The mean of five determinations of this quantity based on calorimetric data is between 63 K and 64 K.

The decomposition pressure of silver oxide at 25° is calculated to be 5×10^{-4} atmospheres.

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THE POTENTIAL OF THE OXYGEN ELECTRODE.

BY GILBERT NEWTON LEWIS.

THERE are no more essential physico-chemical data than the changes of free energy accompanying those important chemical processes in which oxygen takes part. Many of these free energy changes could be calculated directly if the potential of the oxygen electrode, against a given concentration of hydroxyl ion, were accurately known. The purpose of the present paper is to determine the true value of this potential.

An oxygen electrode was first used by Grove in the cell which bears his name. The electromotive force of this cell, which is composed essentially of an oxygen and a hydrogen electrode dipping into an aqueous solution, has been measured by a number of experimentors.[1] The value most frequently met in the literature is 1.07–1.08 volts, as found by Smale,[2] who was the first to show that the electromotive force of such a cell is independent of the nature of the electrolyte used.

This value of 1.07–1.08 volts was generally accepted as the true electromotive force of the oxygen-hydrogen cell, or in other words, the true measure of the free energy of formation of water from its elements, but was later shown to be probably too low, by the work of Bose,[3] Wilsmore[4] and Czepinski,[5] who found that the electromotive force of an oxygen-hydrogen cell in normal sulphuric acid increases after several days' standing to 1.10–1.12 volts.

Assuming that between the substances present in the cell there is no reaction possible which can produce a greater change

[1] See bibliography by Bose: Z. physik. Chem. 34, 730 (1900).

[2] Z. physik. Chem. 14, 577 (1894).

[3] Loc. cit.

[4] Z. physik. Chem. 35, 291 (1900).

[5] Z. anorg. Chem. 30, 1 (1902).

of free energy than is associated with the union of oxygen and hydrogen to form water, then we must assume that the true potential of the oxygen-hydrogen cell is at least as high as the highest value obtained, namely 1.12 volts. This is in fact the value most generally adopted at present.

Westhaver,[1] however, apparently considers the above assumption incorrect when platinum electrodes are used, and prefers to take for the electromotive force 1.06 volts, which he obtains by means of an iridium electrode.

Bose,[2] taking 1.12 volts as only the lower limit of the electromotive force, has tried to find also its upper limit. He concludes that the electromotive force must lie between 1.12 and 1.15 and probably lies nearer the lower value. The method which he used for obtaining the upper limit seems, however, to be quite erroneous. It consisted in increasing the electromotive force artificially by depositing oxygen electrically upon the oxygen electrode, and in noting the lowest point to which the electromotive force then sank after the lapse of considerable time. Bose assumed that this value must be higher than the true electromotive force of the cell, but this assumption is certainly not true. Westhaver found that after charging similarly the iridium electrode with oxygen, the electromotive force fell in a few days to 1.06, the normal value, and even to a lower value, 0.9 volt when the electrode was completely immersed. According to Bose's view the latter figure would have to be taken for the upper limit of the electromotive force, and this is obviously absurd.

A number of other cases might be cited to show that the principle is erroneous. For example, I may mention the following experiment: To a solution of cobaltous sulphate, ammonium sulphate and ammonium hydroxide are added. The mixture shaken with air absorbs a large quantity of oxygen. If it is then immediately acidified it becomes a very powerful oxidizing agent and rapidly evolves oxygen. A platinum electrode dipped into this solution is immediately covered with bubbles of oxygen, but its (oxidizing) potential is several tenths of a volt less than that which an ordinary oxygen electrode would have in a solution of the same acidity.

The only upper limit to the electromotive force of the oxygen-

[1] Z. physik. Chem. 51, 65 (1905).
[2] Z. Elektrochem. 7, 673 (1901); Z. anorg. Chem. 30, 406 (1902).

hydrogen cell which we can obtain from existing data is the lowest electromotive force at which it is possible to electrolyze water and produce definitely recognizable bubbles of oxygen and hydrogen. According to Coehn and Osaka[1] this value is 1.28 volts.

Granting then that the true electromotive force lies between 1.12 and 1.28 volts, what reason have we for believing that the lower of these two values is any more nearly correct than the higher? The belief that the electromotive force actually measured with ordinary oxygen and hydrogen electrodes is the true reversible electromotive force of the oxygen-hydrogen cell is based on two assumptions which are unsupported by any experimental evidence. The first of these assumptions is that when a small current flows through the cell (a current of such magnitude as is used in electromotive force determinations) the accompanying reaction is simply the formation of water from its elements. The second assumption is that this reaction occurs in a perfectly reversible way.

As far as the hydrogen electrode is concerned there is no question but that both assumptions are correct. Hydrogen passes quantitatively and reversibly into hydrogen ion. But it is very doubtful if at the other electrode oxygen passes just as smoothly into oxygen or hydroxyl ion. Richarz and Lonnes[2] studied the products formed when water, in the presence of air, was electrolyzed between electrodes of polished platinum. The conditions of the cathode when a current is passing through this cell are nearly identical with the conditions at the oxygen electrode when it is made the cathode. In both cases hydrogen would be deposited on the electrode if it were not for the presence there of oxygen. In both cases in place of the deposition of hydrogen oxygen goes into electrolytic solution. The only difference in the two cases is that in one the electrode is of platinized platinum, bubbled over with oxygen; in the other the electrode is of polished platinum in contact with dissolved air. Now in their experiments Richarz and Lonnes found that as the dissolved oxygen was consumed at the cathode, not water, but hydrogen peroxide was formed in nearly equivalent amount. Thus with a current density of about 2×10^{-7} amperes per square centimeter, passing for five

[1] Z. anorg. Chem. **34,** 86 (1903).

[2] Z. physik. Chem. **20,** 145 (1896).

obtained 88 per cent. of the theoretical yield of peroxide, and even more than this had probably formed and in part decomposed before the analysis.

Since the conditions at the cathode in this experiment are not identical with those at the oxygen electrode, we cannot conclude necessarily that the reactions going on when a current passes are the same in both cases, but the conditions are so similar that we are at least led to consider the possibility that the main reaction in the oxygen-hydrogen cell is the union of oxygen and hydrogen, not primarily to form water, but to form hydrogen peroxide. If this is the case, the observed electromotive force is the measure of the free energy of formation of hydrogen peroxide, and since this is smaller (even bearing in mind that the peroxide is kept at a low concentration by the presence of the platinum black) than the free energy of formation of water, the electromotive force corresponding to the latter reaction would be considerably higher than the one actually observed.

This assumption is far from improbable. We know indeed that in other cases when oxygen takes part in chemical reactions at ordinary temperatures, it almost invariably enters into combination first as the radical (O_2), forming substances of the type of peroxides.

There is, moreover, another more specific argument in favor of this assumption. It has frequently been observed[1] that upon the addition of hydrogen peroxide to the liquid about the oxygen electrode, the electromotive force of the oxygen-hydrogen cell instead of increasing, as was expected, diminishes. There have been several ingenious attempts to explain this phenomenon, but they are entirely unnecessary if we assume that hydrogen peroxide is formed by the reaction of the cell, for it is a familiar principle that the electromotive force of any cell is lowered by increasing the concentration of any of the products of the electrolytic reaction.

But supposing that in spite of all these facts we assume that the reaction in the cell is simply the formation of water; even then the assumption that this reaction occurs reversibly is quite improbable in view of the slowness of almost all processes of

[1] See, for example, Glaser: Z. Elektrochem. **4,** 374 (1898); Wilsmore: Loc. cit.

oxidation at ordinary temperatures, even in the presence of platinum black.

In this discussion I have attempted to show only that we have at present no satisfactory evidence that the true electromotive force of the oxygen-hydrogen cell may not be much higher than any of the values hitherto obtained by direct measurement. If it is in fact higher, the question is how we are to obtain its true value. Three methods suggest themselves.

If all chemical reactions occurred instantaneously, every galvanic cell would always give the highest possible electromotive force. In other words, of all the reactions possible in the cell, that one evolving the most free energy would alone occur and occur reversibly. It is the slowness of some essential part of the process which causes the condition of irreversibility. One method, therefore, of approaching the true electromotive force of a cell which ordinarily acts irreversibly is to introduce some substance which catalyzes the electrolytic reaction. In our present problem this method would consist in finding for the oxygen electrode some more powerful catalyzer than platinum black.

The second method is based on the principle that when at a given electrode two distinct electrochemical reactions can take place, corresponding to two different potentials, a reaction will tend to occur between the substances concerned, of such a sort as to equalize the two potentials. Thus a platinum electrode dipping into a solution of ferric and ferrous salts has a definite potential. If we introduce a small quantity of potassium iodide at the electrode, iodine will be set free until the potential between iodine and iodine ion is equal to that between the ferric and ferrous ions. So if at the oxygen electrode an oxidizable substance, say a chloride, is added, we should expect chlorine to be set free until the potential between chlorine and chlorine ion equals the true potential between oxygen and the hydroxyl ion at its given concentration. In other words from a strong, slow oxidizing agent an equally strong, but rapid, oxidizing agent may be formed.[1] The reaction may, however, be too slow for the method to be practicable, unless a suitable catalyzer is present.

[1] Spencer and Abegg, Z. anorg. Chem. **44,** 379 (1905), have made application of this principle in determining the electromotive force of the oxygen-hydrogen cell and obtained 1.14 volts, but by a method which appears to me erroneous.

I have made a number of attempts to apply this principle, using various substances such as manganese, cobalt and cerium salts which are known to catalyze the process of autoxidation, but these experiments are still incomplete and their discussion may be postponed.

I may point out in this connection that a phenomenon observed by Wilsmore[1] is probably an illustration of the principle we are considering. He found that the electromotive force of the oxygen-hydrogen cell in normal sulphuric acid is at first 1.08 volts, but rises in the course of a few days to 1.12 volts. The sulphuric acid in the neighborhood of the oxygen electrode then showed on analysis the presence of some oxidizing agent. When it was replaced by fresh acid the electromotive force returned at once to 1.08 volts. Apparently from the sulphuric acid, or from an impurity, the oxygen produced some substance which was a more active, although of course not a more powerful, oxidizing agent than itself.

Both of these methods for determining the true electromotive force are rendered difficult by the extreme slowness which characterizes reactions at ordinary temperatures in which oxygen takes part. The third method, which is the one I have employed, consists in determining at a higher temperature the free energy of some reaction into which oxygen enters, and thus calculating from suitable data the free energy of the same reaction at ordinary temperatures, and the potential of the oxygen electrode.[2] Three reactions appeared especially suitable for this purpose, (1) the decomposition of silver oxide, (2) the decomposition of mercuric oxide, (3) the reaction between oxygen and hydrochloric acid gas (Deacon process). The first of these promised to give the most accurate results and was chosen first for study.

In the paper immediately preceding I have discussed carefully the conditions of equilibrium in the system, $2Ag_2O = 4Ag + O_2$, and have shown that at 25° silver oxide and silver are together in equilibrium with oxygen if the latter has a pressure of 5×10^{-4} atmospheres. I showed that this value is probably not in error

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[1] Loc. cit.

[2] An ingenious attempt of this sort has been made by Preuner, Z. physik. Chem. **42**, 50 (1903), who made use of the equilibria between carbon, oxygen and hydrogen, at high temperatures. He obtained 1.15 volts for the oxygen-hydrogen cell but unfortunately the experimental data are too inaccurate to permit a very reliable calculation of this kind.

by more than one, almost certainly not by more than two units in the significant figure.

From the fundamental laws of energy it is obvious therefore that a galvanic cell at 25° composed of a silver electrode, a saturated solution of silver oxide and an oxygen electrode must have zero electromotive force when the pressure of the oxygen is 5×10^{-4} atmospheres.

It is easy to calculate what electromotive force the same cell will have at the same temperature when the oxygen is at atmospheric pressure. The equation is obviously

$$E = \frac{0.0590}{4} \log \frac{1}{5 \times 10^{-4}}$$

where E stands for electromotive force, log for common logarithm and 0.0590 is the familiar constant occurring in all equations for the electromotive force of a concentration cell at 25°.

Hence we may write,

Ag, Ag$_2$O(sat.), O$_2$(1 atmosphere); E = +0.049 volt.[1]   (1)

Granting that our value for the decomposition pressure of silver oxide is not in error by more than two units at the most, we must regard the above value of E as accurate within 2 or 3 millivolts.

The concentration of the ions in a saturated solution of silver oxide has been determined in a number of independent ways by Whitney and Melcher,[2] by Noyes and Kohr,[3] by Abegg and Cox,[4] and by Böttger.[5] Of these determinations, which are in fairly good agreement with one another, that of Böttger is the only one that was determined by a direct method and is, I believe, the most accurate. He obtained, by measuring the electrical conductivity, the value 1.39×10^{-4} for the equivalent concentration of the ions in saturated silver oxide at 25°. In his work all the customary precautions were taken, and moreover an analysis of the results shows them to be mutually consistent.

[1] All the following values will be for 25° unless the contrary is stated. We will in general call E positive when the positive current tends to pass within the cell from the first electrode to the second. E will be given exclusive of any potentials between the electrolytes of the cell, unless otherwise stated.

[2] This Journal, 25, 69 (1903).

[3] Z. physik. Chem. 42, 336 (1902).

[4] Ibid. 46, 1 (1903).

[5] Ibid. 46, 521 (1903).

Thus for example from the solubility that he gives for silver oxide at 25° and at 20°, I have calculated the heat of solution of silver oxide and obtained a value only a few per cent. different from that obtained calorimetically.
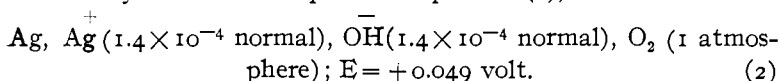
Noyes and Kohr determined accurately the ratio between the concentrations of silver ion in saturated silver oxide and in saturated silver chloride, and found it to be almost exactly ten. From this value and from the solubility of silver chloride given by Kohlrausch and Rose[1] they obtain 1.5×10^{-4} as the ion concentration in saturated silver oxide.

Using instead of the value of Kohlrausch and Rose the ones obtained through electromotive force measurements by Goodwin[2] and by Thiel,[3] we find 1.25×10^{-4} and 1.4×10^{-4} respectively.
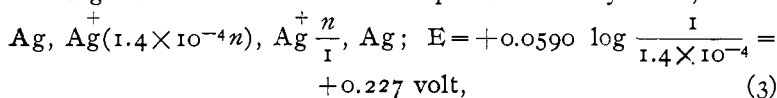
Here, in the case of silver chloride also, I believe that the best determination is that of Böttger. He determined the solubility of silver chloride at 19.95° to be 1.06×10^{-5}. From the known heat of solution of silver chloride I calculate that at 25° this value would become 1.31×10^{-5}. Hence for silver oxide we have 1.3×10^{-4}.

All these determinations show that the value directly obtained by Böttger, 1.4×10^{-4}, can hardly be in error by more than a few per cent. If it were in error by 20 per cent., it would cause an error of one centivolt in our final value for the potential of oxygen.
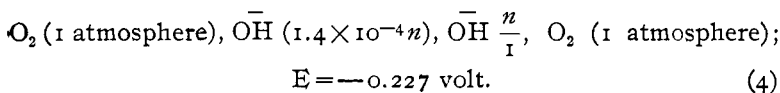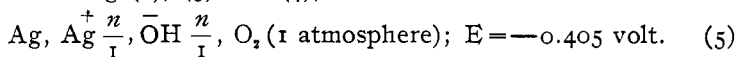
We may now write in place of equation (1),

$$\text{Ag, } \overset{+}{\text{Ag}}(1.4 \times 10^{-4} \text{ normal}), \overset{-}{\text{OH}}(1.4 \times 10^{-4} \text{ normal}), O_2 \text{ (1 atmosphere)}; E = +0.049 \text{ volt.} \quad (2)$$

Using now the familiar Nernst equation we may write,

$$\text{Ag, } \overset{+}{\text{Ag}}(1.4 \times 10^{-4}n), \overset{+}{\text{Ag}} \frac{n}{1}, \text{ Ag; } E = +0.0590 \log \frac{1}{1.4 \times 10^{-4}} = +0.227 \text{ volt,} \quad (3)$$

and

$$O_2 \text{ (1 atmosphere)}, \overset{-}{\text{OH}} (1.4 \times 10^{-4}n), \overset{-}{\text{OH}} \frac{n}{1}, O_2 \text{ (1 atmosphere)}; E = -0.227 \text{ volt.} \quad (4)$$

Combining (2), (3) and (4),

$$\text{Ag, } \overset{+}{\text{Ag}} \frac{n}{1}, \overset{-}{\text{OH}} \frac{n}{1}, O_2 \text{ (1 atmosphere)}; E = -0.405 \text{ volt.} \quad (5)$$

[1] Z. physik. Chem. **12**, 242 (1893).
[2] Ibid. **13**, 577 (1894).
[3] Inaug. Diss., Giessen (1900).

It is obvious that we are now in a position to determine immediately the potential of oxygen against a normal solution of hydroxyl ion, knowing that between silver and a normal solution of silver ion. As no particularly reliable investigation of the latter potential has been made I have determined it anew.

It has been pointed out by Richards and Lewis[1] that satisfactory results for the potentials of solid metals can best be obtained by using the metals in a finely divided state. The employment of this method in the present case has the important advantage that we may use for the silver electrode the very same sort of silver as occurs in the equilibrium upon which our calculations are based. The electrodes were made as follows. A platinum wire was sealed into a glass tube and the projecting part wound into a small spiral. This spiral was inserted in a tube containing silver oxide and the whole was heated at 445° until all the oxide was decomposed. The electrode was then removed from the tube and consisted of a platinum spiral completely enclosed in a loosely cohering mass of finely divided silver. Six of these electrodes were made from two different samples of silver oxide (see preceding paper). For the purpose of comparison five electrodes were also made of the type recommended by Goodwin,[2] consisting of silver foil electroplated with silver.

The individual electrodes were placed in a decinormal solution of silver nitrate in separate vessels of the type commonly used for single electrodes, so that they could be compared either with a standard electrode or with each other.[3] As soon as measurements were begun it became apparent that, although the electrodes of each class did not agree entirely among themselves, there was a much wider difference between the two classes. The average potential of the plated electrodes differed by about one-hundredth of a volt from the average potential of the new type of electrodes, the plated electrodes being more negative.[4] As

[1] Z. physik. Chem. 28, 1 (1899).

[2] Loc. cit.

[3] The following measurements were all made in a thermostat at 30°. As the work was done in the tropics it was difficult to maintain a lower temperature than this.

[4] It was interesting to note that two electrodes plated like the others but with such a large current that the silver came down, not in a smooth film, but in a kind of sponge, gave a potential nearly equal to that of the finely divided silver.

the potentials were measured at intervals for more than a month and this difference persisted throughout, there can be no doubt that the potentials of the two kinds of silver are really different.

In regard to constancy and agreement among themselves the advantage lay with the new electrodes. The six electrodes frequently showed differences between the extremes of 4 or 5 millivolts, but the average deviation from the mean was not over 1 millivolt. Moreover, these electrodes underwent no sudden changes of potential such as the plated electrodes were subject to. They fluctuated in value, but slowly and gradually. The potential of a single electrode would ordinarily change only a few tenths of a millivolt in a day. One of these electrodes was compared with a standard electrode soon after being set up and again after nearly six months. During this time it had changed 2 millivolts.

As standard electrodes I used two decinormal calomel electrodes which were made up at different times out of entirely different materials. They differed from one another by less than 0.2 millivolt.

The cells measured were of the type,

Ag, $AgNO_3$ $n/10$, KNO_3 $n/10$, KCl $n/10$, $HgCl$.
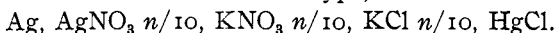
The average electromotive force obtained at 30° with the several finely divided silver electrodes was —0.393 volt, which may be in error by 1 or possibly 2 millivolts. This value includes the potentials between the electrolytes which amount to nearly 2 millivolts. Exclusive of these potentials the electromotive force is therefore —0.391 volt.

I determined the temperature coefficient of this electromotive force between 30° and 0° and found it to be 0.00121 volt per degree, the numerical value of the electromotive force diminishing with increasing temperature. For 25° we have therefore,
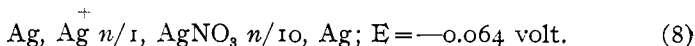
Ag, $AgNO_3$ $n/10$, D. E. (decinormal electrode);
$$E = -0.397 \text{ volt.} \tag{6}$$
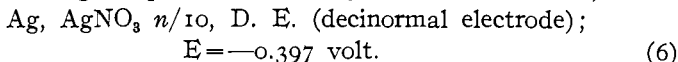
For the difference in potential between the decinormal and normal electrodes we will take,[1]
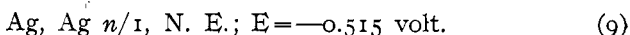$$D. E., N. E.; E = -0.054 \text{ volt.} \tag{7}$$
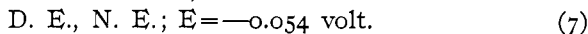
Now assuming that decinormal silver nitrate is 81 per cent. dissociated[2] we find,

[1] See Ostwald-Luther: Phys. Chem. Messungen.

[2] This is the value given by Kohlrausch for 18°. Rudolphi has shown that the degree of dissociation in this case is nearly independent of the temperature: Z. physik. Chem. 17, 385 (1895).

Ag, $\overset{+}{\text{Ag}}$ $n/1$, $AgNO_3$ $n/10$, Ag; $E = -0.064$ volt.   (8)

Combining (6), (7) and (8),

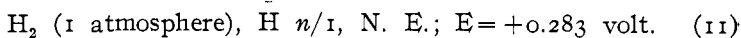Ag, $\overline{\text{Ag}}$ $n/1$, N. E.; $E = -0.515$ volt.   (9)

The true electrolytic potential of silver against normal silver ion is therefore -0.515 volt if we take that of the normal electrode as zero, or -1.079 volts if we give to the latter, as is conventional, the potential -0.560 at $18°$ or -0.564 at $25°$.

Combining now (5) and (9) we find,

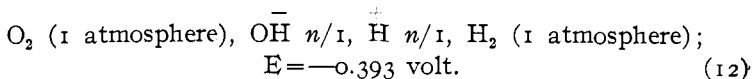O_2 (1 atmosphere), $\overline{\text{OH}}$ $n/1$, N. E.; $E = -0.110$ volt.   (10)
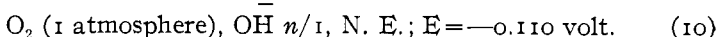
This value, -0.110 volt, is therefore the true potential between oxygen at atmospheric pressure and a normal solution of hydroxyl ion, if the potential of the normal electrode is zero. If the latter is taken as -0.564 volt, we have -0.674 volt for the "absolute" electrolytic potential of oxygen, a value which is probably not in error by more than a few millivolts, and certainly not by more than 1 centivolt unless we have entirely overlooked some possible source of error.

We can also express this potential in terms of the hydrogen potential. Wilsmore[1] has shown that,

H_2 (1 atmosphere), $\overset{+}{\text{H}}$ $n/1$, N. E.; $E = +0.283$ volt.   (11)

Hence from (10)

O_2 (1 atmosphere), $\overline{\text{OH}}$ $n/1$, $\overset{+}{\text{H}}$ $n/1$, H_2 (1 atmosphere);
          $E = -0.393$ volt.   (12)

From this value it is now possible to calculate the true electromotive force of the ordinary oxygen-hydrogen cell if we know the concentration of the hydrogen and hydroxyl ions in pure water. We will take for this concentration at $25°$ the value 1.05×10^{-7}, calculated from the conductivity measurements of Kohlrausch and Heydweiller.[2] This value, as is well-known, has been corroborated by several independent methods so that it is in all probability accurate to within 10 per cent. If it were in error by as much as 20 per cent. an error of 1 centivolt would be caused in our final result.

The concentration of hydroxyl ions in a solution normal with respect to hydrogen ion is $(1.05 \times 10^{-7})^2$ or 1.1×10^{-14}.

[1] Z. physik. Chem. **35**, 291 (1900).
[2] Ibid. **14**, 317 (1894).

Therefore,

O_2 (1 atmosphere), $\overline{OH}$ $n/1$, $\overset{+}{H}$ $n/1$, O_2 (1 atmosphere); E =
+0.824 volt. (13)

From (12) and (13),

H_2 (1 atmosphere), $\overset{+}{H}$ $n/1$, O_2 (1 atmosphere); E = + 1.217 volts.
(14)

This, our final value for the electromotive force of the hydrogen-oxygen cell, is a tenth of a volt higher than the highest value ever obtained by direct measurement. It is quite improbable that it is in error by more than 1 centivolt. Its accuracy depends essentially upon the accuracy of three data, (1) the decomposition pressure at 25° of silver oxide, (2) the solubility of silver oxide, (3) the electrolytic dissociation of water.

It is important finally to determine the temperature coefficient of the potential of the oxygen electrode. I will indicate briefly the essential steps in this calculation.

We have found,

Ag, $AgNO_3$ $n/10$, D. E.; E = —0.397 + 0.00121 $(t—25°)$. (15)

Now Richards[1] has accurately determined the temperature coefficient of the decinormal electrode and found it to be 0.00079 volt per degree. If we take the "absolute" potential of this electrode at 25° as —0.618 volt (N. E. at 25°=—0.564), then at any other temperature it has the value, —0.618—0.00079 $(t—25°)$.

Combining this value with equation (15) we have for the electrode Ag, $AgNO_3$ $n/10$ the potential —1.015 + 0.00042 $(t—25°)$.

From the theory of concentration cells, we have

Ag, $\overset{+}{Ag}$ $n/1$, $AgNO_3$ $n/10$, Ag; E =—0.064—0.00021 $(t—25°)$.

Whence the potential of Ag,.$\overset{+}{Ag}$ $n/1$ is —1.079 + 0.00021 $(t—25°)$.

According to equation (5)

Ag, $\overset{+}{Ag}$ $n/1$, $\overline{OH}$ $n/1$, O_2 (1 atmosphere); E =—0.405 volt.

We can determine by the Helmholtz equation the temperature coefficient of this electromotive force, from the electromotive force itself, and from the heat evolved in the reaction of the cell, which is the heat of formation of silver oxide plus its heat of solution. This amounts, according to the preceding paper, to

[1] Z. physik. Chem. 24, 39 (1897).

—53 Ostwald calories per gram-equivalent. Using this value in our calculations we find,

$$E = -0.405 - 0.00058\ (t-25°).$$

Combining this value with that for the single potential of Ag, Ag $n/1$ given above, we find for the "absolute" potential, O_2 (1 atmosphere), $\overline{OH}$ $n/1$, the value $-0.674 + 0.00079\ (t-25°)$.

The work described in this and in the preceding paper was begun in the Chemical Laboratory of Harvard College, but was carried out for the most part in the Government Laboratory in Manila. It is now being continued in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, where I am investigating the free energy change connected with the action of oxygen on hydrochloric acid gas. In this way I hope to make another independent determination of the potential of oxygen.

SUMMARY.

A consideration of the known facts concerning the potential of the oxygen electrode shows that there is good ground for believing that the present accepted values for the electromotive force of the oxygen-hydrogen cell may all be much too low.

A new form of silver electrode is described and its potential measured.

From this potential, the decomposition pressure of silver oxide, and the solubility of silver oxide, the true potential at 25° of an oxygen electrode against normal hydroxyl ion is found to be —0.674 volt (the normal electrode at 18° being taken as —0.560 volt).

From this value and from the electrolytic dissociation of water the true electromotive force at 25° of the oxygen-hydrogen cell is calculated to be 1.217 volts, a value which is probably correct within less than 1 centivolt.

The temperature coefficient of the oxygen electrode is also calculated.

NOTE.

The last number of the Zeitschrift für Elektrochemie contains a statement by Professor Nernst, to the Bunsen Gesellschaft, that he has calculated the electromotive force of the oxygen-hydrogen cell from the dissociation of water vapor, and obtained

the value 1.23 volts, a value very close to the one found in this paper. A comparison of the two methods will be interesting in order to determine which is better capable of giving the most accurate results.

SOME NOTES ON TRIVALENT COBALT AND NICKEL.

BY STANLEY R. BENEDICT.

IN view of the recent work of Tubandt[1] and Barbiere and Calyolari,[2] describing the formation of trivalent compounds of nickel and cobalt by electrolysis, it has been thought advisable to publish the following paper, preliminary in nature, describing results obtained which indicate more or less conclusively the existence of certain compounds of cobalt and nickel hitherto unprepared. Because of the instability of these compounds, very few have as yet been isolated. In all the instances herein described, however, the reactions given by the solutions seem to the writer to demonstrate the existence of the supposed, or closely allied, compounds. Hence it may not be entirely out of place to publish these partially worked out laboratory notes.

In a previous paper[3] the writer described a method for the detection of nickel which depends upon the formation of cobaltioxalic acid, salts of which had previously been made by both Kehrmann[4] and Marshall,[5] though not in the same way as that described by the writer. It was also mentioned in that paper that by a process analogous to the one described, other new compounds had been made which would be described later. An outline of this work and its continuation follows.

Cobaltioxalic acid may be obtained in solution as follows: A solution of a cobalt salt is treated with a slight excess of sodium peroxide and heated to boiling. The black cobaltic hydroxide thus obtained is filtered off and washed on the filter with hot water a few times, and then with ice water until completely

[1] Z. anorg. Chem. 45, 73 (1905).
[2] Atti. Accad. Lincei Roma, 5, 14, 1, 464. Chem. Centralbl, 1905, 1, 464.
[3] This Journal, 26, 695 (1905).
[4] Ber. 19, 3101.
[5] J. Chem. Soc. 59, 760 (1891).