600°. Test analyses upon standard solutions proved that this method was capable of giving results accurate to within 0.2%.

The copper was determined in the filtrate by electrolytic precipitation from the perchloric acid solution. It was found by experiment that this acid furnishes an excellent medium from which to effect the rapid precipitation of small amounts of copper. Perchloric acid is stable under the electric current and has none of the disadvantages incident to the use of either nitric or sulfuric acid for this purpose. The most favorable conditions were found to require approximately 10 cc. of 6 $N$ perchloric acid in 50 cc. of solution, with a potential of about 6 volts and a current of 1–1.5 amperes. The deposition was made on a platinum dish cathode with a rotating anode revolving at the rate of about 200 revolutions per minute. Test analyses indicated that the accuracy of the method was limited only by the error in weighing the relatively large platinum dish.

The total perchlorate was determined by two methods. The first method consisted in precipitating the metals as sulfides and then titrating the acid liberated. The precipitation was made with hydrogen sulfide under pressure, the air being excluded so as to avoid as far as possible any oxidation of the hydrogen sulfide itself. After filtering off the precipitated sulfides, enough standard alkali was added to neutralize most of the

---

[2] Moser, *Z. anal. Chem.*, **45**, 19 (1916).

perchloric acid present, the excess of hydrogen sulfide was removed by boiling, and the titration completed.

The second method consisted in precipitating the metals by electrolysis and titrating the acid remaining in the solution. Difficulty in securing an adherent coating of the 2 metals simultaneously and loss due to the evolution of gases during the process of precipitation made this method less accurate than the first.

## The Experimental Data

The data obtained are given in Table I below. All concentrations are expressed in atomic weights or moles per liter of solution at 25°, and these units are used throughout this paper. A conversion to moles per 1000 g. of solvent would affect the calculated potentials by less than 1 millivolt. The bismuth concentrations are accurate to within 0.2–0.3%; the copper concentrations, owing to the extremely small amount present in the volume that it was practicable to take for analysis (15–35 mg.), are accurate to within about 2%. The determination of the total perchlorate was somewhat more difficult, and the method subject to more uncertainty; however it is thought that the results are accurate to within 4–5%. It is to be noted that an error of 2% in the determination of the copper concentration would cause a deviation in the calculated copper potential of only about 0.2 millivolt. The concentration of the cuprous ion is negligible, since the ratio of $Cu^{++}$ to $Cu^{+}$, calculated from the molal potentials, Cu(s), $Cu^{++}$, and Cu(s), $Cu^{+}$, is over 1000 to 1. An error of 5% in the determination of the hydrogen ion would cause a deviation of less than 1 millivolt in the calculated value of the bismuth potential.

TABLE I

COMPOSITION OF THE EQUILIBRIUM MIXTURES

| Expt. | Rotation in days | Ion in excess at start | Bi per liter | Cu per liter | $ClO_4$ per liter | Ratio $(Bi):(Cu)^{3/2}$ |
|---|---|---|---|---|---|---|
| 1 a | 60 | Bi | 0.03857 | 0.00121 | 0.115 | 916 |
| b | 60 | Cu | 0.04491 | 0.00144 | 0.125 | 823 |
| 2 a | 60 | Bi | 0.0776 | 0.00282 | 0.237 | 518 |
| b | 60 | Cu | 0.08222 | 0.00297 | 0.258 | 508 |
| 3 a | 65 | Bi | 0.1489 | 0.00552 | 0.473 | 363 |
| b | 65 | Cu | 0.1153 | 0.00429 | 0.376 | 411 |
| 4 a | 65 | Bi | 0.1131 | 0.00211 | 0.241 | 1167 |
| b | 65 | Cu | 0.08315 | 0.00306 | 0.250 | 492 |

In the experiments to whose numbers the letters a and b are attached, the equilibrium was approached from opposite sides in solutions of not far from equal acid concentrations, and the successive pairs of ratios given in the last column show the limits within which equilibrium was attained.

## Calculation of the Electrode Potentials

The results published in the previous paper by D. F. Smith show that most of the bismuth present in solutions similar to those given in Table I exists either as $BiO^+$ or as $Bi(OH)^{++}$. The molal electrode-potential was calculated upon the assumptions (1) that all the bismuth exists as $BiO^+$ and (2) that it all exists as $Bi(OH)^{++}$.

The corresponding chemical equations are

$$3Cu\ (s) + 2BiO^+ + 4H^+ = 2Bi(s) + 3Cu^{++} + 2H_2O. \qquad (1)$$

$$3Cu\ (s) + 2Bi(OH)^{++} + 2H^+ = 2Bi(s) + 3Cu^{++} + H_2O. \qquad (2)$$

The calculation of the molal electrode-potential of bismuth, $E_{Bi}$, was made by equating

$$E_{Cu} - \frac{RT}{2F} \ln Cu^{++} \text{ with } \quad E_{Bi} - \frac{RT}{3F} \ln (\Sigma Bi)\ (\Sigma H)^2 \qquad (1)$$

and with

$$E_{Bi} - \frac{RT}{3F} \ln (\Sigma Bi)\ (\Sigma H) \qquad (2)$$

The molal electrode-potential of copper was taken as $-0.345$ volt.[3] The cupric-ion concentration was calculated upon the assumption that the ionization of cupric perchlorate, $Cu(ClO_4)_2$, is the same as that of cupric nitrate at a concentration equal to that of the total perchlorate present in the solution, and that the ionization values for cupric nitrate are given by the conductance ratios as found by Jones and West.[4]

No attempt was made to correct either for the ionization of the basic bismuth salts, or for the ionization or activity of the acid, as any such corrections would be very uncertain. This is equivalent to making the assumption of complete ionization of these electrolytes.

Table II shows the values at 25° of the molal electrode-potentials obtained under the assumption (1) that all the bismuth exists as $BiO^+$, and (2) that it all exists as $Bi(OH)^{++}$.

TABLE II

THE MOLAL ELECTRODE-POTENTIAL OF BISMUTH AT 25°

| Expt. | ($\Sigma$Bi) | ($\Sigma$H) assuming | | ($Cu^{++}$) | Actual potential of copper | Molal potential assuming | |
|---|---|---|---|---|---|---|---|
| | | (1) $BiO^+$ | (2) $Bi(OH)^{++}$ | | | (1) $BiO^+$ | (2) $Bi(OH)^{++}$ |
| 1 a | 0.03857 | 0.0740 | 0.0354 | 0.00093 | −0.255 | −0.328 | −0.312 |
| b | 0.04491 | 0.0776 | 0.0327 | 0.00109 | −0.257 | −0.328 | −0.313 |
| 2 a | 0.07776 | 0.154 | 0.0760 | 0.00201 | −0.265 | −0.319 | −0.309 |
| b | 0.08222 | 0.170 | 0.0876 | 0.00208 | −0.265 | −0.317 | −0.308 |
| 3 a | 0.1489 | 0.313 | 0.164 | 0.00348 | −0.272 | −0.308 | −0.304 |
| b | 0.1153 | 0.252 | 0.137 | 0.00282 | −0.270 | −0.312 | −0.305 |
| 4 a | 0.1131 | 0.124 | 0.0110 | 0.00149 | −0.261 | −0.316 | −0.319 |
| b | 0.08315 | 0.161 | 0.078 | 0.00216 | −0.266 | −0.319 | −0.309 |
| | | | | | Av. | −0.318 | −0.310 |

It is to be noted that the values of the molal potential derived under the assumption that the bismuth exists as $BiO^+$ are somewhat less constant than those derived under the assumption that it exists as $Bi(OH)^{++}$.

---

[3] Lewis and Randall's, "Thermodynamics and Free Energy of Chemical Substances," **1923.**

[4] Jones and West, *Am. Chem. J.*, **34,** 357 (1905).

(The deviation of the value obtained in Expt. 4a is probably due either to a large amount of dissolved oxygen present at the start or to a slight leak during the period of rotation, which caused the acid concentration to decrease abnormally.) It is also to be noted that the values to which this research has led, though obtained under somewhat more widely varying concentrations of the total bismuth and of the hydrogen ion, are in general agreement with those of Smith, who found under the two assumptions —0.314 and —0.298 volt, respectively.

Slightly different average values of the molal electrode-potentials, namely, —0.323 and —0.314 volt, respectively, are obtained if it be assumed that the ionization of the copper salt is also complete—an assumption which tends to compensate the error involved in regarding the bismuth salts and the acid as completely ionized.

## Summary

Measurements in which the equilibrium was approached from opposite sides were made of equilibrium conditions at 25° in perchloric acid solution of the reaction, $3Cu(s) + 2Bi(ClO_4)_3 = 2Bi(s) + 3Cu(ClO_4)_2$.

From the composition of the equilibrium mixtures were calculated values of the molal electrode-potential of bismuth, under the assumptions that the bismuth exists in such solutions entirely (1) as $BiO^+$, or (2) as $Bi(OH)^{++}$, and that the free perchloric acid present is completely ionized. The following values, referred to the molal hydrogen electrode, were obtained: $Bi(s), BiO^+ + H^+$: —0.318 volt; $Bi(s), Bi(OH)^{++} + H^+$: —0.310 volt

If the copper salt be regarded also as completely ionized, whereby the errors in the ionization assumptions are partially compensated, there result values about 5 millivolts different from these, namely, —0.323 and —0.314 volt.

The results of this research are in fair agreement with the values —0.314 and —0.298 derived by D. F. Smith from electromotive-force measurements, and presented in the preceding paper.

PASADENA, CALIFORNIA