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THE ELECTROMOTIVE FORCE OF METALS

IN CYANIDE SOLUTIONS.

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The Electromotive Force of Metals in Cyanide Solutions.

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(California Meeting, September, 1899.)

THE practice of the cyanide-process of gold-extraction has brought to light many important contradictions of familiar chemical analogies, which still obscure both the theory and the practice of the art with distinctions subtler and more difficult to make or follow than those which delighted the heart of the old-time metaphysician. Yet Nature herself has drawn these distinctions; and if we hope to succeed in this modern search for the Golden Fleece, we must be able to follow her through the winding labyrinth.

There are so many phases of this question that I shall attempt to touch on only one of them at this time, but it is one that lies at the root of many others.

In reviewing my paper "On the Solution and Precipitation of Cyanide of Gold,"[*] Mr. E. B. Wilson contends[†] that "in the solution of gold by the means of alkaline cyanides the various reactions are determined as to their order and intensity by the relative positions of the elements concerned in the electro-chemical series, or series of voltaic tension."

In a modified form this statement is probably true. That is to say, the difference of electrical potential in any closed electrical circuit determines the nature of the reactions which ensue. But the matter is not so simple as Mr. Wilson assumes. Recent investigations show that the order of the metals in the electro-chemical series depends not only on the nature of the elements themselves, but also on the chemical composition of the solution in which they are placed; its degree of concentration; its temperature; and in the case of gases, on the pressure.

Unless all these conditions are taken into account, inferences drawn from the electro-chemical series are likely to prove more

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[*] *Trans.*, xxvi., 735.

[†] *Trans.*, xxvii., 821.

misleading than useful. The series, as quoted by Mr. Wilson from Gore, is as follows:

3. Potassium.
4. Sodium.
8. Calcium.
9. Magnesium.
12. Manganese.
13. Zinc.
15. Iron.
20. Lead.
24. Copper.
25. Hydrogen.
27. Silver.
28. Antimony.
29. Tellurium.
31. Gold.
37. Carbon.
39. Nitrogen.
40. Arsenic.
43. Sulphur.
45. Bromine.
46. Chlorine.
47. Oxygen.

This series correctly shows the difference of potential in many solvents, especially in acid solutions, but the use of it for predicting the action of cyanide solutions involves several grave errors, one of which is the assumption that the nature of the solution in which substances are placed is without effect on the order of the series.

The remarkable effect of solutions of cyanide of potassium upon the relative positions of substances in the electro-chemical series was first shown by Prof. Jacoby, who, on August 21, 1844, called the attention of the St. Petersburg Academy of Sciences to the fact that when silver and cyanide of potassium solution replace the zinc and sulphuric acid in the Daniell cell, a strong current ensues and copper is precipitated. Ordinarily, and according to the usual inference from the above series, copper precipitates silver from its solutions; but here was a combination in which silver precipitated copper.

In the following year, Poggendorff announced* that by his (now well-known) "compensation-method," he had found the electro-chemical series in 1 part of KCy to 8 parts water—*i.e.*, in a 12.5 per cent. solution of KCy, to be:

1. Zinc amalgamated.
2. Zinc.
3. Copper.
4. Cadmium.
5. Tin.
6. Silver.
7. Nickel.
8. Antimony.
9. Lead.
10. Quicksilver.
11. Palladium.
12. Bismuth.
13. Iron.
14. Platinum.
15. Cast Iron.
16. Carbon (*Kohle*).

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* *Annalen*, Bd. 66, s. 597, 1845.

Gore also* investigated this subject with similar results; only he showed that the order depends on concentration and temperature; and that, according to these conditions, gold may be more or less electro-positive than silver.

The variations thus discovered in the relative position of the metals in the electro-chemical series at once cast a cloud on its usefulness for predicting chemical reactions; and though a great mass of experimental data was accumulated, and the most acute minds of the century were brought to bear on the problem, no explanation of these anomalies was found for many years.

It is only within the last decade that anything like a clue to the mystery has been detected; and this result has been made possible only through the combined efforts of a number of men who approached the subject from what may be almost termed its purely speculative side, without any thought of practical applications.

Now that something tangible seems to be resulting from these efforts, I have thought that a brief outline of the rapid progress made in the electro-chemical theory during the last decade might be of service to those who have been too much occupied with practical details to follow theoretical investigations for themselves. Such an outline will also render more clear the bearing of the experimental work which follows.

I.—Outline of the Development of the Modern Electro-Chemical Theory.

Analytical Research.—In the development of this subject, the efforts of investigation in the line of pure mathematics have been combined with the experimental methods of the chemist and the physicist with the happiest results.

Chief among the mathematicians in this particular field is Prof. J. Willard Gibbs, of Yale University, whose work is too little known and appreciated by his countrymen, or even by his own colleagues. His essays, published in the *Transactions* of the Connecticut Academy of Science, being purely mathematical, attracted but little attention in this country, but, being translated into German by Prof. Ostwald, were introduced to a public capable of appreciating them. He is now recognized in

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* *Proc. Royal Soc.*, Lond., vol. xxx., p. 45, 1879.

Europe as having anticipated many important discoveries with which Helmholtz had been credited. His predictions concerning the laws governing matter and energy have been verified as far as they have been tested, and are even yet far ahead of experimental verification. It is impossible to give here an adequate account of the work of this great man, but he will always be recognized as a leader in the application of mathematical analysis to the most profound physical and chemical problems.

The "Ions."—While Gibbs and Helmholtz were busy with the mathematical side of the question, Daniell, Kohlrausch, Hittorf and many others were busy in following the experimental lines opened up by Faraday. Faraday had always assumed that the electric current was transported through a solution by discrete particles of matter, each bearing its own electric charge. To these moving particles of matter he gave the name of "ions." Those which move in the solution in the same direction as the positive electricity he called "cathions," and those which move in the opposite direction, "anions." The electrodes he distinguished as the "cathode," to which the cathions move, and the "anode," to which the anions move. These distinctions have proved of the greatest service; their value and meaning have been made yet more clear by the work of Daniell, and most of all by the classic experimental researches of Hittorf. The latter showed beyond question that the passage of the current was accompanied by an actual transfer of the cathions and anions through the solution in opposite directions. He and those who followed him were able to determine that these ions were sometimes simple elements, like sodium, potassium, silver, copper, etc., and at other times compound molecules like SO_4, NH_4, NO_3, etc. Thus, while common salt would have for its cathion sodium, and for its anion chlorine, sodium nitrate would have for its cathion sodium, and for its anion NO_3. He proved these propositions by ingenious experimental methods which are still admired for their simplicity and certainty.

Hittorf showed also that, in the case of potassium argentocyanide, the principal cathion was not silver, but potassium, which alone traveled in the direction of the positive current. The silver traveled in the opposite direction, with the cyanogen and the negative electricity, and formed the anion ($AgCy_2$). He explained the reduction of the silver which takes place at the cathode by proving that all (but a trace) is due to the secondary reaction which ensues when the potassium ion is deposited at the cathode and displaces an equivalent of silver from the silver cyanide there adjacent.

This experiment is so important that it will be considered more extensively below. It is sufficient in this place to say that he proved that, while an equivalent of silver was deposited at the cathode, the adjacent solution was robbed of that equivalent, and at the same time there was found an extra equivalent of potassium in the form of caustic potash, while about the anode there was an increase of one equivalent of silver and two equivalents of cyanogen. The conclusion is irresistible that the principle ions are, cathion (K), anion ($AgCy_2$). He proved also that the ions migrate with different, moderate and easily measured velocities.

Molecular Conductivity.—Meanwhile Kohlrausch, Ostwald and others were making a tedious and apparently useless investigation on the electrical conductivity of solutions of increasing dilution. The specific conductivity of dilute solutions is usually much smaller than that of more concentrated ones; but when the comparison was made on the basis, not of specific, but of molecular conductivity, a new and important law was discovered.

For the purpose of comparing the molecular conductivities of solutions, a unit known as the "gramme-molecule" was employed. A given volume v of solution is said to contain a "gramme-molecule" of a given substance whenever it contains a number of grammes of the substance equal to its molecular weight. Thus a "gramme-molecule" of potassium cyanide would be 65 grammes supposed to be dissolved in v liters of water. When v is one liter we should have a solution of one "gramme-molecule" per liter. In this case, for univalent substances, the "gramme-molecule per liter" is of course identical with one "equivalent" or a "normal solution."

Now, when we compare the total conducting power of a gramme-molecule of all electrolytes, we find that, as the volume v increases, and the solution becomes more dilute, the total, or molecular, conductivity of the whole volume of solution increases instead of diminishing with dilution, as the specific conductivity does. This increase is at first quite rapid; then the conductivity becomes nearly constant and increases only very slightly, to reach its maximum value for $v =$ infinity.

Kohlrausch proved by a comparative study of these results that the total conductivity of a dilute solution is due to the velocity of the ions, and also that it is made up of the sum of the velocities of the cathions and anions moving in opposite directions.

Osmotic Pressure.—Meantime progress was being made in an apparently totally different field. Pfeffer, professor of botany at the University of Leipzig, made an extensive study of the osmotic transfer of solutions through the walls of plant-cells, and devised in 1878 a method by which it was shown that osmotic action was capable of producing certain definite pressures. His method consisted in using a "semi-pervious membrane" through which the solvent, but not the solid in solution, can pass. When, for instance, a glass tube, closed at the bottom with a plug of porous earthenware coated with the semi-pervious membrane of ferrocyanide of copper, is filled with a strong solution of sugar and the lower end is placed in distilled water, the latter, being able to pass through the pores of the filter, does so; while the sugar particles, being unable to pass out, remain in the tube, and hence the solution column actually rises in the tube. Pfeffer showed that the pressure, as measured by the height of the column, was proportional to the amount of sugar in the solution and increased with the temperature.

The Gas-Law and Osmotic Pressure.—These phenomena had long been supposed to be due to an attraction of the sugar for water; but the fact that the osmotic pressure was proportional to the sugar-content, and increased with the temperature, suggested to Prof. Van't Hoff, the brilliant Hollander, that the dissolved substance acted just as a gas would do.

His reasoning was something like this: A dissolved substance exerts an osmotic pressure against the bounding surface of the liquid, just as a gas does against the walls of the vessel that contains it. But the surface of the liquid presses inwards with a pressure of above a thousand atmospheres (the *Binnendruck* of the Germans, which prevents the liquid from evaporating instantaneously into space). This surface-tension of the liquid resists the comparatively slight osmotic pressure, and ordinarily the latter produces no noticeable effect.

But when a semi-pervious membrane, through which water may pass, but which will filter out the sugar molecules, is interposed between the sugar solution and the clear water, the pressure of sugar molecules against the semi-pervious membrane and the upper surface of the solution raises the latter just as it would a piston; and as the sugar is unable to exert any pressure on the surface of the water on the other side of the semi-pervious membrane, the clear water freely enters the tube through the membrane as fast as the upper surface rises.

Of course, according to the gas-law, the osmotic pressure should increase with the concentration. Hence Van't Hoff applied the gas-law, $pv = RT$, in which p represents the pressure, v the volume containing a gramme-molecule; T, the absolute temperature; and R, the "gas-constant." When this formula was applied to Pfeffer's results an almost perfect agreement was discovered; and the same result was obtained with numerous other solutions *of organic substances.* But when it was applied to inorganic salts, or electrolytes, it was found that the osmotic pressure was greater than that indicated by the molecular concentration. Van't Hoff expressed this fact by the formula, $pv = iRT$, in which i is a coefficient greater than unity.

Here was an apparent anomaly; the osmotic pressure was apparently greater than that due to the number of molecules, that is, greater than the gas-law would indicate. Progress seemed to be stopped by a stone wall. But it was not delayed long.

Dissociation.—Arrhenius, the masterly Swedish physicist, suggested a new idea. Perhaps the gas-law still holds, only the number of molecules has been increased by the dissociation of some of the dissolved substance. If a part of the molecules were supposed to be split, so as to double their number, the total number of molecules present would be increased and the gas-law might still hold. It was soon shown by Arrhenius that there was a close relation between the size of the coefficient i and the "chemical activity" of the substance. For instance, in the case of the inorganic acids, this coefficient was particularly large in those chemically most active, like hydrochloric and nitric acids. Assuming that in these cases the dissociation was most complete, he made another brilliant generalization. He distinguished between "chemically active" and "inactive" molecules, and claimed that the dissociated molecules were the only "chemically active" ones. This distinction has proved to be sound.

The next step was to show that the increase of molecular conductivity of dilute solutions was due to this same dissociation, and that the dissociated molecules alone took part in the transfer of the electrical current. Arrhenius concluded that the dissociated molecules formed the "ions" which Faraday had shown to be instrumental in conveying the current; that each dissociation produced a cathion which carried the positive electrical current, and an anion which carried the negative current in the opposite direction; that these alone were active in the electrical transfer; that when a substance was entirely undissociated it would be a non-conductor; and that its conducting power was directly proportional to the number of ions present.

This view was strongly contested at first. It was argued, in opposition, that such strongly combined substances as, for instance, potassium chloride, could not possibly split up in solution, even in part, into potassium and chlorine ions—that the potassium would decompose the water. But the reply was: "What if it did? The only effect would be to produce HCl and KHO; these would again dissociate into H and Cl and K and HO; and the potassium and chlorine ions would still exist as before." It was also suggested by Prof. Ostwald, of the University of Leipzig, that the ions were an allotropic modification, different from the ordinary elements, in that to the cathion was attached a positive charge, and to the anion an equal negative charge, of electricity; and that when these electrical charges were given up at the electrodes, the ions changed into the ordinary elemental form.

Ostwald was the first to defend these new views, and the position now held by the theory is largely due to his remarkable genius for outlining, executing and interpreting experimental work. Together with his students, inspired by his example, he has accomplished a great work in clearing up many difficult points as fast as they were raised.

Fig. 1 illustrates an ingenious experiment devised by Ostwald to show the bearing of the new theory. Two vessels, A and B, filled with a solution of KCl, are connected electrically by the column of solution contained in the siphon C. If the theory be correct, a large insulated conductor D, charged with negative electricity, and brought near the vessel A, will act by induction on the ions contained in A and B. The electrically positive, potassium cathions, will migrate through C and collect in A, being attracted by the negative charge on D. At the same time the electrically negative chlorine anions, repelled by the negative charge on D, will accumulate in B.

On removing C, so that A and B are disconnected electrically, and then removing D, the vessel A will contain an excess of positively electrified potassium ions, and the vessel B an excess of negatively electrified chlorine ions. So long as the vessels are not connected with each other or the earth, they will inductively remain in equilibrium and there will be no reaction between them. But according to the theory, if their contents be connected by a platinum wire, the potassium ions will give up their positive charge on the end immersed in A (hydrogen being set free by the reaction of the potassium on the water as soon as the ions have given up their electric charge), and the chlorine ions will give up their negative charge on the end immersed in B (ordinary gaseous chlorine being similarly set free on that end of the wire).

Fig. 1

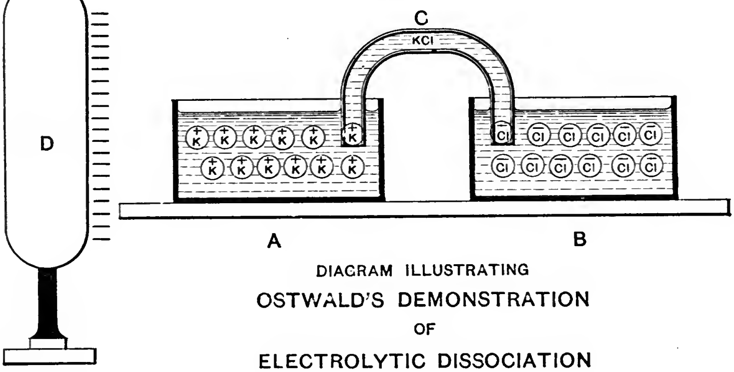

DIAGRAM ILLUSTRATING
OSTWALD'S DEMONSTRATION
OF
ELECTROLYTIC DISSOCIATION

The above experiment is difficult of actual execution on account of the enormous amount of electricity (96,540 *coulombs*) required by each gramme-molecule; but in a modified form of it, using a capillary mercurial cathode, Ostwald and Nernst were able to demonstrate the correctness of this view by traces of hydrogen, distinctly visible under the microscope.

Fig. 1 is therefore not so much a record of actual experimental demonstration as an ideal diagram, serving to explain the nature of the conception involved.

Altered Freezing and Boiling Points.—Another important confirmation of the ideas of Arrhenius came from an entirely different quarter. It had long been known that the boiling point of an aqueous solution was raised and its freezing point lowered in proportion to its molecular concentration; and the method had even been used to determine molecular weights in cases of doubt. But here again dilute solutions proved an exception, showing variations in excess of what was due, according to the rule, to their molecular concentration. But when the behavior of dilute solutions was examined in the light of the new theory, it was found that the assumption of an increase by dissociation in the number of molecules present explained in these cases, also, the apparent anomally. That is to say, when the rise of boiling and fall of freezing points of dilute solutions were expressed in terms of the total molecular concentration (allowing for the increase in number of molecules by dissociation, as determined by the method of electric conductivity), the observed facts accorded with the rule.

Heat of Neutralization.—Another argument in favor of the dissociation hypothesis is furnished by the remarkable fact that the heat of neutralization of a gramme-molecule of all dilute acids is the same. When strong solutions of acids are neutralized with strong solutions of the several alkalis, the heat of the reaction per gramme-molecule is usually quite different; but when dilute solutions are used, the heat of neutralization per gramme-molecule is found to be practically the same for all the electrolytic salts.

This fact, inexplicable according to the usual views of chemical affinities, is a natural consequence of the dissociation-theory. The heat of combination in all these cases is practically equal to that due to the formation of a gramme-molecule of water—that is, to the combination of the atom of H in the acid with the molecule of OH in the alkali. The O and OH ions existing in water are infinitesimal in amount. Hence, when two solutions containing both in equivalent amounts are brought into contact, they unite, and the heat produced results from their combination. No heat results from the combination of the acid and alkali radical, because they were separated into ions before neutralization, and remain in the same state afterwards.

Hence, as the heat results solely from the reaction $H_2 + O = H_2O$, according to the new theory, it ought to be the same for all dilute solutions of acids and alkalies.

Solution-Pressure.—Professor Nernst, now of the University of Goettingen, made the next great forward step in explaining the anomalies in the electro-chemical series. He investigated very carefully the so-called "concentration-cells." The concentration-cell contains two electrodes of the same metal, each immersed in a solution of the same salt of the metal of its electrodes; the only difference between the solutions being that one has a greater molecular concentration than the other. When such a cell is arranged like a Daniell cell (except that both electrodes are, say, of silver, one immersed in a normal, the other in a deci-normal solution of silver nitrate), and the electrodes are connected, a current of electricity results. From the electrode immersed in the dilute nitrate solution an equivalent of silver is dissolved, and at the same time on the electrode immersed in the concentrated solution an equivalent of silver is precipitated. The positive current flows from the electrode in the weak solution to that in the strong solution.

An electric current is thus produced from two electrodes of the same metal immersed in its own salt. Evidently, therefore, it can no longer be deemed necessary to have two different metals, or even the salts of two different metals, in order to produce a galvanic couple. But whence comes the electromotive force in this case?

An attempt to answer this question led Nernst to propose the brilliant hypothesis which commonly bears his name and rounds out the modern theory of electromotive force. Briefly stated, it is that, for a given temperature, each metal has a certain definite "solution-tension," as he first called it, or "solution-pressure," as it has been more aptly named by Ostwald. According to Nernst's idea, every metal immersed in a solution containing none of its ions possesses, at a given temperature, a certain "solution-pressure" with which its particles tend to go into solution and assume the ionic state. In doing this, each takes from the remaining metal a charge of positive electricity which it imparts to the solution. At the same time the remaining metal receives an equal charge of negative electricity. This causes the formation of Helmholtz's "double layer" of oppositely electrified particles on the surface of the metal, and the process goes on until the attraction of the positively electrified ions for the negative metal just balances the solution-pressure of the metal. By reason of the enormous electrical charges of the atoms (96,540 *coulombs* to the gramme-molcule), it follows that only unweighable traces of the metal have to go into solution to bring about this equilibrium, which, once assumed, remains, unless a charge of positive electricity be imparted to the negatively electrified metal. When this is done, as happens when the circuit of a galvanic battery is closed, the formation of ions and the solution of the metal go on continuously. On the other hand, when a metal is immersed in a solution already charged with its own ions, these at once set up an osmotic pressure opposite to the solution-pressure, and hence, dependent on the concentration of the solution, there are three possible cases:

1. The osmotic pressure of the ions already in solution may be less than the solution-pressure of the metal. Here the case is similar to the one described above, but the difference of pressure will be smaller than when no ions were originally present in the solution.

2. The osmotic pressure of the ions in solution is exactly equal to the solution-pressure, and no double layer or difference of electrical pressure results between the metal and the solution. In this case the metal remains indifferent to the solution.

3. The osmotic pressure of the ions already in solution is greater than the solution-pressure of the metal. In this case the ions in solution tend to precipitate themselves on the surface of the metal; and at the same time they impart their charge of positive electricity to the metal, which becomes positively electrified, while the solution which had contained an equal number of positive and negative ions becomes negatively electrified. This soon produces a new double layer of oppositely electrified ions, which brings about an equilibrium, unless

a continuous stream of negative electricity is imparted to the positively electrified metal (as by completing the circuit of a galvanic battery), when the precipitation of the ions goes on continuously. The equilibrium of the double layer is brought about (for the same reason as given before) by the precipitation of unweighable traces of the ions.

According to this view, the electromotive force of a galvanic cell is just as much due to the difference of pressure between the metals tending to assume the ionic state, and the ions tending to assume the metallic state, as the force of a steam or compressed-air engine is due to the differences between the steam- or air-pressures acting on either side of the piston.

Hence, Nernst applied the laws of thermodynamics, which had been already worked out so thoroughly for gases, to this problem also, and with the most remarkable results. It is impossible to enter here into all the refinements of the subject; but the following condensed statement will give an idea of the reasoning involved.

Starting with the well-known gas-law

$$(1) \qquad \mathrm{pv} = \mathrm{RT}.$$

(p and P being pressures in grammes per square centimeter; V and v, the corresponding volumes in ccm. to contain one gramme-molecule; T, 273 + t degrees Centigrade; and R, the "gas-constant" = 1.96 calories), we can easily determine the maximum amount of work, A, in gramme-centimeters, done by a perfect gas, expanding at a constant temperature from a volume v to a larger volume V, and at the same time falling from a pressure P to a smaller pressure p. We have:

$$(2) \qquad \mathrm{A} = \int_p^{\mathrm{P}} v\,dp.$$

But, from (1), $v = \frac{\mathrm{RT}}{p}$; hence

$$(3) \qquad \mathrm{A} = \mathrm{RT}\int_p^{\mathrm{P}} \frac{dp}{p};$$

and, integrating this, we have

$$(4) \qquad \mathrm{A} = \mathrm{RT \ nat.\ log.}\ \frac{\mathrm{P}}{p}.$$

If we now suppose the gas-law to apply to the diffusion of the ions from the electrode into the solution; let P represent the "solution-pressure" and p the "osmotic pressure" of the ions of the given metal in solution; and further assume that work is done only in falling from the pressure P to the lower osmotic pressure p, and not in changing from a solution-pressure P to an equal osmotic pressure P, it follows that equation (4) will apply directly to this case also.

But we can also express the maximum work A in electrical units. If we assume that to a "gramme equivalent" of a univalent element is given its unit charge of $e = 96{,}540$ coulombs of electricity, and represent by the Greek letter π the potential difference in volts between the metal and the solution, we may also represent the work A done, by the product πe. Hence we have:

$$(5) \qquad \pi e = \mathrm{RT \ nat.\ log.} \frac{\mathrm{P}}{p};$$

or, changing, for convenience of calculation, from natural to common logarithms, we have

$$(6) \qquad \pi e = \frac{\mathrm{RT}}{0.4343} \log. \frac{\mathrm{P}}{p}, \quad \text{and hence}$$

$$(7) \qquad \pi = \frac{\mathrm{RT}}{e \times 0.4343} \log. \frac{\mathrm{P}}{p}.$$

Now $\mathrm{R} = 1.96$ calories, or in electrical units, $\mathrm{R} = 1.96 \times 4.24$; $e = 96{,}540$ coulombs; and for ordinary temperatures $t = 17°$ C. or $\mathrm{T} = 273 + 17 = 290°$ C. Substituting these values, we have:

$$(8) \qquad \pi = \frac{1.96 \times 4.24 \times 290}{96{,}540 \times 0.4343} \log. \frac{\mathrm{P}}{p} = 0.0575 \log. \frac{\mathrm{P}}{p} \text{ volts.}$$

For ions that have a valency $n > 1$, each gramme-molecule will require $n \times e$, or $n \times 96{,}540$ electrical units, and this must be substituted in the formulas (5) to (8) instead of e; when this is done we have the general formula:

$$(9) \qquad \pi = \frac{0.0575}{n} \log. \frac{\mathrm{P}}{p} \text{ volts.}$$

This formula, of course, is only true for $t = 17°$ C.

I have plotted this curve in Fig. 2. It will serve for any metal in which the ratio $\frac{P}{p}$ is the same. If we study the ratios of $\frac{P}{p}$ we see that when P is greater than p, π always has a positive value; that is, the liquid is positively electrified by the ions which go into solution, and the remaining mass of metal is, in consequence, negatively electrified. As a further consequence, when $p = 0$, $\frac{P}{p} =$ infinity; hence log. $\frac{P}{p}$, and hence π, equals infinity.

This, of course, is interpreted to mean that a metal brought into the presence of a solution containing none of its ions would have an infinite potential with regard to that solution; but this could only last for an infinitesimal period, after which the liquid would be impregnated with the ions of the metal. Experiment shows that none of the metals give an infinite potential in any known solution. It follows, therefore, that traces of the ions of all the metals must exist in all solutions, even though they may not be recognizable by any other chemical or physical test. The same mathematical difficulty exists with regard to the conception of a perfect vacuum, and a similar conclusion may be drawn, namely, that such a thing as a perfect vacuum is physically impossible.

When $P = p$, then $\frac{P}{p} = 1$, and log. $\frac{P}{p} = 0$. In this case, the potential is 0, and there is no tendency either to dissolve or to precipitate the metal.

When P is less than p, log. $\frac{P}{p}$ is negative, and the solution is negatively electrified, owing to the positive ions precipitating themselves with their positive charges upon the metal, which becomes positively electrified. If p could become infinity, log. $\frac{P}{p}$ would become minus infinity. As a matter of fact, these values are never reached, for the simple reason that as p depends on the number of ions in a unit-volume, it follows that, on dilution, p reaches nearly a maximum value for very moderate dilutions, when dissociation of the liquid is nearly complete; and, after that, the value of p is reduced rather than increased by further dilution.

According to this view, the electromotive force of the metals in their solutions depends, for a given temperature:

1. Upon the "solution-pressure" peculiar to each metal.

2. Upon the number of ions of the given metal present in the solution in which it is immersed.

If the "solution-pressure" peculiar to each metal were accurately known, we might write out an absolute electromotive series for the metals. Le Blanc[*] proposes, on the basis of the work of Neumann, and on the supposition that the osmotic pressure of a totally dissociated normal solution (containing one gramme-molecule in the dissociated state) is equal to 22 atmospheres, a series of this kind, as follows:

Electromotive Series of Metals in Solution.

(Value of P at 17° C.)

	Atmospheres.		Atmospheres.
Zinc,	9.9×10^{18}	Lead,	1.1×10^{-3}
Cadmium,	2.7×10^{6}	Hydrogen,	9.9×10^{-4}
Thallium,	7.7×10^{2}	Copper,	4.8×10^{-20} (?)
Iron,	1.2×10^{4}	Mercury,	1.1×10^{-16}
Cobalt,	1.9×10^{0}	Silver,	2.3×10^{-17}
Nickel,	1.3×10^{0}	Palladium,	1.5×10^{-36}

But it is in the varying number of ions present in solution that the true explanation of the apparent anomalies in the electromotive series was found. According to this theory the position of the metal in the series ought to vary in different solutions in accordance with the number of ions of the given metal that can exist in the given solution.

Complex Ions.—The anomalous position of copper, gold and silver in cyanide solutions is here explained for the first time. According to this view, there are very few metallic ions of these metals in solutions of their cyanides. For example, the double cyanide of gold and potassium (potassium auro-cyanide) dissociates, in part, first into a positive ion K(+)[†] and a nega-

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[*] *Elements of Electro-chemistry*, p. 228.

[†] The expression (+) means that the ion after which it is written carries a positive charge of electricity; the expression (—) means that the ion carries a negative charge, and (±) that it is neutral, or not electrified.

Fig. 2

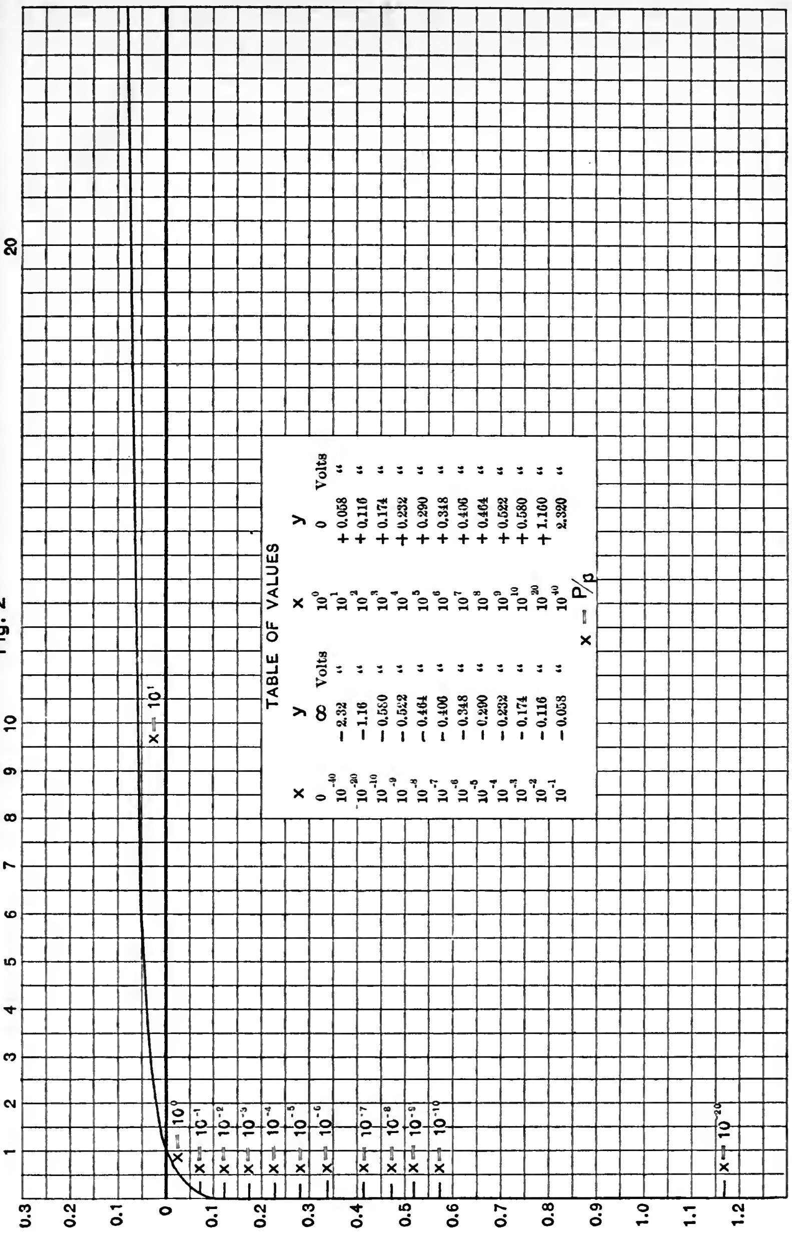

TABLE OF VALUES

x	y		x	y	
0	∞	Volts	10^{0}	0	Volts
10^{-40}	−2.32	"	10^{1}	+0.058	"
10^{-20}	−1.16	"	10^{2}	+0.116	"
10^{-10}	−0.580	"	10^{3}	+0.174	"
10^{-9}	−0.522	"	10^{4}	+0.232	"
10^{-8}	−0.464	"	10^{5}	+0.290	"
10^{-7}	−0.406	"	10^{6}	+0.348	"
10^{-6}	−0.348	"	10^{7}	+0.406	"
10^{-5}	−0.290	"	10^{8}	+0.464	"
10^{-4}	−0.232	"	10^{9}	+0.522	"
10^{-3}	−0.174	"	10^{10}	+0.580	"
10^{-2}	−0.116	"	10^{20}	+1.160	"
10^{-1}	−0.058	"	10^{40}	2.320	"

$x = P/p$

NERNST'S CURVE OF ELECTROMOTIVE FORCE.

$\pi = Y = .058 \text{ Log } P/p = .058 \text{ Log } x.$ Volts.

tive ion $AuCy_2$ (—). The latter, in accordance with the "mass-law," also dissociates, to a very slight extent, into AuCy (±) and Cy (—) and the AuCy, in accordance with the same mass-law, dissociates, to an almost infinitesimal extent, into Au (+) and

Cy (—). The metallic gold ions, thus existing to an almost infinitesimal extent in cyanide solutions, are the only ones that exert an osmotic pressure against the solution-pressure of the gold. Hence, in spite of the low solution-pressure of the gold, the still lower osmotic pressure of the few gold ions present renders the potential of the gold in cyanide solutions remarkably high. Its solubility, also, is thereby explained.

But a high potential difference does not necessarily indicate the great solubility of a metal; it may, in fact, indicate the opposite. For instance, the electromotive force of silver in cyanide of potassium solutions is high; but in sulphide of potassium solutions it is still higher—owing, in this case, to the extreme insolubility of the sulphide of silver. This extreme insolubility of the sulphide of silver reduces to a minimum the number of metallic silver ions that are present in the solution, diminishes the osmotic pressure of the ions, and hence increases the electromotive force.

The explanation of these remarkable exceptions that "prove the rule," is due to the work of Ostwald, who, more than any one else, has filled in the gaps and explained away the difficulties presented by the new views.

Beyond doubt, the gold, the silver and the copper in the cyanide solution are mainly combined with Cy_2 to form electronegative ions $AuCy_2$(—), $AgCy_2$(—), and $CuCy_2$(—). As to silver, this conclusion is to be drawn, in fact, from Hittorf's early experiments, and, as to gold and copper, from those of Ostwald, already described.* These ions have been termed by Ostwald "complex ions," to indicate that they contain the metals in a combination in which their ordinary chemical reactions are entirely masked. There are many other such combinations: the thiosulphites of gold and silver, the ferrocyanides and ferricyanides, the platinochlorides, etc., all fail to answer the ordinary tests for the gold, silver, iron, and platinum that they contain. The alkaline sulphhydrates of many of the metals are also examples of the same fact.

It is for this reason that all of the ordinary reagents fail to precipitate the gold and silver from cyanide solutions. For

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* See Christy, "The Solution and Precipitation of the Cyanide of Gold," *Trans*, xxvi., 758 *et seq.*

this reason, also, the electric current causes a transfer of the electronegative ion from the negative to the positive pole, or anode, in the opposite direction to that ordinarily taken by the metals, and only the comparatively few electropositive gold ions present in the solution travel towards the cathode or negative electrode of the deposition-box. As already shown in my paper, just cited, this necessarily retards the electrodeposition of the gold from cyanide solutions. However, the potassium ions, on giving up their electric charge to the cathode, precipitate gold from the adjacent solution, and this helps matters out. Nevertheless, the travel of the $AuCy_2(-)$ ions to the anode considerably retards the precipitation of the gold.

To illustrate the great difference in the osmotic pressure exerted by the complex ions as compared with the ordinary case of dissociation, the following examples are cited from the work of Ostwald and his pupils:

Ordinary dissociation is represented by the cases of solutions of potassium chloride, copper sulphate, silver nitrate, and hydrochloric acid. These are found to be dissociated as follows:

$KCl = K(+) + Cl(-)$ Practically wholly dissociated at $\frac{M}{10{,}000}$

$CuSO_4 = Cu(+) + SO_4(-)$ Practically wholly dissociated at $\frac{M}{10{,}000}$

$AgNO_3 = Ag(+) + NO_3(-)$ Practically wholly dissociated at $\frac{M}{1{,}000}$

$HCl = H(+) + Cl(-)$ Practically wholly dissociated at $\frac{M}{100}$

The above characteristic cases show that the degree of dissociation varies extremely with different salts, but with many substances, like silver nitrate and hydrochloric acid, is practically complete at very moderate dilutions.

Let us take in contrast the case of a complex ion, that produced, for instance, by the dissociation of potassium argentocyanide. According to an investigation of Morgan,*, the dissociation takes place in three steps. Of these, the first is very complete:

$$KAgCy_2(\pm) = K(+) + AgCy_2(-).$$

(The latter is the "complex ion.")

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* *Zeitsch. für Phys. Chemie,* Bd. xvii., S. 513.

The second occurs in very small amount:

$$AgCy_2(-) = AgCy(\pm) + Cy(-).$$

The third is in almost infinitesimal traces:

$$AgCy\ (\pm) = Ag\ (+) + Cy(-).$$

In the case of $\frac{M}{20}$ $KAgCy_2$, Morgan shows that the first step is almost complete; the second step is 2.76×10^{-3} M = 5 per cent. dissociated; and the third step shows of Ag (+) ions, $3.65 \times 10^{-11}\ M = 3.65 \times 108 \times 1000 \times 10^{-11} = 3.94 \times 10^{-6}$ mg. per liter;—that is, there are only about four millionths of a milligramme of silver in the ionic state in a liter of such a solution.

Let us compare this with the dissociation in a $\frac{M}{20}$ $AgNO_3$ solution. Morgan finds this to be 86.5 per cent. dissociated, hence a liter of such solution will contain $0.865 \times 108 \times \frac{1000}{20} = 4.36 \times 10^{3}$ mg. of Ag(+) ions per liter.

The ratio of silver ions in the cyanide solution to those in the nitrate solution is therefore:

$$\frac{4.36 \times 10^3}{3.94 \times 10^{-6}} = 1.11 \times 10^9.$$

Hence, there are over a billion times as many silver ions in $\frac{M}{20}$ silver nitrate as in silver cyanide.

This makes clear at once the reason of the great difference between the osmotic pressure of the silver ions in the nitrate and in the cyanide solution, and consequently the reason why the electromotive force of silver is so much greater in the cyanide solutions. The case of potassium aurocyanide and other complex salts is entirely similar to that of potassium argento-cyanide. It should be further stated that, according to this view, ions can only form or disappear in infinitesimal traces, sufficient to bring about a static equilibrium, unless they appear or disappear in pairs, positive and negative, as they do in the continuous passage of the current through the electrolytic cell. It is for this reason that it is necessary to have two electrodes to any galvanic cell, one to receive the discharge of electricity from the positively electrified cathions, and the other to receive that from the negatively electrified anions. Without both of these, a continuous current is impossible.

In considering this case of the Daniell cell, for instance: If we represent the solution-pressure of the zinc by P_1, the osmotic pressure of the zinc ions present in the zinc sulphate by p_1, and the similar values for the copper by P_2 and for copper ions in the copper sulphate by p_2, we shall have for the electromotive force of the zinc in zinc sulphate:

$$\pi_1 = \frac{0.0575}{2} \log. \frac{P_1}{p_1},$$

and for the copper in copper sulphate,

$$\pi_2 = \frac{0.0575}{2} \log. \frac{P_2}{p_2}.$$

Either of these alone can give, not a continuous current, but only a static charge of ions, which prevents further action; but when they are combined on a closed circuit, as in the Daniell or gravity-cell, we have a resulting difference of potential:

$$\pi = \pi_1 - \pi_2 = \frac{0.0575}{2}\left(\log. \frac{P_1}{p_1} - \log. \frac{P_2}{p_2}\right) =$$
$$\frac{0.0575}{2} \log. \frac{P_1 \times p_2}{p_1 \times P_2}.$$

On the other hand, in a concentration-cell, with either of these metals (copper electrodes, for instance), one in a strong and the other in a weak solution of copper sulphate, we should have $P_1 = P_2$ in the above formula, and the only difference would be in the differing concentration of the ions p_1 and p_2 in the strong and weak solutions. Making these substitutions in the formula, we should have, in this case:

$$\pi = \frac{0.575}{2} \log. \frac{p_2}{p_1}.$$

In this case it is evident that the solution-pressure of the metal itself plays no part in creating the electromotive force of the combination. It is entirely due to the relative number of ions present in the strong and weak solutions. The solution containing the smaller number of ions per unit-volume will oppose to the solution-pressure of the metal immersed in it the smaller resistance, and that metal will dissolve and the other will precipitate.

The above outline gives only in the briefest way a summary of some of the hardest thinking and closest reasoning that has been done of late in one of the most important departments of physical chemistry. It is, perhaps, too much to hope that the conclusions reached are all final. But they rest on such a firm foundation of experimental work, and explain so much that is otherwise inexplicable, that it is certain that they contain a large amount of truth. The details will probably be filled in quite differently from what we now expect, but the great mass seems to be solid gain. The importance of these new views in the study of chemical geology and the deposition of ores, in every branch of the metallurgical art and in all departments of practical chemistry, has hardly begun to be appreciated and utilized. It is not too much to say that ionic action lies at the bottom of all plant- and animal-life; and that the new views are sure to create a revolution in the study of physiological chemistry, biology, pathology and therapeutics. In every department of physical science where they have been applied, they have acted like a new ferment; this speaks volumes for their usefulness and virility.*

Objections to the New Electrolytic Theory.—The above theories have not been received without opposition from many chemists and physicists of no little weight. Many of the first opponents to the theory have been overthrown, and point by point has

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* Those who are interested in following up these ideas more at length will find the subject treated *in extenso* in Ostwald's *Elektrochemie, ihre Geschichte und Lehre*, Leipzig, 1896 (1150 pp.), his *Chemische Energie*, Leipzig, 1893 (1090 pp.), and Nernst's *Theoretische Chemie*, Stuttgart, 1893 (580 pp.). An admirable summary of these views appears in *The Elements of Electro-chemistry*, translated into English by W. R. Whitney, from the German of Le Blanc. Macmillan & Co., London and New York, 1896 (pp. 282). Since this paper was presented, another excellent work has appeared: *Theory of Electrolytic Dissociation*, by H. C. Jones. Macmillan & Co., 1900, pp. 283.

been won against the strongest opposition. But the field is by no means clear of weighty objectors. The English school, led by Pickering with his "hydrate theory," has opposed most bitterly the new theory of "dissociation. Others, such as Crompton in England, and Bucherer in Germany, have proposed what may be termed the "association" as opposed to the "dissociation" theory. The battle still rages. While the issue seems certain in the main to be in favor of the new views, there is not wanting evidence of the wisdom of a compromise on certain minor but important points.

It will be noticed that the adherents of the dissociation theory neglect *in toto* the effect of the solvent. Formerly, chemists fixed their eyes on the mystic power of the solvent to clear up any doubtful question. The new theorists ignore the solvent entirely. It is indeed astonishing what they have been able to explain without it, but, like Banquo's ghost, "it will not down." They have assumed the solvent to be without action in bringing about dissociation and electrolysis. They have regarded it simply as of the nature of a vacuum into which the ions were free to expand, and everything has been supposed to be due to the pressure of the ions, nothing to the medium.

But already there are signs of reaction. It has been noticed that not all solvents are capable of changing salts into electrolytes. Some are almost without effect in this respect. In other words, not all liquids are capable of becoming vacua into which the ions may evaporate. This fact of itself is enough to show that the nature of the solvent is not without influence on the dissociation.

It was next noticed that most of the solvents which enable electrolysis to take place contain oxygen, and that of these, those possess the power most strongly which contain the most oxygen. Next, it was suggested that in all probability oxygen is quadrivalent rather than bivalent, as usually supposed. The fact that carbon, which is never known to be anything but quadrivalent, combines with oxygen to form carbon monoxide (CO), favors this view. If oxygen be regarded as at least potentially quadrivalent, an explanation is at once found for the well-known variations in the water of crystallization of salts; for Pickering's remarkable series of "hydrates;" and last, but not least, the idea suggests itself: "May not the ions be, not merely a dissociation of the dissolved salt, but an association of the dissociated ions with one or more water molecules?"

It was first supposed that all solvents capable of forming electrolytes contained oxygen. This was disproved by the discovery cited by Ostwald, that liquefied ammonia (NH_3), a non-conductor, becomes a conductor when salts are dissolved in it. This was cited to prove that the ionizing force was not due to the presence of oxygen. But it was pointed out by Bruehl,* that, like oxygen, the nitrogen in NH_3 has two unsatisfied valencies, which are thus capable of acting like it in producing ionization. He predicts that anhydrous HCN when liquefied, as well as PCl_3 and $AsCl_3$, will be likely to have similar effects for similar reasons. Nernst† has also called attention to the sigular proportionality between the dissociating power of solvents and their dielectric constant. The latter are as follows for certain solvents:

Dielectric Constants (Nernst).

Gases,	1.00
Hydrocarbons,	1.7 to 2.6
CS_2,	2.6
Ether,	4.1
Esters,	6.9
Acetic Acid,	9.7
Alcohol,	26.0
Water,	80.00

This series might almost serve as showing the relative dissociating-power of these substances.

Thuring‡ had also called attention to the remarkable difference of the dielectric constants between water and ice, that of water at 0° C. being 79.46, and that of ice at −2° C. being 3.36 only. He also gives 10.30 as the constant for liquid acetic acid, and 2.79 for solid. In all these cases, the dissociating power increased with the dielectric constant. This points to relations worth following to a conclusion.

It does seem, then, as if the adherents of the dissociation theory had ignored too much the effect of the solvent, and as if the final theory must be enlarged to include it. Why should

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* *Z. f. Phys. Ch.*, xxvii., 319, (1893).

† *Z. f. Phys. Ch.*, xiv., 622 (1894).

‡ *Z. f. Phys. Ch.*, xiv., 286 (1894).

the action of the solvent be ignored? Its chemical action, it is true, is often slight, but when we take into account the effect (in dilute solutions), of its relatively great mass, does not this explain why dilute solutions are more dissociated than strong ones? In the latter, the cohesion of the solid still maintains, even in solution, a certain effect; but as the mass of the salt diminishes, and that of the solvent increases, the latter makes up by its mass what it lacks in intensity.

If the solvent is without effect, why does not the solution-pressure of the metals cause them to ionize as freely into a vacuum, or into the air? And why should one solvent be effective and not another?

The dissociation-controversy in England waxed particularly warm in the numbers of *Nature* published in 1897.*

One can hardly read this discussion without feeling that, on the whole, the dissociation theory has the better of it. But the associationists, led by Pickering, are not wholly wrong. Pickering cites one experiment that is worth quoting. He says that when a solution of propyl-alcohol in water is placed within a semi-permeable membrane, the water from without passes through the membrane into the interior. This seems to prove that the membrane is pervious to water but not to propyl-alcohol. But, he adds, when the same vessel is immersed in propyl-alcohol the propyl-alcohol passes in through the membrane, but the water cannot get out. This would seem to prove that the membrane was pervious to the propyl-alcohol but not to the water. He considers this a *reductio ad absurdum*. But Wetham points out that the experiment may be interpreted to mean that the membrane is pervious to either water or to propyl-alcohol, but not to their associated molecules or to the solution of one in the other.

Wetham also points out that the assumption that the ions are dissociated from each other does not in any way contradict the assumption that they are severally associated in some, as yet unkown, manner with the solvent.

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* *Nature*, vol. lv., Dr. H. E. Armstrong, p. 78, against; Prof. O. J. Lodge, p. 151, for; W. C. D. Wetham, for, p. 152; Spencer Pickering, against, p. 223; Lord Raleigh, p. 253, for; Lord Kelvin, p. 273, agnostic, if not wholly skeptical; Prof. J. Willard Gibbes, p. 461, for, answers some of Lord Kelvin's objections; W. C. D. Wetham, p. 606, for, answers Pickering. The discussion is continued in *Nature*, vol. lvi., p. 29.

Lord Kelvin (*loc. cit.*, p. 273) takes an agnostic, if not skeptical, position. After stating the problem of osmotic pressure, he says:

> "No molecular theory can, for sugar or common salt or alcohol dissolved in water, tell us what is the true osmotic pressure against a membrane permeable to water only, without taking into account laws, quite unknown to us at present, regarding the three sets of mutual attractions or repulsions: (1) between the molecules of dissolved substance; (2) between the molecules of the water; (3) between the molecules of the dissolved substance and the molecules of the water."

He follows this with a warning against undue haste in accepting theoretical views as settled while they are still open to debate.

On p. 461 (*loc. cit.*) Prof. J. Willard Gibbes shows that in the case cited by Lord Kelvin, for dilute solutions, where the relation of the density and pressure of the dissolved substance becomes like that of a gas, it is only necessary to have a single numerical constant in addition to the relation between the density and the osmotic pressure to solve the problem.

It must be remembered that the greatest triumphs of the new theory are confined to dilute solutions, but a complete theory of solutions must, of course, include all states from the dilute solution through the saturated solution to the solid substance with its various hydrates.

In describing the condition of affairs assumed in the new theory of ionic dissociation, Le Blanc says:*

> "The parts resulting from the dissociation (the ions) are electrically charged, and contain equivalent amounts of positive and negative electricity. It is natural to ask: Whence come these sudden charges of electricity? They seem to be produced from nothing. An answer that seems satisfactory is not difficult to give. It is known that metallic potassium and iodine combine to form potassium iodide. In this combination heat is generated, which shows that the two have entered into a state in which they contain less energy than before. A certain amount of chemical energy doubtless still remains in the compound, and when the salt is dissolved in water, the greater part of this chemical energy is changed into electrical, *through the influence of the solvent.*† This energy is seated in the charges of the ions. The potassium ion is positively, and the iodine negatively electric. By the aid of the electric current, it is possible to add to these ions the energy in the form of electricity necessary to give them the energy they originally possessed as elements. In such a case, they separate in the ordinary molecular forms at the electrodes."

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* Le Blanc, *Elements of Electro-chemistry*, p. 60.

† The italics are mine.—S. B. C.

It will be noticed that in this explanation of the mode of formation of the ions on the dissociation hypothesis, Le Blanc uses the phrase: "*through the influence of the solvent.*" That is, he seems to recognize the need of bringing this influence into the problem. He does not attempt to show how it acts. But if it is able to alter such strong affinities as those of potassium and chlorine, or even of potassium and iodine, by changing the chemical into electric energy, such action is surely worth studying most closely.

I am firmly convinced that the next great advance will be made when the effect of the solvent is more closely studied. But while believing that the association or loose combination of the water-molecules with the dissociated ions plays an important, though as yet unknown, part in electrolysis, I shall, in what follows, continue to use the method of nomenclature already in use for the ions, in the absence of a better system.*

II.—Methods Used in This Investigation.

In looking about for some means of determining the relative affinities of the metals for cyanide solutions, I long ago came to the conclusion that the determination of the relative electromotive forces of the metals in solutions of different strengths was the simplest, readiest, and most certain that could be selected. For, properly considered, it shows the actual tendency of the metal to go into solution. My first experiments were made in this direction in August, 1896. I made at that time a large number of preliminary determinations, the results of which were presented in a lecture given February 1, 1897, before the California Academy of Sciences, in San Francisco. At that time, the curves shown in Fig. 5 were projected on the screen by a stereopticon before an audience of 300 persons.

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* H. C. Jones, *Z. f. Phys. Ch.*, xiv., 346, gives some interesting determinations of the EMF of the combination Ag, $AgNO_3$ Aq, $AgNO_3$, ethyl-alcohol, Ag, which seem to show that the solution-pressure P may not be a constant for a given temperature, but may also be a function of the solvent.

See also J. J. Thomson, *Phil. Mag.*, xxxvi., 320, on the action of the dielectric in bringing about dissociation by its inductive influence.

For other attempts to explain the influence of the solvent, see Bredig, *Z. f. Phys. Ch.*, iv., 444 (1889), "Kinetic Nature of Osmotic Pressure;" also Noyes, *Id.*, v., 53 (1890), and Kistiakowsky, *Id.*, vi., 115 (1890), "Specific Attractions in Salt Solutions."

The results of these experiments have filled me with constant surprise, when I have noticed what apparently slight causes were capable of making great changes in the electromotive force of the same metal. The great delicacy of the method proved to be the chief source of difficulty in its application, while at the same time it reported faithfully the facts as they exist in nature.

Two methods have been used in these determinations, the first being what I have, for brevity, called the "Deflection" method, and the other the "Compensation" or "Zero" method of Poggendorf.

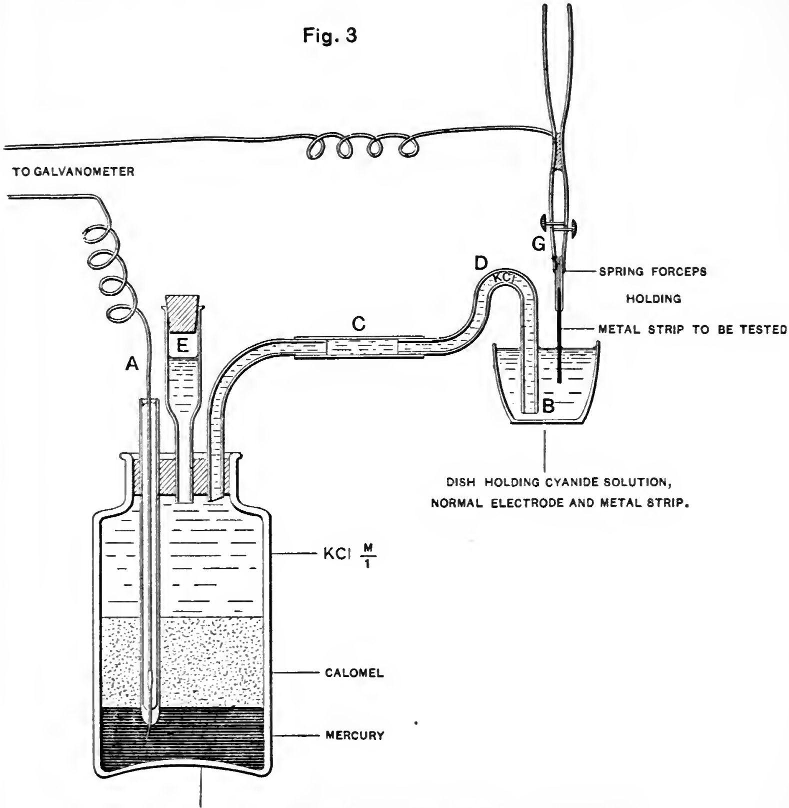
In each case an electrolytic cell is constructed with two electrodes, each immersed in a separate solution. One, consisting of the metal to be tested, was held in the points of a platinum-tipped pair of forceps, electrically connected with a galvanometer, and was immersed in a vessel containing the cyanide solution of the given strength. The other was in all cases the "normal" electrode of Prof. Ostwald, consisting ot mercury, electrically connected with the galvanometer by means of a glass-coated platinum wire. The surface of the mercury is covered with a layer of mercurous chloride, a couple of inches thick; and a solution of chloride of potassium of one gramme-molecule $\frac{M}{1}$ (in this case also a normal solution).

The two vessels containing the electrodes are connected, as shown in Fig. 3, by means of the tube C and the siphon D, the latter being filled with $\frac{M}{1}$ KCl solution, like that in the normal electrode. I have added a small tube E, ordinarily closed with a cork, for the purpose of displacing at intervals the solution in the siphon D with fresh KCl solution, to avoid the diffusion of the cyanide solution through the latter back into the normal electrode. For the same reason the position of the normal electrode is ordinarily a little higher than that shown in the figure, so that any accidental action of the siphon shall be rather away from the normal electrode than into it.

The purpose of the normal electrode of Ostwald is to have a non-polarizable electrode in a solution of known strength and electromotive force. This is fixed at —0.560 volts. That is, in the case of the normal electrode, the quicksilver ions tend to precipitate themselves on the surface of the mercury, and the solution is therefore negative to the metal by 0.560 volts. That is, the positive current tends to flow through the solution to the mercury, which becomes positively electrified, while the solution itself becomes negatively electrified.

Now, if we neglect the slight electromotive force due to the contact of the two solutions, the resulting electromotive force of the combined cell is the algebraic sum of the electromotive forces active at the two electrodes. Hence, if we subtract 0.560 from the EMF of the cell, we have the EMF of the metal under consideration. The algebraic sign indicates the direction of the positive current.

Fig. 3

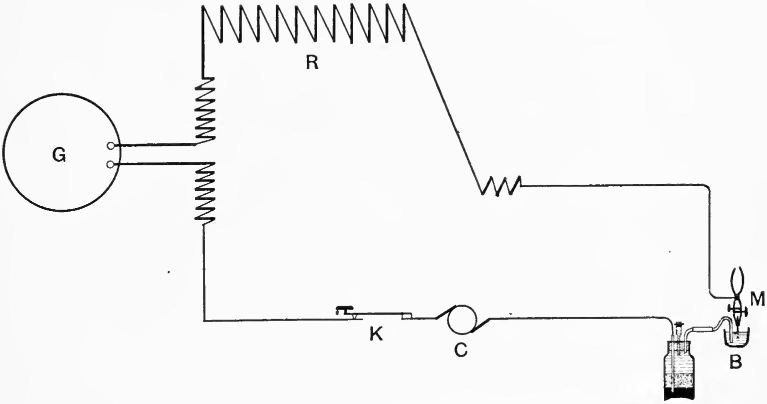


OSTWALD'S NORMAL ELECTRODE

The Deflection Method.—This method is much the most convenient for such investigations, particularly in the first roughing-out of a large amount of material. With proper precautions, it gives results not less reliable than those of the zero method; and it has the great advantage over the latter that the rapid changes of electromotive force may be followed almost as they occur.

The method is illustrated in Fig. 4. B is the cell containing the cyanide solution and the metal M to be tested; NE is Ostwald's normal electrode; R is a resistance which varied in the tests from 30,000 to 200,000 ohms; G is a Wiedemann reflecting galvanometer; K, a make-and break-circuit key; and C, a commutator.

Fig. 4



THE DEFLECTION - METHOD.

B,	Cell Containing Cyanide Solution;	R,	Resistance of from 30,000 to 200,000 Ohms;
M,	Metal to be Tested;	G,	Wiedemann's Reflecting Galvanometer;
NE,	Ostwald's Normal Electrode;	K,	Make - and Break - Circuit Key.

The galvanometer was calibrated by replacing the cells B and NE with a Latimer-Clark cell, prepared according to the directions of Ostwald, and noting the deflection produced by its voltage through the given resistance of 30,000 to 200,000 ohms. The voltage was taken as $EMF = 1.438 - 0.001 \times (t^\circ - 15^\circ \text{ C.})$ volts.

Most of the concentrations of potassium cyanide were $\frac{M}{1}$ (one gramme-molecule, 65 grammes per liter, or 6.5 per cent.), or fractional multiples of this in tenths. Thus the series used was frequently $\frac{M}{1}, \frac{M}{10}, \frac{M}{100}, \frac{M}{1000}, \frac{M}{10{,}000}, \frac{M}{100{,}000}, \frac{M}{1{,}000{,}000}$.

As there is no little difference in the methods of notation in use, and much resulting confusion, the following methods of notation will always be used in this paper: We shall follow the motion of the positive ions through the solution, and the mode of notation will depend entirely on that. When the motion of the positive ion *in the solution* is from the metal to the solution, the metal is said to be electropositive, because it gives up positive ions to the solution and causes the solution to become positively electrified, itself becoming at the same time negatively electrified. Such, for instance, is the case of zinc in a solution of zinc sulphate. When, on the other hand, the solution gives up positive ions to the metal immersed in it, as is the case with copper in a solution of copper sulphate, the metal is said to be electronegative, for it causes the solution in which it is immersed to become electronegative, itself, at the same time, becoming positively electrified. The quicksilver in Ostwald's normal electrode is another example. The + or — sign, then, here indicates the direction of ionic motion, and simply shows whether the given positive ions tend to flow away from the metal into the solution or towards the metal from the solution. That is, whether the "solution-pressure" of the metal is greater or less than the "osmotic pressure" of the ions in solution.*

Now, when an electropositive and an electronegative metal are coupled, the direction of flow of the ions of both through the solution is the same, and the electromotive force of the combination is the arithmetic sum of those of the ingredients. When two electropositive or two electronegative metals are coupled, the ions tend to flow through the solution in opposite directions; hence, the electromotive force of the combination is equal to the arithmetical difference between the separate electromotive forces, the direction of motion, and hence the sign, being that of the greater.

In combinations in which the Ostwald normal electrode is one member, we know the amount and direction of one electromotive force; and hence, when we measure that of the combination, it is easy to calculate that of the other (neglecting the slight electromotive force due to the contact of the solutions).†

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* With regard to the anions, the + and — signs have an inverse meaning.

† This, except in cases of great differences in the concentration of the solutions, has been shown to cause an error of only a few thousandths or hundredths of a volt.

Thus, if, against the normal electrode, aluminum in a $\frac{M}{1}$ solution of KCy gives an EMF = + 1.55 volts,—that is, if the current flows from the aluminum to the mercury, the same as in the case of mercury,—it follows that the EMF of the aluminum in $\frac{M}{1}$ KCy will be + 1.55 — 0.560 = + 0.99 volts.

Again, if a strip of amalgamated zinc under similar circumstances gives a voltage of + 1.49 volts, the EMF of amalgamated zinc in a $\frac{M}{1}$ KCy solution will be + 1.49 — 0.560 = + 0.93 volts.

In making the determinations, it must be evident from the formula that, if there are few ions of the given metal present in the solution at the start, the introduction of a very few more will make great changes in the value of the EMF.

For in log. $\frac{P}{p}$ it must be evident that, as P is constant (for a given temperature), the value will depend entirely on p; and the smaller p is, the greater will be the effect due to slight changes in p. Hence, it will be impossible to get constant values for the EMF, unless the value of p is nearly constant; that is, when the solution is saturated with ions at the given temperature. That is the case with the normal electrode, where the mercury lies in a saturated solution of mercurous chloride. The mercury is thus in equilibrium with its ions, and a constant EMF results.

To get perfectly constant results with cyanide solutions, it would be necessary to have the solution saturated with the cyanide of the metal in question. But while this would give us a very satisfactory electromotive series, it would not give us a measure of the action of the unsaturated cyanide solution, just as it acts on the ores. We must, therefore, be content with results that are not entirely concordant, and take the best of a large number of determinations.

The strips used were always freshly burnished with sandpaper, cooled, and touched to a grounded platinum wire to discharge any electricity with which they might have been charged in burnishing.

Preliminary Results with the Deflection Method.—The following preliminary results were obtained in October to December, 1896,

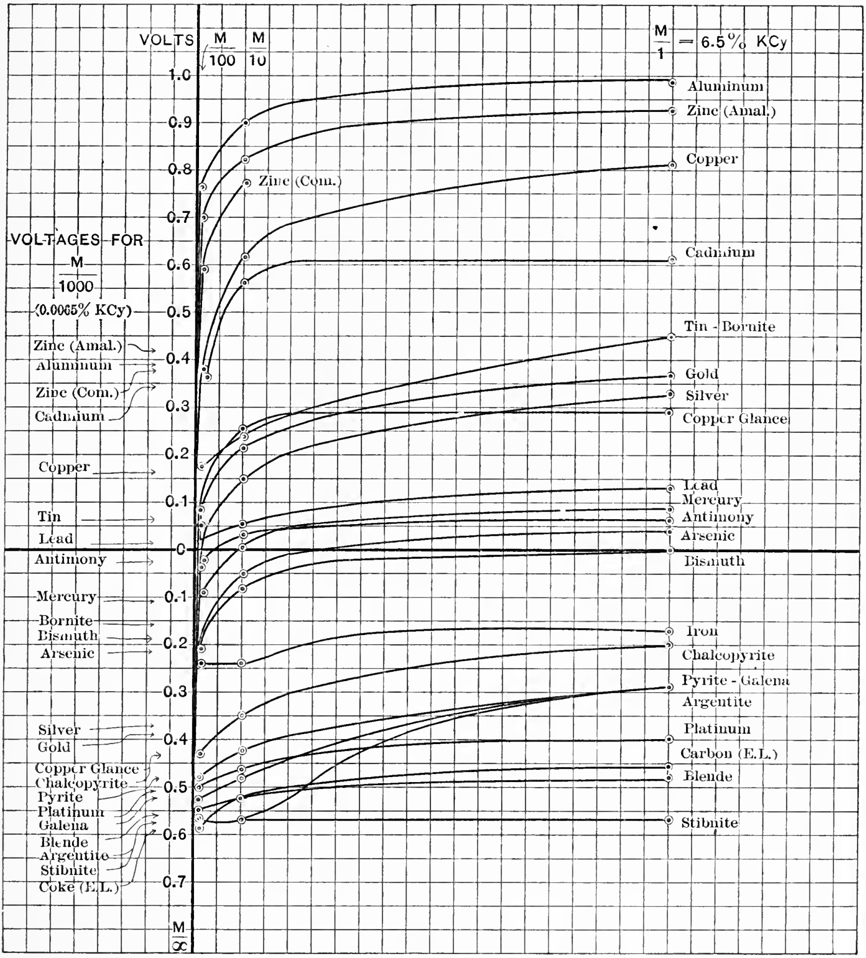
TABLE I.—*Electromotive Force of Metals in Cyanide Solutions. Deflection Method. Preliminary Experiments. October–December,* 1896.

	Ostwald's Normal Electrode = — 0.560 Volts.			
	$\frac{M}{1}$ KCy	$\frac{M}{10}$ KCy	$\frac{M}{100}$ KCy	$\frac{M}{1000}$ KCy
	Volts.	Volts.	Volts.	Volts.
*Aluminum	+0.99	+0.90	+0.76	+0.40
*Zinc, amalgamated	+0.93	+0.82	+0.70	+0.44
*Zinc, commercial	Not determ.	+0.77	+0.59	+0.39
*Copper	+0.81	+0.62	+0.37	+0.16
*Cadmium	+0.61	+0.57	+0.35	....
Cadmium, amalgamated	+0.55	+0.31	+0.19	....
*Tin	+0.45	+0.24	+0.17	+0.06
*Bornite	+0.45	+0.25	—0.16	....
Copper, amalgamated	+0.39 (?)	+0.41	—0.14 (?)	—0.12 (?)
*Gold	+0.37	+0.23	+0.09	—0.38
*Silver	+0.33	+0.15	— 0.05	—0.36
*Copper-Glance	+0.29 (?)	+0.25	+0.05	—0.44
*Lead	+0.13	+0.05	+0.01	....
Tin, amalgamated	Not determ.	+0.01	—0.07	—0.12
Lead, amalgamated	Not determ.	....	—0.03	....
*Quicksilver	—0.09	+0.01	—0.11	....
Gold, amalgamated	....	....	—0.13	—0.26
*Antimony	+0.06	+0.03	—0.03	....
*Arsenic	+0.04	—0.05	—0.21	....
*Bismuth	+0.00	—0.06	—0.20	....
Niccolite	—0.11	—0.17	—0.44	....
*Iron	—0.17	—0.24	—0.24	....
*Chalcopyrite	—0.20	—0.34	—0.44	....
*Pyrite	—0.28	—0.42	—0.48	....
*Galena	—0.28	—0.48	—0.52	....
*Argentite	—0.28	—0.56	—0.55 (?)	....
Berthierite	—0.30	—0.52	—0.52	....
Speisscobalt	—0.30	—0.33	—0.50	....
Magnetopyrite	—0.30	—0.40	—0.54	....
Fahlore	—0.36	—0.52	—0.52	....
Arsenopyrite	—0.40	—0.45	—0.54	....
*Platinum	—0.40	—0.46	—0.50	....
Cuprite	—0.43	—0.55	—0.57	....
*Electric Light Carbon	—0.46	—0.52 (?)	—0.57	....
*Blende	—0.48	—0.52	—0.55	....
Boulangerite	—0.50	—0.55	—0.55	....
Bournonite	—0.50	—0.55	—0.56	....
Coke	—0.52	—0.52	—0.42 (?)	....
Ruby Silver-Ore	—0.54	—0.53 (?)	—0.54	....
Stephanite	—0.54	—0.55	—0.52 (?)	....
*Stibnite	—0.56	—0.56	—0.56	....

with some of the common metals and minerals. The metals were good commercial articles, such as are in use in the arts, except in the case of gold, silver and quicksilver, which were chemically pure. In the case of some of the minerals, such as zincblende, stibnite, etc., the electrical resistance was probably so high in comparison with that of the intercalated resistance that the results may be somewhat low.

Nevertheless, they give at once some important relations which must exist whenever the cyanide process is applied in the treatment of ores.

Fig. 5



PRELIMINARY RESULTS. OCT.-DEC. 1896.

The electromotive forces of the metals and minerals marked with an asterisk in the above table have been plotted in Fig. 5. The Y axis shows the potential in volts, the X axis the concentration in gramme-molecules and also in percentage of KCy.

It will be noticed that in most cases the curves approximate quite closely to the logarithmic curve which theory would give (see Fig. 2), supposing the osmotic pressure of the metallic ions present to be inversely proportional to the concentration of the free potassium cyanide present; but they have different origins.

It will be noticed that the electromotive force of commercial sheet-zinc is increased by amalgamation, probably by reducing local action with some of its impurities, by which some of the current produced is short-circuited. In all the other experiments, amalgamation reduces the electromotive force of the combination.

With some substances, particularly aluminum, copper, iron, platinum and gas-carbon, it was very difficult to get concordant results; with aluminum and copper this seemed to be due to a tendency to form an insoluble film on the surface of the metal, which put a stop to further action. With copper and iron it was also possibly due to a tendency of the metals to a change of valency, which is accompanied by a change in the electrical state. With platinum and gas-carbon, it was not improbably due to a varying content of absorbed gas.

In testing the minerals, it was in all cases difficult to get a complete electrical contact between the tips of the platinum forceps and the rough surface of the mineral fragment, so that the results are only provisional, particularly as the resistance in some of these cases was very high. Nevertheless, the results are very interesting. They show, for instance, that not all copper minerals have a strong action on the current. Pure chalcopyrite, for instance, has hardly more action than pure pyrite, while bornite and copper-glance have a very decided tendency to go into solution. Cuprite is also apparently very little acted on, though this may be due to its high resistance rather than to a lack of tendency to dissolve. The soluble salts and minerals of copper could not be tested in this manner, owing to their non-conductivity.

It is plain, however, that pure chalcopyrite, galena, argentite, magnetopyrite, fahlore, arsenopyrite, blende, boulangerite, bournonite, ruby silver-ore, stephanite and stibnite, when free from their oxidation-products, are apparently very little acted on by cyanide solutions.

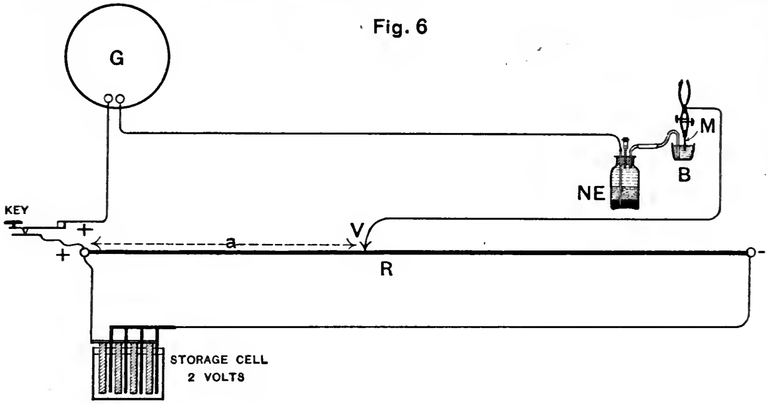
It is also plain that a particle of metallic gold, in contact with a particle of pyrite, forms a galvanic couple in $\frac{M}{1}$ or 6.5 per cent. KCy solution, equal to + 0.65 volts: in $\frac{M}{10}$ or 0.65 per cent. KCy solution, + 0.65volts, and in $\frac{M}{100}$ or 0.065 per cent. KCy solution, + 0.57 volts. With zinc under the same circumstances (if we take for the $\frac{M}{1}$ KCy solution the figures for amalgamated zinc), taking the zinc as the more electropositive metal, and subtracting the potential of gold, we have differences of + 0.56 volts, + 0.54 volts, and + 0.50 volts. In short, these figures would measure the tendency of the zinc to dissolve, or of the gold to precipitate in KCy solutions of these strengths.

According to these figures, the precipitating power of the zinc seems to hold up quite well for the dilute solutions. The actual failure to precipitate the gold, sometimes met with in dilute solutions, is no doubt due to films of cyanide or hydrate of zinc, which form incrustations on the surface of the zinc and thus prevent contact. The fact that the use of a small amount of fresh cyanide or of caustic potash in the zinc-boxes starts precipitation again, seems to favor this explanation.

The Zero-Method.—This method is shown in outline in Fig. No. 6. NE is the Ostwald normal electrode. B is the cell containing the cyanide solution in which, as before, is immersed the metal M to be tested. At G is a galvanometer. At R is a resistance, graduated, in my experiments, into 10,000 parts. A storage-battery of two volts and the combination-cell NE–B are so connected that their positive poles are both connected at the same end of the resistance R. The negative pole of the storage-battery is attached to the other end of the resistance R, so that the whole current of the storage-battery discharges constantly through R. The latter should be great enough to avoid heating, and to maintain a constant potential between the ends of R. The other terminal of the combination (the negative pole) is then moved along the resistance R till some distance, *a*, is reached at which the EMF force of NE–B is exactly balanced by the EMF force of the storage-battery for that fraction of R represented by *a*. In this case there is no deflection of the galvanometer; at other points the galvanometer will be deflected either to the right or left, according as too much or too little EMF is used to balance NE–B. The EMF of the storage-battery, is, of course, first calibrated by comparing it with a standard Latimer-Clark cell, placed where NE–B is.

This method of determining the EMF of a cell is deservedly considered one of the most reliable. With non-polarizing cells, it certainly leaves nothing to be desired. But, in investigations of this kind with cells that are easily polarized, accurate results are obtained only by a long number of very tedious approximations, which render the work almost interminable. For it is, of course, impossible to hit the right balance at first; and, if the connection is made at any point except the right one, the metallic electrode will receive either a positive or negative charge from the storage-battery, and a true reading will be thus made impossible. It is necessary to change the entire solution in B, put in new electrodes at M, drive out the diffused cyanide solution from NE, and so on, till these operations have been repeated perhaps a dozen times. If this is not done, the results are very unreliable. With the deflection method, on the other hand, the observations may be made very rapidly, and though there is a tendency for the readings to be a little low unless they are quickly madé, still, with a high intercalated resistance, and a delicate reflecting galvanometer, this method seems to be reliable for these quickly polarizing electrodes.

Fig. 6



POGGENDORF'S COMPENSATION - METHOD.

B,	Cell Containing Cyanide Solution;	R,	Resistance Graduated into 10,000 Parts;
M,	Metal to be Tested;	V,	Movable Contact;
NE,	Ostwald's Normal Electrode;	G,	Wiedemann's Reflecting Galvanometer.

As I have already stated, and as was first pointed out by Ostwald, strictly concordant results are possible only when the electrode is surrounded with a medium already saturated with its ions.

I had intended to verify the results in Table I. with the zero method before publication, but although I had all the apparatus set up for over two years, ready to begin at any time, I was prevented by the constant pressure of routine-work from touching it, till shortly before the time set for the San Francisco meeting of the Institute, in September, 1899. Meantime Prof. A. von Oettingen, professor of physics in the University of Leipzig, read a very valuable paper on this subject before the Chemical and Metallurgical Society of South Africa, in January and February, 1899. In this paper he gives the results of a large number of determinations which he made of the electromotive force of metals in cyanide solutions by means of Poggendorf's compensation method, or, as I shall call it for brevity, the zero method.

Professor von Oettingen's results are given in Table II.

TABLE II.—*Potentials of Different Metals in Contact with KCy Solutions, at 25° C.*

Experiments of Prof. A. von Oettingen, *Jour. Chem. and Metallurgical Soc. S. Africa*, January and February, 1899.

	$\frac{M}{1}$ KCy	$\frac{M}{10}$ KCy	$\frac{M}{100}$ KCy	$\frac{M}{1000}$ KCy	$\frac{M}{100}$ KCy + $\frac{M}{.670}$ Au
	Volts.	Volts.	Volts.	Volts.	Volts.
Au	+0.340 to +0.306	+0.180 to +0.218	—0.092 to —0.056	—0.414 to —0.474	—0.020 to —0.170
Ag.........	+0.330 to +0.314	+0.176 const.	—0.020 const.	—0.340 to —0.200	—0.308 to —0.330
Cu.........	+0.890 to +0.924	—0.680 to +0.648	—0.212* to +0.380	—0.550 to —0.230	
Hg.......	+0.162 to +0.200	+0.008 to +0.024	+0.056 const.	....	
Ni.........	—0.290 to +0.194	—0.466 to —0.392	—0.550 to —0.488	—0.560	
Co.........	+0.182 to +0.196	+0.118 to —0.220†	—0.168 to —0.240	....	
Fe.........	+0.056 to —0.146	+0.034 to —0.012	—0.054 to +0.022	—0.008 to +0.050	
Fe_2O_3....	—0.674 to —0.700	—0.796 to —0.720	—0.824 to —0.750	....	
PbO_2.....	+0.160 const.	+0.110 to +0.118	—0.062 to +0.070	—0.006 const.	
Pb.........	+0.164 const.	+0.128 const.	+0.120 const.	+0.120 const.	+0.126 const.
Zn	+0.924 const. +0.940	+0.780 to +0.800	+0.560 to +0.604	+0.480 const.	

* On moving the fluid the potential suddenly rises.

† The potential changed suddenly from —0.121 to +0.118, then remained constant.

(Note the discrepancy between —0.220 in the table and —0.121 in the footnote.)

The above results were all obtained by the Poggendorff compensation or zero method, the Lippman capillary electrometer being used as an indicator instead of a galvanometer.

Prof. von Oettingen says of these results:

> "The two figures in each column refer to the first and last observations on each metal, the intermediate values being omitted. The time occupied by the change is very variable; Cu, for instance, took an hour. When no changes occur, this is indicated by a constant. The changes of potential are not always in the same direction; sometimes decreasing, sometimes increasing. But the direction of the changes in any given metal is always the same."

It will be noticed on examining the table that this last sentence is not correct (unless there should be a typographical error in his table). For gold, silver, copper, cobalt, ferric oxide and lead peroxide, the highest value for the same metal is sometimes the first and sometimes the second value. In the case of copper in $\frac{M}{100}$ KCy the results jump from —0.212 volts to + 0.380 volts—a difference of 0.592 volts. I shall speak of the probable cause of these differences later.*

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* There are some other potential differences given by Prof. von Oettingen which I include here.

$\frac{\mathrm{Hg}}{\mathrm{Hg_2SO_4}} = -0.99$ volts. (Ostwald), $\frac{M}{1}$ Solutions.

$\frac{\mathrm{Zn}}{\mathrm{ZnSO_4}} = +0.524$ " " "

$\frac{\mathrm{Mg}}{\mathrm{MgSO_4}} = +1.243$ " " " 18° C.

$\frac{\mathrm{Cd}}{\mathrm{CdSO_4}} = +0.158$ " " " "

$\frac{\mathrm{Pb}}{\mathrm{Pb\,(C_2H_3O_2)_2}} = -0.089$ " " "

$\frac{\mathrm{Cu}}{\mathrm{CuSO_4}} = -0.582$ volts. " " "

$\frac{\mathrm{Ag}}{\mathrm{Ag_2SO_4}} = -1.024$ " " " "

$\frac{\mathrm{Hg}}{\mathrm{Hg_2Cl_2}} = -0.560$ (Ostwald's normal electrode.)

Prof. von Oettingen himself determined the following also (all at 25° C.).

$\frac{\mathrm{Au}}{\mathrm{AuCl\ (conc.)}} = -1.64$ to 1.42 volts, variable.

$\frac{\mathrm{Au}}{\frac{M}{1}\mathrm{AuCl_3}} = -1.134$ volts.

$\frac{\mathrm{Au}}{\mathrm{Aqua\ Regia}} = -1.09$ volts.

In order to make more clear the meaning of Prof. von Oettingen's results, I have plotted them in Fig. 7 as mine are plotted in Fig. 5. In the figures, x is made to mark the molecular concentration $\frac{M}{1}, \frac{M}{10}, \frac{M}{100}, \frac{M}{1000}$; the y axis shows the potential in volts. The designation Zinc 1 means that this was the first value obtained with zinc, the designation Zinc 2, the final value, etc. It will be noticed that sometimes the first value is higher than the second and sometimes *vice versa;* but the results are not consistent throughout, sometimes crossing each other.

The first curves of each metal, except mercury, approximately follow the logarithmic law (on the assumption that the number of metal ions is inversely proportional to the potassium cyanide concentration). Evidently the curves will cross the X axis at different points, and not usually at a molecular concentration M = 1, unless it should accidentally happen that $\frac{P}{1} = 1$ for M = 1. The second curves of zinc, copper, gold and silver, also approximately follow it. But the second curves of mercury, cobalt, nickel and iron depart considerably from it. It is possible that these departures are due to polarization effects, as already explained. The irregularities are much more marked than with the deflection-method. With that method, provided a sufficiently large resistance is used, the first deflection is the greatest, and is taken as the reading nearest to the truth. The deflection then gradually falls (often quite rapidly, if there is a formation of gas on the face of the electrode); but the electromotive force never rises unless the first effect of the current is to produce a film of gas or insoluble

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$\frac{\text{Au}}{\text{KCyS (sat.)}}$ = —0.26 to +0.03, very variable.

$\frac{\text{Au}}{\frac{M}{1}\text{KCyS}}$ = —0.36, variable volts.

$\frac{\text{Au}}{\frac{M}{10}\text{KCyS}}$ = —0.40 volts.

$\frac{\text{Au}}{\text{KCy (sat.)}}$ = +0.50 volts.

$\frac{\text{Au}}{K_2S}$ = +0.14 volts.

$\frac{\text{Au}}{K_2S_7}$ = +0.21 volts.

$\frac{\text{Au}}{Na_2S}$ = 0 to 0.136 volts.

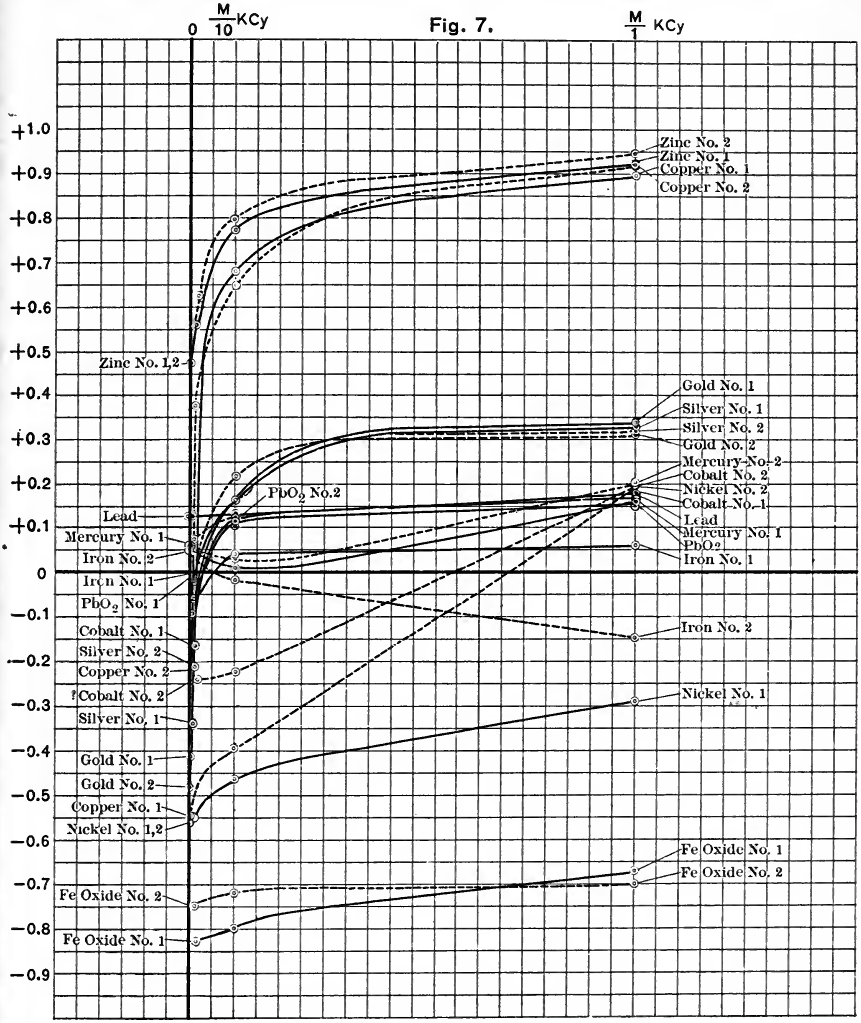
$\frac{\text{Ag}}{\text{KCy (sat.)}}$ = +0.536 volts.

$\frac{\text{Cu}}{\text{KCy (sat.)}}$ = +1.154 volts.

$\frac{\text{Zn}}{\text{KCy (sat.)}}$ = +1.193 volts.

cyanide which puts a stop to the current, either by setting up an opposing EMF or by preventing or reducing contact by its resistance. In this case, shaking the solution or jarring the electrode usually gives an increase of the EMF by destroying the film in part; but, if the metallic surface is untarnished to begin with, the EMF rarely rises again to its first value.

Fig. 7.



E.M.F. OF METALS IN CYANIDE-SOLUTIONS.

by Prof. v. Oettingen of Leipzig.

(J. Chem. & Met. Soc. S. A. Feb. 1899.)

$x = M.$ $y = \pi - .058 \log P/p$ Volts.

New Method of Plotting Results.—The method of plotting results hitherto used, while it shows very well the near approach of the curve to the true logarithmic curve, has the disadvantage that only three or four values for the tenth ratio can be plotted. If, however, instead of making $x = \frac{P}{p}$, as we have done, we let $x = \log. \frac{P}{p}$, and plot the curve $y = 0.058 \log. \frac{P}{p}$ volts, the curve becomes a straight line passing through the origin at 0. For $x = 0$, $y = 0$.

This curve is plotted in Fig. 8 for values of $x = \log. \frac{P}{p}$ from + 13 to — 12, which gives voltages from + 0.755 to — 0.696, and the table shows values from $x = \log. \frac{P}{p} =$ minus infinity to 40. It shows what an enormous change in the value $\frac{P}{p}$ is necessary to produce a very moderate change in the voltage. Thus, to produce a change of 2.32 volts, a change in the ratio $\frac{P}{p} = 10^{40}$ (or ten to the fortieth power) is necessary.

In our experiments, of course, we do not know the value of $\frac{P}{p}$, but as a first approximation we may assume it inversely proportional to the molecular concentration $M \times 10^n$.

On the axis of x is plotted the logarithm of the molecular concentration expressed in the powers of 10. Thus: $x = \log. M = \log. 10^{\pm n}$. The y axis gives the EMF in volts. For comparison the theoretic formula of Nernst is also given.

If we plot Prof. von Oettingen's results, as in Fig. 9, on this plan, they become at once more intelligible. We see at once that all the curves do not remain straight lines. The zinc follows along very nearly in the theoretic straight line. The copper starts well, but soon falls quite rapidly, due probably to increasing dissociations. The gold and silver approximate fairly well, also; but the rest depart from it considerably.

Comparison of the Deflection and Zero Methods.—Since the results of Prof. von Oettingen were published, I have thought best to try the zero method as well as the deflection method, and to compare the results so far obtained with each other. I have also decided to plot the results by the same method as shown in Fig. 8, as it enables us to compare the results over a wider range of dilution than the former method of tabulation would cover.

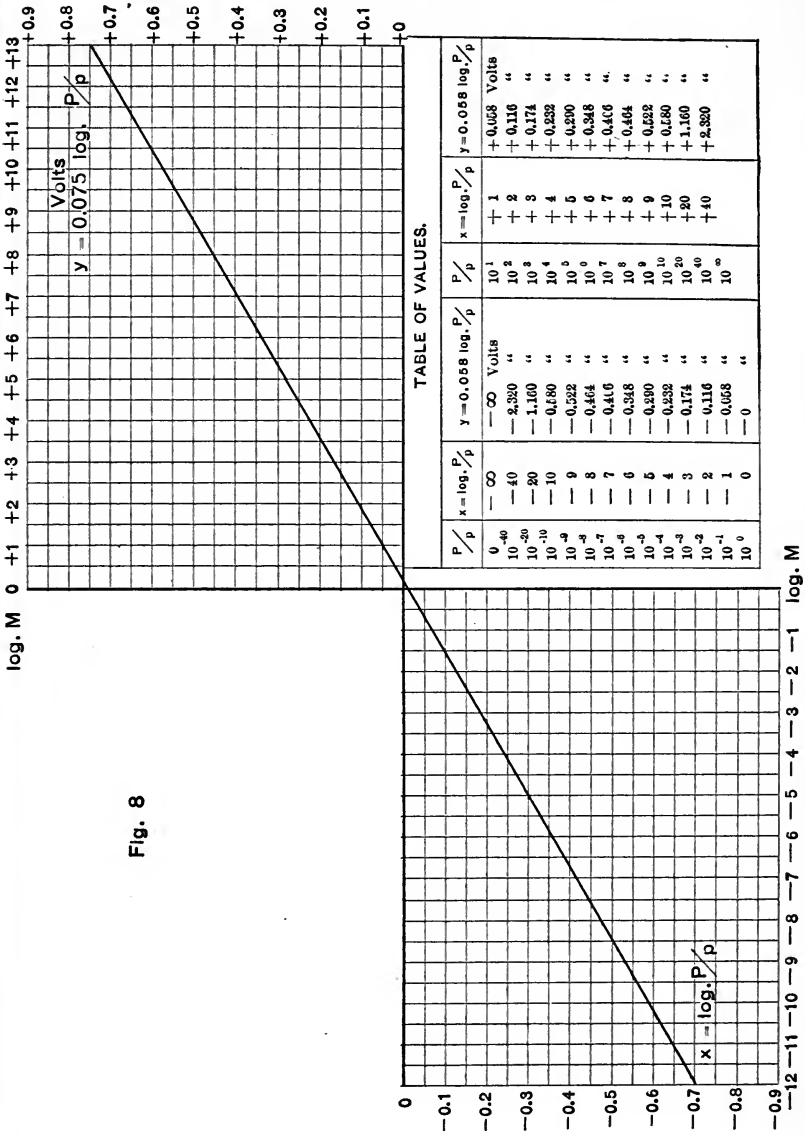


TABLE OF VALUES.

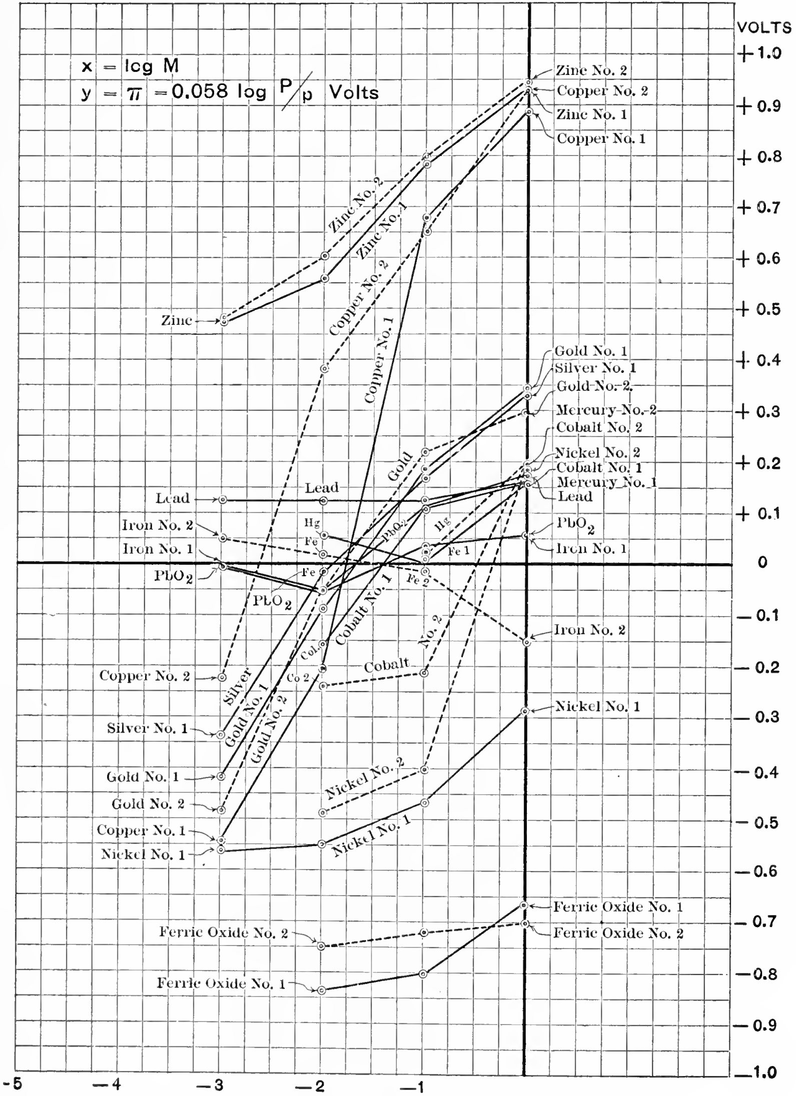
P/p	$x = \log. P/p$	$y = 0.058 \log. P/p$	P/p	$x = \log. P/p$	$y = 0.058 \log. P/p$
0	$-\infty$	$-\infty$ Volts	10^1	+1	+0.058 Volts
10^{-40}	−40	−2.320 "	10^2	+2	+0.116 "
10^{-20}	−20	−1.160 "	10^3	+3	+0.174 "
10^{-10}	−10	−0.580 "	10^4	+4	+0.232 "
10^{-9}	−9	−0.522 "	10^5	+5	+0.290 "
10^{-8}	−8	−0.464 "	10^6	+6	+0.348 "
10^{-7}	−7	−0.406 "	10^7	+7	+0.406 "
10^{-6}	−6	−0.348 "	10^8	+8	+0.464 "
10^{-5}	−5	−0.290 "	10^9	+9	+0.522 "
10^{-4}	−4	−0.232 "	10^{10}	+10	+0.580 "
10^{-3}	−3	−0.174 "	10^{20}	+20	+1.160 "
10^{-2}	−2	−0.116 "	10^{40}	+40	+2.320 "
10^{-1}	−1	−0.058 "	10^{∞}		
10^0	0	−0 "			

Fig. 8

NERNST'S LAW OF ELECTROMOTIVE FORCE
When $x = \log. P/p$ $y = 0.058 \log. P/p$ Volts

After the foregoing description and discussion of the various methods employed in this investigation, the reader will be able

Fig. 9.



E.M.F. OF METALS IN CYANIDE-SOLUTIONS.

Prof. v. Oettingen of Leipzig. (J. Chem. and Met. Soc. S. A. Feb. 1899.)

On the horizontal (x) axis are laid off the values of log. $M = \log. 10^n$; on the vertical (y) axis, the actual volts.

to study intelligently the tabulated results of the tests hereinafter stated.

III.—Results of Experiments.

The following tables show, for the several metals tested, my own results, obtained at different times and by different methods, as well as those of Prof. von Oettingen. In every case, each observation was made independently, without regard to the ultimate result of its reduction. But the later readings are more reliable than the earlier, because a certain knack in catching the needle at its maximum position, before the voltage begins to fall, was acquired during the work. The tables give the readings as reduced from the actual observations, without attempted correction; but when any anomaly rendered the observation uncertain, this is indicated by a (?). Such was the case particularly in the readings with distilled water (M divided by ∞), which were very uncertain, especially for easily oxidizable metals like zinc and iron.

Table III.—*Electromotive Force of Zinc* (*Commercial Sheet, Burnished*) *in KCy.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).	(*f*).	(*g*).
Note-book B1. page..	67	176	177	186	193	Publsh'd.	Publsh'd.
Date	Oct. 19,'96	A'g. 30,'99	A'g. 30,'99	Sep. 4, '99	Sep. 8, '99	Feb., '99	Feb., '99
Method	Deflect.*	Zero.†	Deflect.†	Deflect.‡	Deflect.	Zero.	Zero.
Resis. ohms..............	100,000	....	100,000	100,000	200,000	....	....
Temperature...........	22° C.	19° C.	19° C	19° C.	198 C.	25° C.	25° C.
Observer..................	Christy.	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF........................ (N. E. = —0.560)........	Volts.	Volts.	Volts	Volts.	Volts.	Volts.	Volts.
Concentration :							
KCy $\frac{M}{1}$....................	....	+0.946	....	+0.906	+0.914§	+0.924	+0.940
$\frac{M}{10}$....................	+0.770	+0.861	....	+0.815	+0.836§	+0.780	+0.800
$\frac{M}{100}$....................	+0.585	+0.772	....	+0.730	+0.735§	+0.560	+0.604
$\frac{M}{1,000}$....................	+0.385	+0.415	+0.386	+0.300	+0.371‖	+0.480	+0.480
$\frac{M}{10,000}$....................	....	+0.385 (?)	+0.326	+0.270	+ 0332	....	....
$\frac{M}{100,000}$....................	....	+0.355	+0.320	+0.270 (?)	+0.332 (?)	....	....
$\frac{M}{1,000,000}$....................	....	+0.383 (?)	+0.312	+0.282 (?)	+0.332 (?)	....	....
$\frac{M}{\infty}$ (= H_2O).......	+0.041 (?)	+0.372 (?)	+0.256 (?)	+0.240 (?)	+0.293 (?)	....	....
				+0.350 (?)			

* Used same strip of zinc throughout experiments, burnishing each time. Tested from strong to weak solutions. † Used new burnished strip each time.

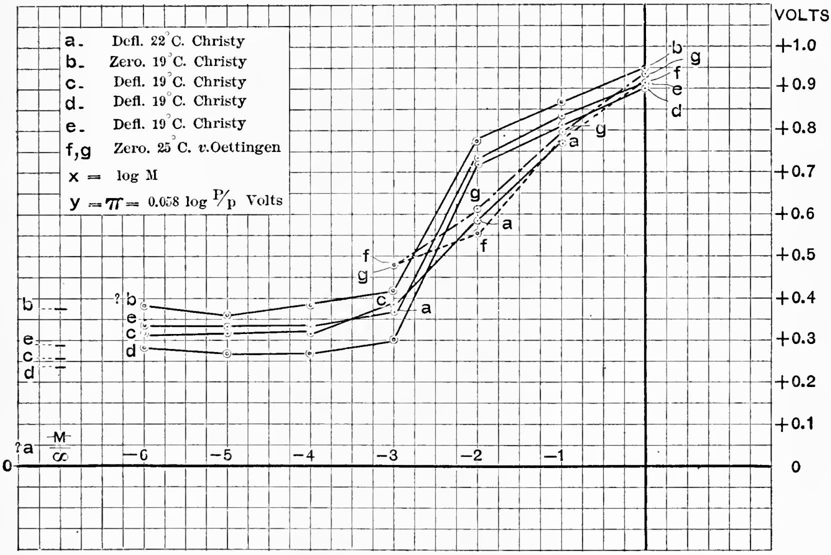
‡ Same strip, burnished each time. Tested from weak to strong solutions.

§ Fine bubbles form on zinc and then voltage falls. Shaking causes bubbles to escape, and voltage rises. ‖ Below this, no gas-bubbles visible to naked eye; but voltage falls, and then rises on shaking.

Experiments with Commercial Sheet-Zinc.—Experiments were made at different times, with both the zero and the deflection method, on the ordinary commercial sheet-zinc, such as is actually used in making zinc-shavings for precipitating gold. The results are given in Table III., and those of Prof. von Oettingen have been introduced into the same table, for comparison.

These results are plotted together for comparison in Fig. 10. It will be evident that from $\frac{M}{1}$ to $\frac{M}{100}$, or from 6.5 to 0.065 per cent., the curve nearly follows the theoretic straight line. Curves *a*, *f* and *g* appear to follow it to $\frac{M}{1000}$ or 0.0065 per cent., but for more dilute solutions beyond that point the curve approximates a horizontal straigh tline. This, according to the Nernst theory, would mean that the number of zinc ions in such solutions remains nearly constant. In spite of all the irregularities in the curves, the point — 3 or $\frac{M}{1000}$ or 0.0065 per cent. KCy is evidently a critical or inflection-point in the curve.

Fig. 10.



E.M.F. OF ZINC IN KCy. SOLS.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

The results obtained with high dilutions of cyanide and with distilled water were very uncertain, probably because of the formation of insoluble films of oxide of zinc and occluded hydrogen, which prevented the accurate reading of the needle.

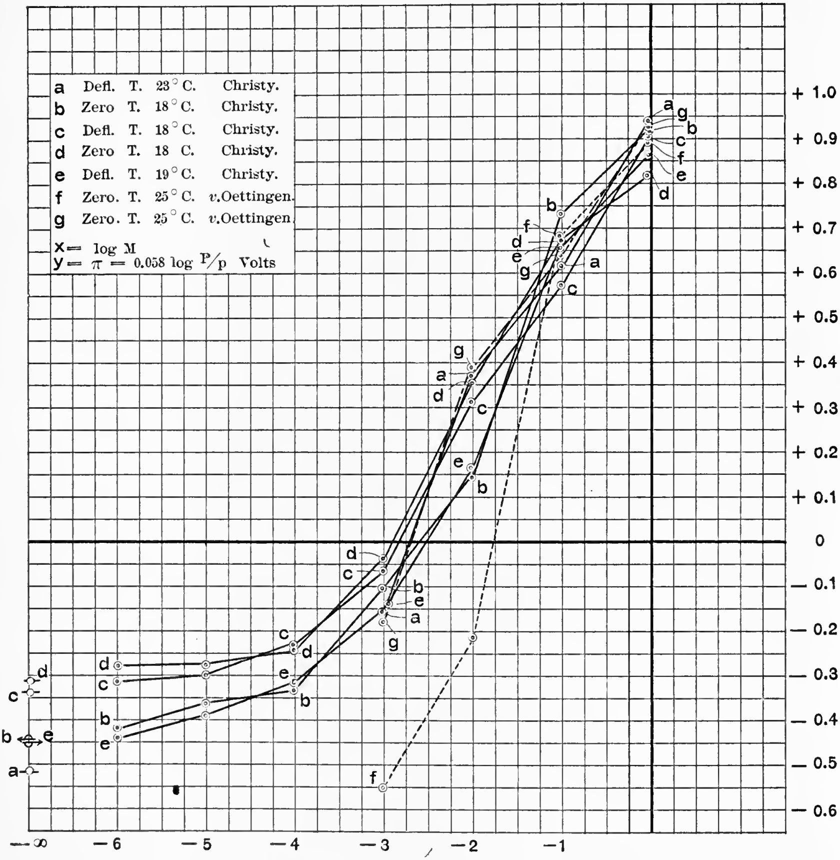
TABLE IV.—*Electromotive Force of Copper (Burnished Sheet) in KCy.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).	(*f*).	(*g*).
Note-book Bl. page..	68	178	188	189	190	Publsh'd.	Publsh'd.
Date	Oct. 20,'96	A'g. 30,'99	Sep. 6, '99	Sep 6, '99	Sep 7, '99	Jan., '99	Jan., '99
Method	Deflect.	Zero.	Deflect.	Zero.	Deflect.	Zero.	Zero.
Resis. ohms	100,000	....	100,000	....	200,000	....	....
Temperature	23° C.	18° C.	18° C,	18° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF.... (N. E. = —0.560)	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.
Concentration :							
KCy $\frac{M}{1}$	+0.930	+0.910	+0.905	+0.811 (?)	+0.860	+0.924	+0.890
$\frac{M}{10}$	+0.620	+0.731	+0.310	+0.663	+0.660	+0.680	+0.648
$\frac{M}{100}$	+0.370	+0.146	+0.310	+0.356	+0.149	—0.212	+0.380
$\frac{M}{1,000}$	+0.158	—0.104	—0.068	—0.048	—0.151	—0.550	—0.230
$\frac{M}{10,000}$	....	—0.332	—0.241	—0.230	—0.324	....	....
$\frac{M}{100,000}$	....	—0.360	—0.299	—0.272	—0.387	....	....
$\frac{M}{1,000,000}$	....	—0.426	—0.314	—0.282	—0.442	....	....
$\frac{M}{\infty}$(= H_2O)	—0.560 (?)	—0.444	—0.328	—0.313	—0.450	....	....

In my results with the deflection method, I have always taken the highest reliable reading as the most probable result. It was often quite difficult to make sure of the proper reading, as a slight insoluble film of cyanide of copper formed almost instantly, and this lowered the potential almost before a reading could be taken. On agitating the copper, so as to bring it into contact with fresh solution, the potential would gradually rise to a maximum, after which, on being left at rest, it would again fall off more gradually. It is possible, also, that the tendency of copper to form cupric, as well as cuprous cyanide, may in part explain the discordant results, such, for instance, as that obtained by Prof. von Oettingen with $\frac{M}{100}$ KCy solution. He says in a footnote concerning this case, "On shaking, the potential suddenly rises from — 0.212 to + 0.380."

The results contained in the above table have all been plotted in Fig. 11. The mean results of these curves show a tendency to follow the course of a straight line from $\frac{M}{1}$ down to $\frac{M}{1000}$; or perhaps to $\frac{M}{10,000}$; that is, from 6.5 down to 0.00065 per

Fig. 11



E.M.F. OF METALS IN KCy SOL.
COPPER.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

cent., when it breaks off sharply and runs along flat again, just as the zinc-curve did.

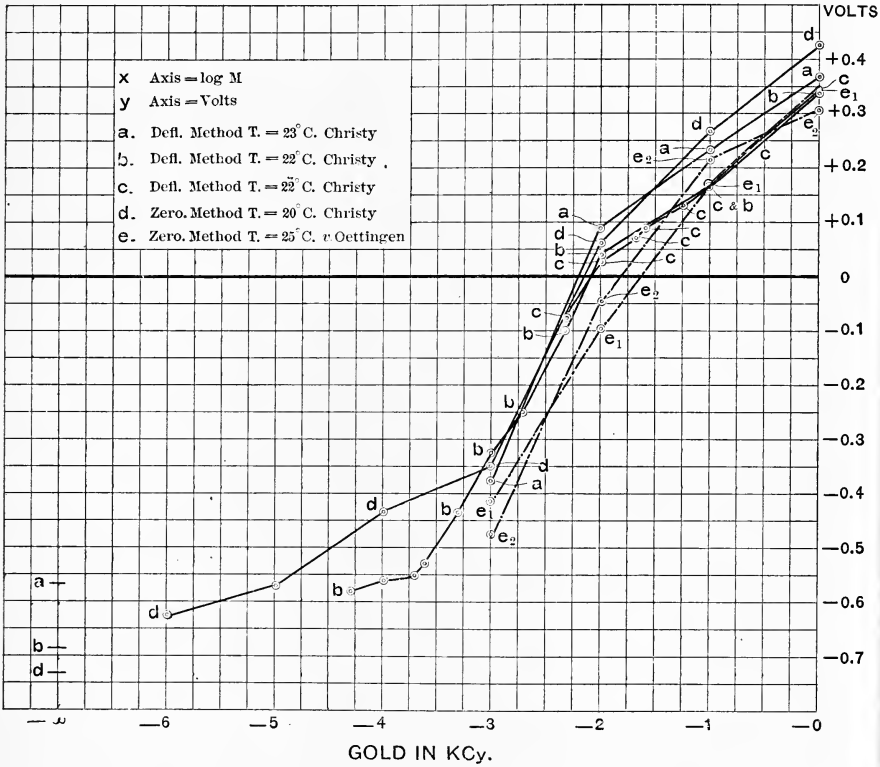
On plotting the gold-curves, as has been done in Fig. 12, it is evident that the gold follows the logarithmic law fairly well

Table V.—*Electromotive Force of Gold in KCy Solutions.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).	(e_1).	(e_2).
Note-book, B1. page	71	86	88	172	Published.	Published.
Date	Oct. 20, '96	Dec 12, '96	Dec. 14, '96	Aug. 26, '99	Feb., '99	Feb.. '99
Method	Deflect.	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resis. ohms	100,000	50,000	50,000	....	....	....
Temperature	23° C.	22° C.	22° C.	20° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E. = —0.560)	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.
Concent'n. KCy:						
6.4M	....	....	+0.468	....	....	....
3.2M	....	....	+0.420	....	....	....
1.6M	....	....	+0.357	....	....	....
$\frac{M}{1}$	+0.366	+0.334	+0.336	+0.418	+0.340	+0.306
$\frac{M}{2}$	....	....	+0.288	....	....	....
$\frac{M}{4}$	....	....	+0.239	....	....	....
$\frac{M}{10}$	+0.233	+0.176	+0.176	+0.264	+0.180	+0.218
$\frac{M}{20}$	....	....	+0.135	....	....	....
$\frac{M}{40}$	....	....	+0.093	....	....	....
$\frac{M}{50}$	....	....	+0.073	....	....	....
$\frac{M}{100}$	+0.087	+0.045	+0.037	+0.065	—0.092	—0.056
$\frac{M}{200}$	....	—0.099	—0.073	....	....	....
$\frac{M}{500}$	....	—0.244	....	....	....	....
$\frac{M}{1,000}$	—0.380	—0.326	....	—0.348	—0.414	—0.474
$\frac{M}{2,000}$	....	—0.436	....	....	....	....
$\frac{M}{4,000}$	....	—0.533	....	....	....	....
$\frac{M}{5,000}$	....	—0.554	....	....	....	....
$\frac{M}{10,000}$	....	—0.560	....	—0.439	....	....
$\frac{M}{20,000}$	....	—0.581	....	....	....	....
$\frac{M}{100,000}$	....	....	—0.567	....	....	....
$\frac{M}{1,000,000}$	....	....	—0.622	....	....	....
$\frac{M}{\infty}$ (= H_2O)	—0.560 (?)	—0.698	....	Sep. 4, '99 Deflection. —0.724 —0.620 —0.709	....	....

as far as $\frac{M}{100}$ or 0.065 per cent. KCy. A considerable fall of potential occurs, according to my experiments, between $\frac{M}{100}$ and $\frac{M}{1000}$, or 0.0065 per cent. KCy, indicating an increase of osmotic pressure, probably due to an increasing dissociation of the potassium aurous cyanide. This point seems again a critical point in the curve, which, beyond it, runs off more flatly, indicating an approach to a constant osmotic pressure of the gold ions.

Fig. 12.



On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

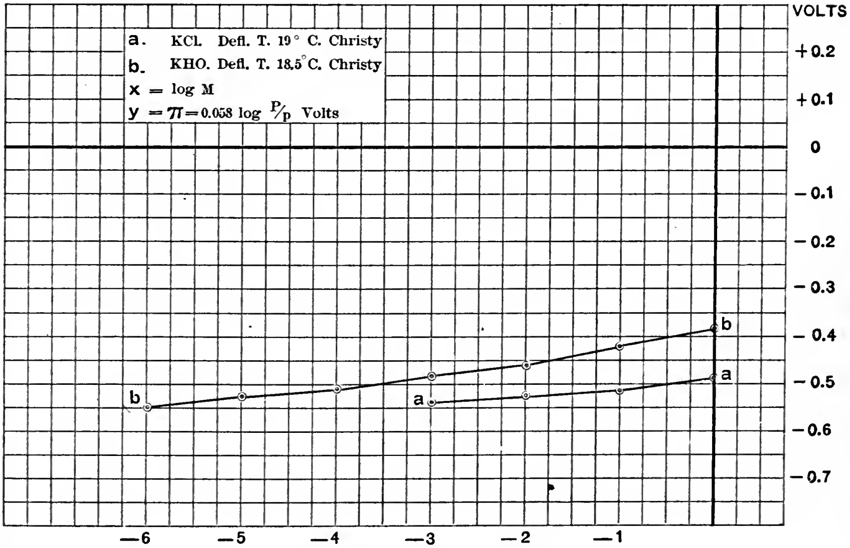
Electromotive Force of Gold in KCl and KHO.

In order to bring out the effect of the potassium cyanide in reducing the osmotic pressure of the gold ions in the solution (according to the Nernst theory), I append the following experiments on the electromotive force of gold in solutions of potassium chloride and potassium hydrate. These results are given in Table VI., and are plotted in Fig. 13. It is evident that there is a very much smaller electromotive force in each of these cases. It is particularly low in the case of potassium chloride. According to the Nernst theory, the solution-pres-

TABLE VI.—*Electromotive Force of Gold in KCl and KHO.*

Curve.	(*a*).	(*b*).
Note-book B1, page	160	159
Date	Aug. 10, '99	Aug. 10, '99
Resistance, ohms	30,000	30,000
Temperature	19° C.	18.5° C.
Observer	Christy.	Christy.
EMF. (N. E. = −0.560)	Volts.	Volts.
Solution	KCl.	KHO.
Concentration :		
$\frac{M}{1}$	−0.487	−0.381
$\frac{M}{10}$	−0.510	−0.422
$\frac{M}{100}$	−0.523	−0.468
$\frac{M}{1,000}$	−0.533	−0.486
$\frac{M}{10,000}$	......	−0.505
$\frac{M}{100,000}$	......	−0.526
$\frac{M}{1,000,000}$	......	−0.551

Fig. 13.



E.M.F. OF GOLD IN KCl AND KHO SOLUTIONS.
On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

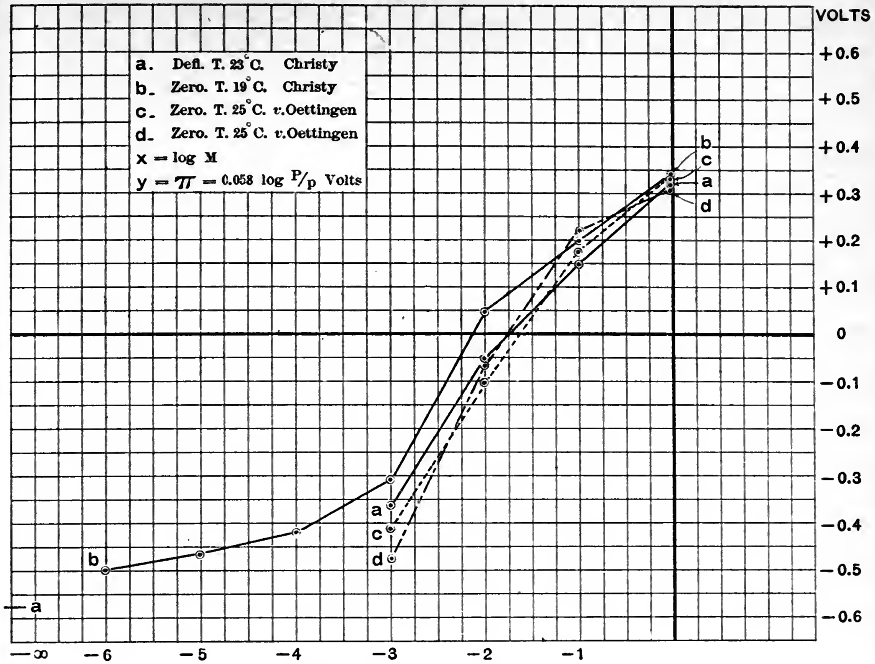
sure of the gold is the same in each of these solutions; that is, the pressure with which the gold tends to go into solution is exactly the same (at a given temperature), whether the gold is immersed in either potassium cyanide, potassium chloride or potassium hydrate. But the number of gold ions in each solution, and hence the resulting osmotic pressure, is very different. According to this theory, it is least in potassium cyanide, much greater in potassium hydrate, and greatest of all in potassium chloride. Consequently, the EMF varies inversely as p, according to the ratio $\log. \frac{P}{p}$.

The curves in both cases run rather flat, indicating an approach to a constant osmotic pressure for high dilutions.

TABLE VII.—*Electromotive Force of Silver in KCy.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).
Note-book B1, page	71	170	Published.	Published.
Date	Oct. 20, '96	Aug. 19, '99	Jan., '99	Jan., '99
Method	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms	100,000	......	......	......
Temperature	23° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E. = —0.560)	Volts.	Volts.	Volts.	Volts.
Concentration KCy:				
$\frac{M}{1}$	+0.326	+0.345	+0.340	+0.306
$\frac{M}{10}$	+0.152	+0.194	+0.180	+0.218
$\frac{M}{100}$	-0.054	+0.058	-0.092	-0.156
$\frac{M}{1,000}$	-0.360	-0.308	-0.414	-0.474
$\frac{M}{10,000}$	......	-0.417	......	......
$\frac{M}{100,000}$	......	-0.457	......	......
$\frac{M}{1,000,000}$	......	-0.498	......	......
$\frac{M}{\infty}$ (= H_2O)	-0.572	......	......	......

Fig. 14.



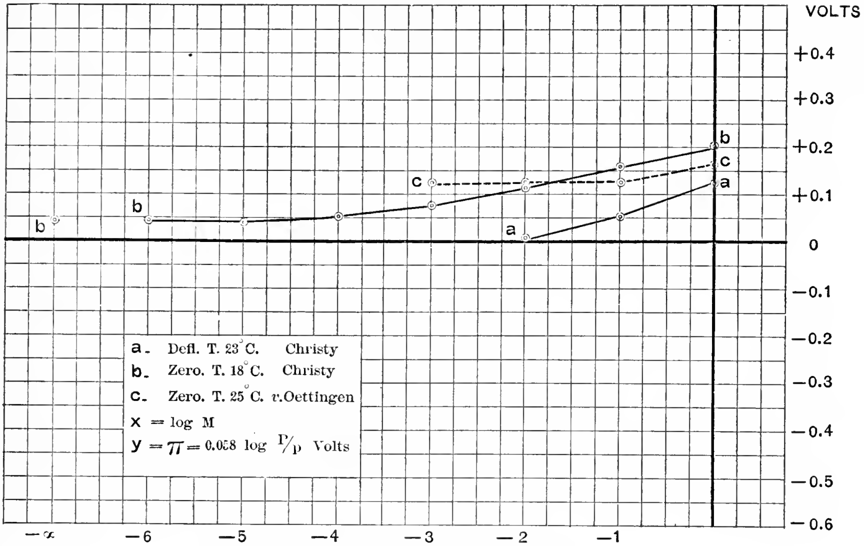
E.M.F. OF SILVER IN KCy.

On the horizontal (x) axis are laid off the values of log. M = log. 10_n; on the vertical (y) axis, the actual volts.

TABLE VIII.—*Electromotive Force of Lead in KCy.*

Curve.	(*a*).	(*b*).	(*c*).
Note-book B1, page	68	183	Published.
Date	Oct. 20, '99	Sep. 2, '99	February, '99
Method	Deflect.	Zero.	Zero.
Resistance, ohms	100,000	......	......
Temperature	23° C.	18° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen.
EMF (N. E. = —0.56)	Volts.	Volts.	Volts.
Concentration KCy:			
$\frac{M}{1}$	+0.125	+0.200	+0.164 const.
$\frac{M}{10}$	+0.050	+0.158	+0.128 "
$\frac{M}{100}$	+0.006	+0.112	+0.120 "
$\frac{M}{1,000}$	......	+0.070	+0.120 "
$\frac{M}{10,000}$	......	+0.046	......
$\frac{M}{100,000}$	......	+0.040	......
$\frac{M}{1,000,000}$	......	+0.040	......
$\frac{M}{\infty}$ (= H_2O)	......	+0.040	......

Fig. 15.



E.M.F. OF LEAD IN KCy SOLUTION.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

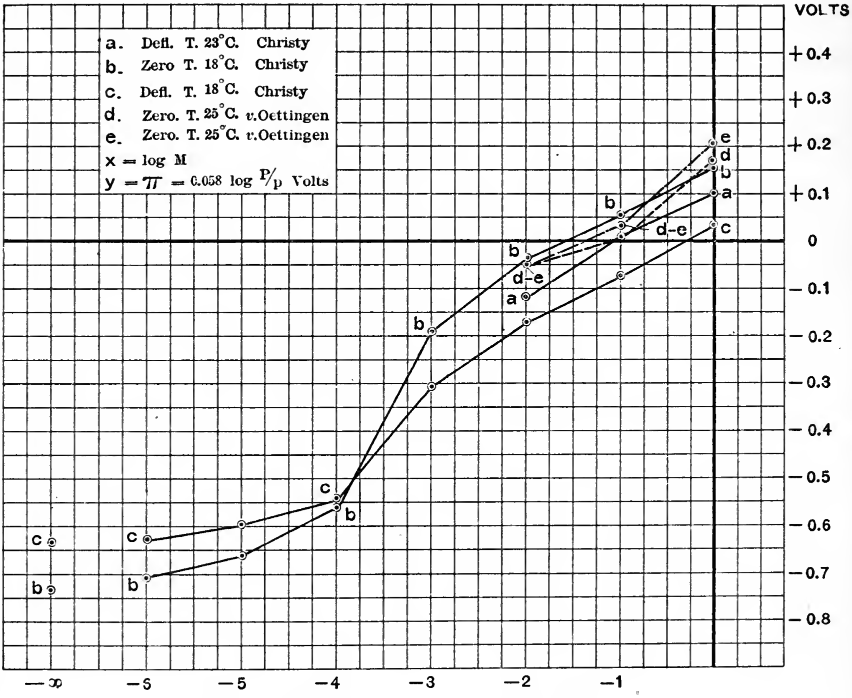
Table IX.—*Electromotive Force of Mercury in KCy.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).
Note-book B1, page...	67	184	184	Published.	Published.
Date........................	Oct. 19, '96	Sep. 2, '99	Sep. 2, '99	Feb., '99	Feb., '99
Method....................	Deflect.	Zero.	Deflect.	Zero.	Zero.
Resistance, ohms......	100,000	......	100,000	......	......
Temperature............	23° C.	18° C.	18° C.	25° C.	25° C.
Observer..................	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E.=−0.560) Concentration KCy:	Volts.	Volts.	Volts.	Volts.	Volts.
$\frac{M}{1}$..........................	+0.091	+0.154	+0.032	+0.162	+0.200
$\frac{M}{10}$..........................	+0.010	+0.047	−0.073	+0.008	+0.024
$\frac{M}{100}$..........................	+0.115	−0.043	−0.176	−0.056	......
$\frac{M}{1,000}$....................	......	−0.193	−0.309	......	......
$\frac{M}{10,000}$......	......	−0.560	−0.545	......	......
$\frac{M}{100,000}$..................	......	−0.664	−0.594	......	......
$\frac{M}{1,000,000}$...............	......	−0.705	−0.634	......	......
$\frac{M}{\infty}$ (= H_2O)............	......	−0.735	−0.640	......	......

The normal electrode, checked on $\frac{M}{1}$ KCl, showed −0.560, as it should do.

As a check on the foregoing results, I am able to quote the observations of an independent observer, Brandenberg.* He conducted a number of experiments with mercury in various depolarizing solutions. Instead, however, of using Ostwald's normal electrode, he used as one electrode mercury covered with sulphate of mercury (instead of the chloride used in Ostwald's). This electrode was then connected, by means of a siphon containing a neutral salt in solution, with a vessel containing mercury covered with the various solutions to be experimented on.

Fig. 16.



E.M.F. OF MERCURY IN KCy SOLUTION.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

The solutions he experimented on to find their ion destroying-power, or their power to form complex ions with mercury, were: potassium sulphide, potassium cyanide, potassium sulphocyanate, sodium hyposulphite, potassium ferrocyanide and potassium

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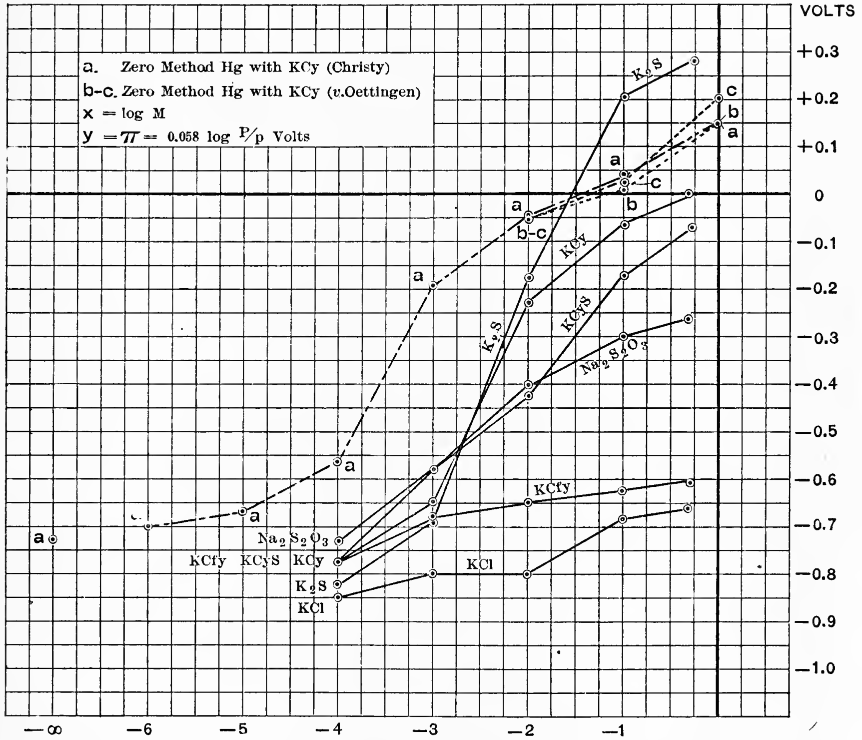
* *Zeitschrift für Physikalische Chemie*, xi., p. 570, etc.

chloride. As he did not use the same strengths that I have found most convenient, I have had to plot his results, reduce them to zero potential,* and interpolate the results for the strengths I have used. The results so obtained are compared

Fig. 17.



QUICKSILVER

Mercury Depolarizer/$HgSO_4$/Hg.

The Results of Brandenberg, (Z.f.Ph.Ch.xi.570. &c.)

Plotted, Interpolated, Replotted and Reduced to 0 Potential, by S.B.Christy.

To which are added, for comparison, curves with Normal Electrodes.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

with the results obtained by Professor Oettingen and myself with the normal electrode. The results obtained by us for potassium cyanide are higher than Brandenberg's, but show the curves to be of the same general nature. They are shown in Fig. 17.

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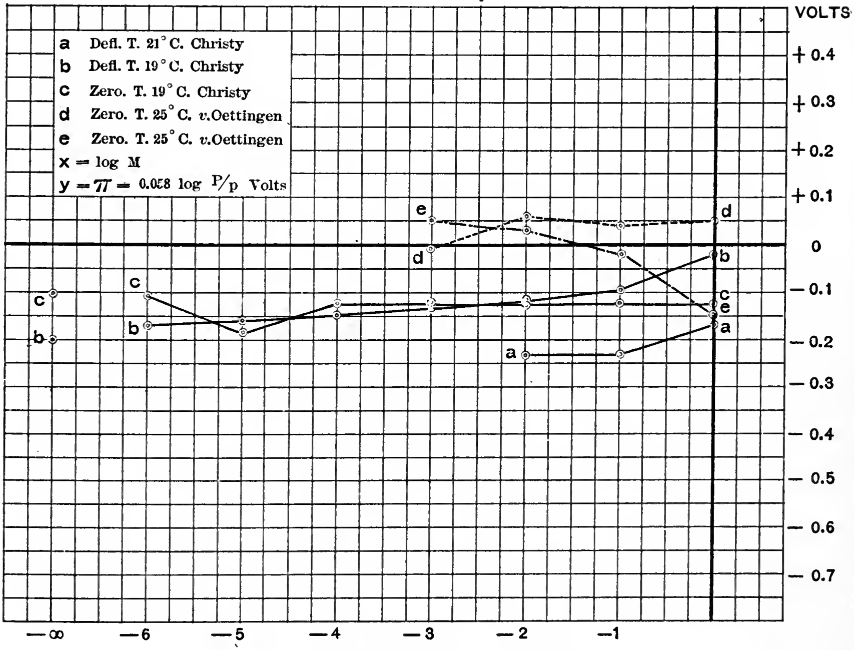
* On the supposition that $\frac{Hg}{HgSO_4}$ has a potential of — 0.93 instead of — 0.560 for $\frac{Hg}{Hg_2Cl_2}$.

TABLE X.—*Electromotive Force of Iron in KCy.*

Curve.	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).
Note-book B1, page...	68	182	180	Published.	Published.
Date.........................	Oct. 21, '93	Sep. 1, '99	Sep. 1, '99	Feb., '99	Feb., '99
Method....................	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms......	100,000	100,000	......	......	......
Temperature	21° C.	19° C.	19° C.	25° C.	25° C.
Observer..................	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF. (N. E. =−0.56)	Volts.	Volts.	Volts.	Volts.	Volts.
Concentration KCy :					
$\frac{M}{1}$..........................	−0.169	−0.028	−0.124	+0.56	−0.146
$\frac{M}{10}$..........................	−0.236	−0.082	−0.124	+0.34	−0.120
$\frac{M}{100}$..........................	−0.236	−0.116	−0.124	+0.054	+0.022
$\frac{M}{1,000}$......................	......	−0.131	−0.124	−0.008	+0.050
$\frac{M}{10,000}$....................	......	−0.146	−0.124	......	......
$\frac{M}{100,000}$..................	......	−0.160	−0.184	......	......
$\frac{M}{1,000,000}$................	......	−0.160	−0.104	......	......
$\frac{M}{\infty}$ (= H_2O).............	......	−0.206	−0.104	......	......

Fig. 18.



E.M.F. OF IRON IN KCy SOLUTION.

On the horizontal (x) axis are laid off the values of log. M = log. 10^n; on the vertical (y) axis, the actual volts.

In order to bring out more clearly the nature of the relations existing between EMF of the different metals, I have combined, from the plotted curves of each metal, what appear to be the most probable values for each metal. These results are contained in Table XI.

TABLE XI.—*Electromotive Force of Metals in Cyanide of Potassium Solution.*

CONCENTRATION.		COMBINATION OF MOST PROBABLE VALUES.						
$M = 10^n$	Log. 10^n	Zinc.	Copper.	Gold.	Silver.	Lead.	Mercury.	Iron.
$M = 10^0$	0	+0.945	+0.930	+0.420	+0.340	+0.200	+0.150	−0.030
$M = 10^{-1}$	−1	+0.870	+0.680	+0.265	+0.195	+0.160	+0.050	−0.090
$M = 10^{-2}$	−2	+0.775	+0.430	+0.090	+0.055	+0.110	+0.040	−0.120
$M = 10^{-3}$	−3	+0.415	−0.050	−0.340	−0.310	+0.070	−0.190	−0.130
$M = 10^{-4}$	−4	+0.385	−0.250	−0.450	−0.420	+0.050	−0.590	−0.140
$M = 10^{-5}$	−5	+0.355	−0.270	−0.565	−0.460	+0.040	−0.600	−0.150
$M = 10^{-6}$	−6	+0.330	−0.280	−0.620	−0.495	+0.040	−0.635	−0.160
Dist. water..	$-\infty$	+0.280	−0.320	−0.720	−0.570	+0.040	−0.640	−0.200

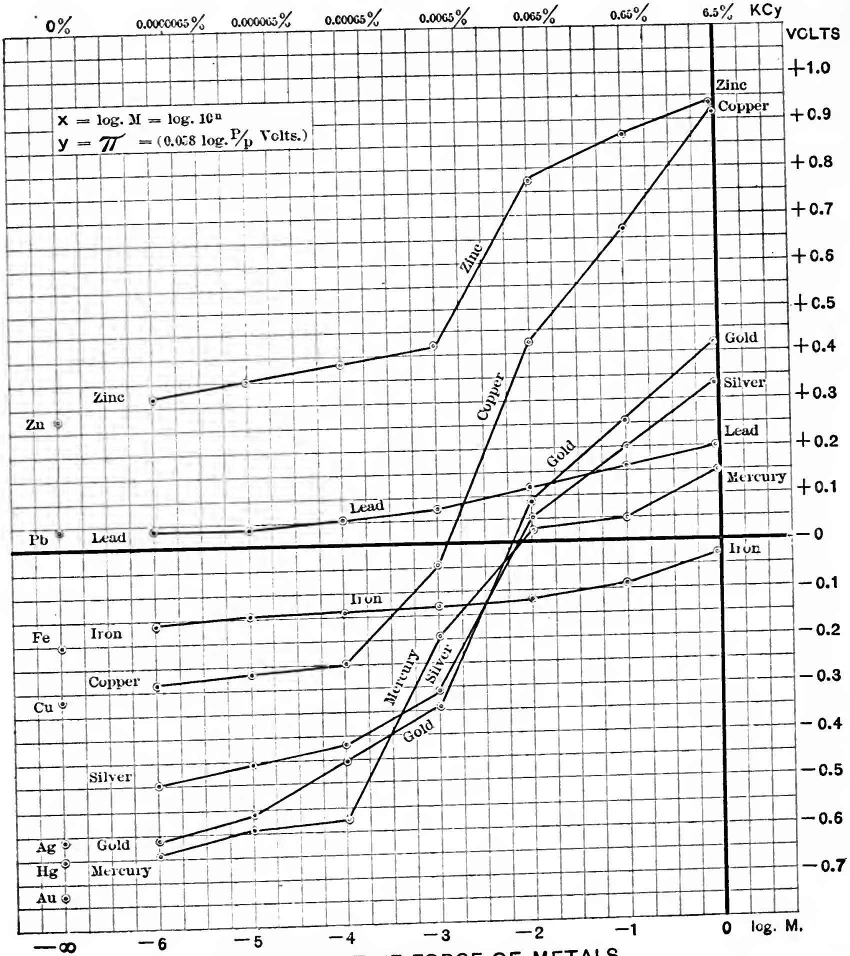
These results have been plotted in Fig. 19. These curves all show critical points at either log. M = — 2, — 3 or — 4. Most of them show the greatest amount of inflection at log. M = — 3. In fact, most of them seem to change in character at this point. According to the Nernst-Ostwald theory, this would be explained by the assumption that below say $\frac{M}{1000}$ KCy, the dissociation of the complex ion containing the metal in point is practically complete, so that the osmotic pressure p of the given metallic ions in the dilute solutions becomes practically constant below this point, so that as the ratio $\frac{P}{p}$ is nearly constant, so its logarithm, and hence the voltage, becomes also nearly constant, as is shown in the figure.

The curves for lead and iron are very remarkable; at first quite low, they maintain themselves at a higher level than either of the other metals except zinc. This is explainable on the supposition that the values of P for lead and iron are for these metals rather low, but that the values of p reach a nearly constant value sooner than for the other metals, so that the resulting curves flatten earlier.

These curves also show a number of remarkable crossings.

Copper, which starts at a voltage slightly less than that of zinc, rapidly falls off, crosses the curve of lead a little below log. M = — 2.5, and that of iron a little before log. M = — 3.5, and then remains permanently below these metals. The gold-

Fig. 19



ELECTROMOTIVE FORCE OF METALS
IN POTASSIUM CYANIDE.
Combination of Most Probable Values.

curve crosses the curves of mercury, silver and iron at just about log. M = — 2.5. Gold and silver both cross mercury again at about log. M = — 3.5. Gold finally crosses mercury again at a point beyond log. M = — 6, and remains permanently below it after that.

It will be observed that the metals change their sequence from that of zinc, copper, gold, silver, lead, mercury, iron, which they possess in a $\frac{M}{1}$, or 6.5 per cent. KCy solution, to the order zinc, lead, iron, copper, silver, mercury, gold, in distilled water, which is the usual electrochemical series in acid solutions quoted by Wilson except that iron is placed above lead. The determination of iron in my experiments was not entirely satisfactory, by reason, apparently, of the formation of films; and the results are probably too low. Water, also, appears to act like a weak alkali.

All the metals show a critical point somewhere between log. M = —3 and —4, at which dilution they seem to change from the voltage due to the cyanide solution to that which they ordinarily possess.

From a study of these curves there seems to be little support for the so-called " selective affinity " of dilute cyanide solutions for gold and silver, except in the case of copper down to log. M = —4, or 0.00065 per cent. KCy. In the case of zinc, lead, iron and mercury the strong solutions give a better relative voltage in favor of the gold than do the dilute cyanide solutions. But in the case of copper, there seems to be a distinct advantage in favor of the gold in dilute solutions down to 0.00065 per cent. Then the curves widen again. These facts will appear from the following table taken from the figure:

TABLE XII.—*Differences in Electromotive Force Between Gold and Copper in Potassium Cyanide Solutions.*

Log. M = Log. 10^n.	Value of 10^n.	KCy.	Difference Between Gold and Copper.
		Per cent.	Volts.
0	1 ÷ 1	6.5	0.51
-1	1 ÷ 10	0.65	0.42
-2	1 ÷ 100	0.065	0.32
-3	1 ÷ 1,000	0.0065	0.30
-4	1 ÷ 10,000	0.00065	0.20
-5	1 ÷ 100,000	0.000065	0.30
-6	1 ÷ 1,000,000	0.0000065	0.34
-∞	1 ÷ Infinity (H_2O)	0.	0.40

It should be remarked that if we had an independent method of determining the number of metallic ions in cyanide solutions, and were thus able to plot the EMF in terms of the actual ionic concentration instead of the molecular concentration, we should probably reach a more perfect agreement with the logarithmic law than in the curves here shown. Nevertheless, even as it is, a general agreement is certainly evident.

Relation Between the Strength of Cyanide Solutions and Their Dissolving Power.

It has already been shown by Maclaurin,* that the dissolving power of a cyanide solution saturated with oxygen increases with its strength until a strength of 5 or 10 per cent. is reached, and diminishes again as the strength in cyanide increases beyond that point. But, so far as I am aware, no one has proposed the question: "At what point of dilution does the cyanide solution cease to act on the gold?"

According to the Nernst theory, gold should cease to dissolve in cyanide solutions, *provided no force acts except its own solution-pressure*, at the point at which its electromotive force is zero, for then its solution-pressure will be just balanced by the osmotic pressure of the ions already in solution. At this point (provided no other force acts) the solution of the gold should cease.

It seemed interesting to ascertain if there were such a point. In order to do so, it was necessary to expose the gold to the cyanide solution, in the presence of air, under circumstances most favorable for rapid solution. Hence I devised a rotating apparatus, consisting of three pairs of rollers, driven by a small Pelton water-motor, on which a couple of 2½-liter bottles, such as are used for holding nitric acid, could be laid and rotated about their long axes. The number of revolutions of the middle axis being recorded, the distance traveled was known. This precaution was taken to be able to allow for the irregularities of the motor.

Standard strips of fine gold were prepared by repeated precipitation with sulphurous acid from a diluted chloride solution. These were rolled out thin and cut to a standard size of 2 in. by ¼ in. They weighed from 250 to 330 mg., according to their thickness. The strips were boiled in sulphuric and muriatic acids, washed, and ignited before use. The first set of experiments was undertaken with 2 liters of solution and ½ liter

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* *Journ. Chem. Soc.*, 63, p. 731.

of air, the bottles being stoppered. The weighed gold strips were then added; the bottles were rotated for 24 hours; and the strips were then washed and dried and weighed again. The number of rotations made in 24 hours ranged from 4000 to 24,000, and as the interior diameter of the bottles was 4½ in., the distance traveled in this time by the gold strip was from one to six miles. It was found impossible to get a uniform rotation-rate, owing to constant changes in the water supply. But so long as the solution was kept gently agitated these variations did not seem to have any appreciable effect on the result.*

Table XIII. shows the results of these experiments. The first pair were undertaken with distilled water, to see if there was any loss due to erosion. The apparent loss of 0.01 mg. was almost at the limit of accuracy of the balance, but seemed to show the possibility of a slight loss due to that cause. It will be observed that up to $\frac{M}{2000}$ or 0.00325 per cent. the gold-loss is merely nominal, never more than 0.29 mg., often zero; and the results vary in the most irregular manner. No. 18, with $\frac{M}{10,000}$ or 0.00065 per cent., gave a loss of zero, and No. 20, with $\frac{M}{4000}$ or 0.0016 per cent., only 0.08 mg. It is believed that these small losses below $\frac{M}{4000}$ were chiefly mechanical. It was noted that while most of the bottles used were perfectly smooth inside, some seemed to have small sharp grains of sand, or slivers of glass, projecting above the smooth inner surface. In many cases it was impossible to detect these without breaking the bottles. The loss in No 12, which was not rotated, cannot be set down to this cause. The explanation in this case, and perhaps in some others, may have been an imperfect mixing of the solution. The solutions were made up by adding the proper volume of strong solution to the proper amount of distilled water. In case the mixture of the solutions was not thoroughly made before the gold strip was added, the gold

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* In making these solubility-experiments, I was aided by my former assistant, now Assistant Professor, E. A. Hersam. I wish also to acknowledge the aid of my present assistant, Mr. Geo. E. Young, in the preparation of the standard solutions used in these experiments, and of the illustrations.

TABLE XIII.—*Solubility of Gold in Cyanide of Varying Strength.*

In twenty-four hours. Gold strips, standard size. Fine gold, 2 in. x ¼ in. Weight, 250 to 330 mg. 2½ liter bottles, 4½ in. diameter, making 4000 to 24,000 revolutions in twenty-four hours, and containing 2 liters cyanide solution and ½ liter air.

No.	Strength of Cyanide.	KCy. Per Cent.	Revolutions in 24 Hours.	Loss Gold in 24 Hrs., Milligrms.	Remarks.
1	$\frac{M}{\infty} = (H_2O)$		24,461	0.01	
2	$\frac{M}{\infty} = (H_2O)$		13,595	0.01	New strip.
3	$\frac{M}{100,000}$	0.000065	15,403	0.01	
4	$\frac{M}{100,000}$	0.000065	10,344	0.008	$\frac{24}{46}$ of 0.2 milligramme, the loss in 46 hours.
5	$\frac{M}{60,000}$	0.000109	23,750	0.00	
6	$\frac{M}{50,000}$	0.00013	14,430	0.00	
7	$\frac{M}{50,000}$	0.00013	11,315	0.06	
8	$\frac{M}{40,000}$	0.00016	7,920	0.02	
9	$\frac{M}{40,000}$	0.00016	8,490	0.11	
10	$\frac{M}{40,000}$	0.00016	10,180	0.19	
11	$\frac{M}{30,000}$	0.000216	14,850	0.02	
12	$\frac{M}{30,000}$	0.000216	Not rotated.	0.11	
13	$\frac{M}{30,000}$	0.000216	8,030	0.29	
14	$\frac{M}{20,000}$	0.000325	6,490	0.20	
15	$\frac{M}{20,000}$	0.000325	17,746	0.01	$\frac{24}{45}$ of loss in 45 hours.
16	$\frac{M}{20,000}$	0.000325	17,746	0.025	Same as above.
17	$\frac{M}{10,000}$	0.00065	9,780	0.08	Treated 24 hours.
18	$\frac{M}{10,000}$	0.00065	9,780	0.00	Duplicate of No. 17.
Total loss Nos. 3 to 18 inclusive				1.133	Average loss, 0.07 mg.
19	$\frac{M}{4000}$	0.0016	14,423	0.26	Mean loss, 0.17 mg.
20	$\frac{M}{4000}$	0.0016	14,423	0.08	
21	$\frac{M}{2000}$	0.00325	14,423	9.68	
22	$\frac{M}{1000}$	0.0065	4,260	24.86	Mean of two, 23.03 mg.
23	$\frac{M}{1000}$	0.0065	4,260	21.21	
24	$\frac{M}{500}$	0.013	5,790	81.74	Mean of two, 84.60 mg.
25	$\frac{M}{500}$	0.013	5,790	87.48	
26	$\frac{M}{100}$	0.065	5,270	143.64	Mean of two, 146.91 mg.
27	$\frac{M}{100}$	0.065	5,270	150.18	

would at first lie in a layer of stronger solution that might have a slight solvent effect until the dilution was effected by rotation. The fact that the mean loss up to $\frac{M}{10,000}$ is only 0.07 mg.; that even at $\frac{M}{10,000}$ (Exp't No. 18), no loss, and in No. 20 a loss of only 0.08 mg. was obtained, renders it extremely probable that the solution-loss up to $\frac{M}{10,000}$ or 0.00065 per cent. is absolutely nil. *Thus much is certain : these experiments demonstrate that for all practical purposes the cyanide of potassium solution ceases to act at a strength below* 0.001 *per cent.*

Going to higher strengths we find a sudden jump at $\frac{M}{2000}$; here the loss has risen to 9.68 mg., and beyond this it rapidly increases; the strips in the $\frac{M}{100}$ or 0.065 per cent. solution being eaten through in 24 hours.

The next set of experiments was devised to show the effect of a smaller volume of cyanide solution, and an unlimited supply of air. The same bottles as before were used, but they contained only 500 cc. of solution, and were left open to the air so that the latter was free to enter. The results, as shown in Table XIV., are in general the same as before. No appreciable loss occurs up to $\frac{M}{2000}$, but at that point, and for greater strengths, the loss rapidly increases, finally rising a little higher than before. In Experiments Nos 4 and 6 the entire solution was filtered and the washed filter was scorified and cupelled. In No. 4, where the gold-loss was 0.07, none was found. In No. 6 (the loss being 0.23 mg.), 0.02 mg. of abraded gold was found. Whether the rest was fine enough to pass the filter, or was dissolved before the strong solution was diluted, is a conjecture.

The next experiments were made without agitation and in the following manner: The gold strips were suspended in perforated glass tubes just below the surface of the solution, so that although the solution was at rest, circulation by convection was possible. The volume of the solution was 250 cc. The time of action was in each case 48 hours. The losses are

TABLE XIV.—*Solubility of Gold in Potassium Cyanide of Varying Strength in Twenty-four Hours.*

Standard fine gold strips, 2 in. × ¼ in. Weight, 250 to 330 mg. 2½-liter bottles, 4½ in. diameter, making 4000 to 24,000 revolutions in twenty-four hours. Half a liter cyanide solution, 2 liters air. Freely open to air.

No.	Strength of Cyanide.	KCy. Per Cent.	Revolutions in 24 Hours.	Gold Loss in 24 Hours, Milligrammes.
1	$\frac{M}{\infty}$ (= H_2O).........	....	5110	0.01
2	$\frac{M}{\infty}$ (= H_2O).........	....	5110	0.00
3	$\frac{M}{12,800}$................	0.0005	8440	0.43 (!)
4	$\frac{M}{12,800}$................	0.0005	6600	0.07*
5	$\frac{M}{6400}$..................	0.001	8440	0.19
6	$\frac{M}{6400}$..................	0.001	6600	0.23†
7	$\frac{M}{4000}$..................	0.0016	6790	0.16
8	$\frac{M}{3200}$..................	0.002	5450	0.44
9	$\frac{M}{2000}$..................	0.00325	6790	1.77
10	$\frac{M}{1600}$..................	0.004	5450	4.29
11	$\frac{M}{800}$....................	0.008	5540	48.43
12	$\frac{M}{400}$....................	0.016	5540	74.96
13	$\frac{M}{200}$....................	0.0325	28,230	150.54
14	$\frac{M}{100}$....................	0.065	28,230	168.12

given in Table XV.; they are somewhat smaller than before, and again negligible below $\frac{M}{1000}$. In this case $\frac{M}{2000}$ was not determined. The advantage of the position near the surface near the air is well shown in comparing Nos. 5 and 8. When the gold was suspended near the surface of a $\frac{M}{400}$ solution, the loss was 21. 44 mg. in 48 hours, or nearly half a milligramme

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* In order to see whether or not these losses might not be due in part, or wholly due to abrasion, the solution was filtered and the filter scorified and cupelled. No gold was found in the filter.

† This solution was also treated as above, and 0.02 mg. of abraded gold was found.

per hour; when the strip was put at the bottom of the same volume of a similar solution, the total loss in the same time was only 8.70 mg., or hardly one-third as much.

TABLE XV.—*Solubility of Gold in Potassium Cyanide of Varying Strength in Forty-eight Hours. At Rest.*

Standard fine gold strips, 2 in. × ¼ in. Weight, 250 to 330 mg. Suspended in open glass tubes, near surface, of 250 c.c. Cyanide solution at rest, but so that convection currents were possible.

No.	Strength of Cyanide.	KCy. Per Cent.	Gold Loss in 48 Hours, Milligrammes.
1	$\frac{M}{100,000}$	0.000065	0.00
2	$\frac{M}{10,000}$	0.00065	0.06
3	$\frac{M}{1000}$	0.0065	4.33
4	$\frac{M}{800}$	0.008	3.86
5	$\frac{M}{400}$	0.016	21.44*
6	$\frac{M}{200}$	0.0325	36.57
7	$\frac{M}{100}$	0.065	42.79

All these results have been plotted together with the voltage of the gold in curves *a*, *b*, *c* and *d*, in Fig. 20. According to the voltage-curve the voltage becomes zero for a cyanide solution of 0.00675 M, or about 0.044 per cent., and it is a curious fact that this is very near the limit of strength that practice has so far justified. Nevertheless, solutions as low as 0.01 per cent., and even less, have been employed in practice; and my experiments show that the solution acts perceptibly down as low as $\frac{M}{2000}$ or 0.00325 per cent., and perhaps to $\frac{M}{4000}$ or 0.0016 per cent. KCy.

An Apparent Contradiction.—Although it will be seen that the solubility-curves all follow very closely the voltage-curve, the fact that action does not cease for the zero of potential of gold

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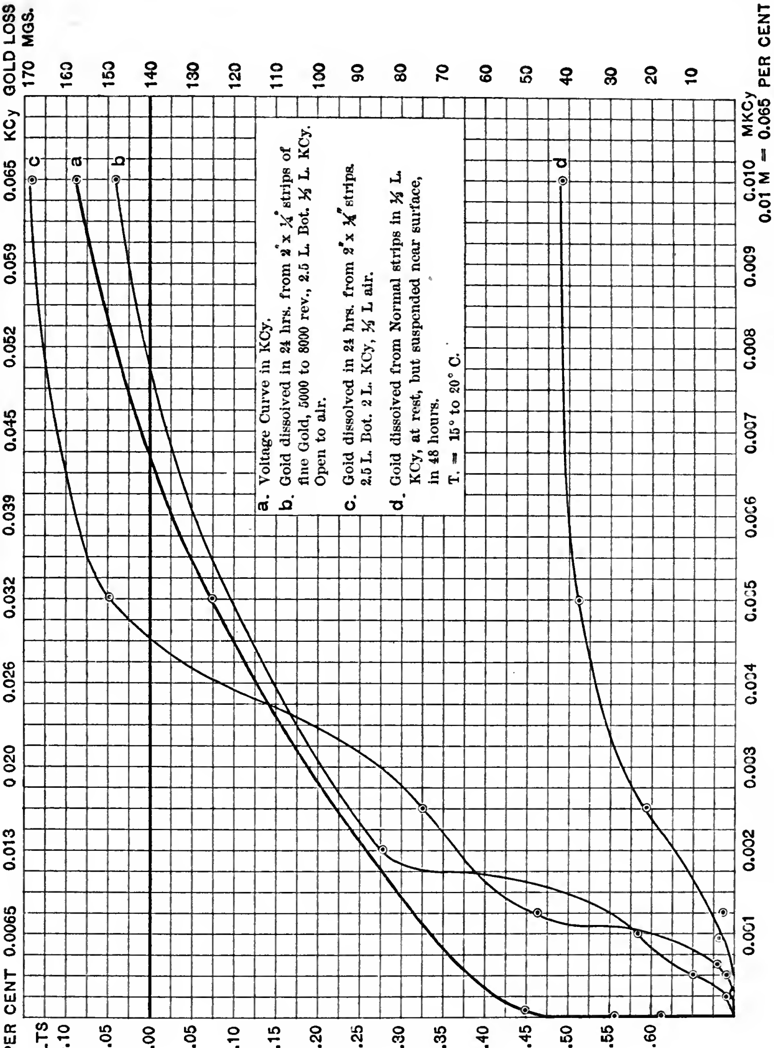
* 8. A similar experiment with same conditions as to strength and volume of solution as No. 5, only that the strip of gold rested at the bottom of the vessel, gave a gold loss of only 8.7 mg.

in KCy solution seems to contradict the Nernst law. But this contradiction is only apparent and not real. It is part of the new theory that (except the infinitesimal amounts necessary to produce the state of static tension) ions cannot come into existence or disappear except in pairs. That is, for every ion with a positive charge of electricity there must be one with an equal negative charge. Hence, when a positive ion appears, another positive ion must disappear, or else a negative one must also

Fig. 20.



VOLTAGE AND SOLUBILITY OF GOLD IN POTASSIUM CYANIDE.

Mining Laboratory, University of California, Jan. 1897.

The values of MKCy on the lower margin, and the corresponding percentages of KCy at the top, belong to each fourth vertical line (*i.e.*, to the 4th, 8th, 12th line, etc.) of subdivision. These lines should have been made heavier in the engraving.

appear simultaneously. (In the case of ions with varying valency, an ion having a double or treble valency is, of course, equivalent to two or three oppositely electrified univalent ions.)

For instance, in my experiments for determining the electromotive force of gold in potassium cyanide solution against the normal electrode, the couple is composed of

$$\frac{\text{Gold} : \text{KCy}}{\text{KCl, HgCl} : \text{Hg}}.$$

When the gold dissolves, the positive gold ions travel from the gold with their positive charge, and in order that the solution may continue, a similar flow of positive ions must continue by means of potassium ions through the solution to the mercury. The potassium ions finally drive out some of the mercury ions which precipitate into the mercury forming the electrode, at the same time giving up their charge of positive electricity to it. Simultaneously there is a corresponding flow of negative ions in the opposite direction. Thus: first chlorine and then cyanogen move in the opposite direction to meet the gold, and the latter forms with the cyanogen the complex negative ion $(\text{AuCy}_2)(-)$. Thus: $\text{Au}(+) + \text{Cy}(-) + \text{Cy}(-) = (\text{AuCy}_2)(-)$.

The action of this couple will go on *so long as the electromotive force of the combination is greater than zero*, and, as we have seen in my experiments, long after the electromotive force of the gold in the dilute cyanide solution has become zero. For the tendency of the mercury ions to discharge into the mercury electrode can only affect its purpose and cause a current by the simultaneous solution of the gold. That is, the tendency of the positively electrified ions of mercury to discharge themselves can cause the gold to dissolve long after its own electromotive force has ceased.

The Electromotive Force of the Oxygen of the Air the Sufficient Cause of the Solution of Gold in Cyanide Solutions.

We have another substance at hand with a great tendency to form negative ions. This is the oxygen of the air. In the presence of water, the molecule of oxygen, O_2, tends to assume the ionic state, combining with water to form four negatively electrified ions, thus: $O_2(\pm) + 2H_2O(\pm) = 4(OH)(-)$. Or, as has been suggested by Traube, when metals dissolve in the presence of oxygen, a molecule of the latter combines directly with two atoms of potentially nascent hydrogen thus: $O_2 + 2H = H_2O_2$. Later, the peroxide of hydrogen dissociates into two negative hydroxyl ions, which, entering the solution with their negative charges of electricity, tend to produce a current in the same direction as the positively electrified mercury ions do when they leave the solution. That is, oxygen can play the same part in causing the solution of the gold as the mercury ions did in the normal electrode above cited.

The controlling importance of an abundant supply of oxygen is well shown by the curves in Fig. 20. In curve *c*, although there is only one-fourth as much cyanide present as in curve *b*, the amount of gold dissolved is greater, except for the very dilute solutions. The evident reason is that the aeration is greater. The cyanide-supply being ample in both cases, the oxygen-supply determines the rate of solubility. For dilute solutions, the amount of dissolved oxygen being sufficient in *b*, the greater volume of cyanide is the determining factor, and the amount dissolved in *b* is in this case greater than in *c*.

Interesting confirmation of these views is found in Maclaurin's experiments on the solubility of gold in a solution of cyanide of potassium saturated with oxygen.* He conducted two sets of experiments with gold strips in solutions of different strengths. The first set was left at rest for three hours, the second set was agitated. The losses are given in the following table:

TABLE XVI.—*Maclaurin's Table of Losses of Gold in KCy Saturated with Oxygen.*

At Rest in Solution Saturated with Oxygen. Time, Three Hours.

KCy, per cent....................	1	5	10	20	30	40	50
Gold loss, mg.†...................	8.45	13.55	15.40	11.15	8.55	5.8	5.05

Agitated for Two Hours in Solution Saturated with Oxygen.

KCy, per cent....................	1	4.9	9.4	19.93	29.9	39	47.3
Gold loss, mg.‡...................	18.7	47.2	39.1	31.4	21.1	14.2	10.8

Maclaurin deems the results in the second table more reliable than those in the first. In both it will be seen that there is a

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* *Journal Chemical Society,* lxiii., p. 731.

† Curve A, Fig. 21.

‡ Curve B, Fig. 21.

rapid increase of the dissolving power up to about 5 or 10 per cent. KCy; then it gradually falls off till at 50 per cent. the solubility of the gold is less than at 1 per cent.

The importance of the remarkable relation thus discovered by Maclaurin has, I think, never before been appreciated. Is it not a little remarkable that the strong cyanide solution should dissolve less gold than a weak one, while the electromotive force of the gold goes on steadily increasing?

But in the light of the new theory the reason is not far to seek, for at no time does the electromotive force of the gold rise high enough to displace without external aid any other positive ions, such as those of the potassium in the cyanide or the hydrogen in the water; and unless this be done, the gold ions cannot continue to form, nor the gold to dissolve. For this reason (as Maclaurin, myself and others have shown), in the absence of oxygen or some equivalent agency, gold does not dissolve in cyanide solutions. In other words, unless some negative ion like (OH) (—), (Cl) (—), or (Br) (—) is added, or some other positive ion as (K) (+) etc. is removed by some external source of energy, the action cannot go on. Ordinarily the oxygen of the air furnishes this energy; as we have seen above, it dissolves in the solution and furnishes the negative ions necessary to cause the solution of the gold.

Again, Maclaurin has found the key to the anomalous action of strong cyanide solutions. It is in the fact which he demonstrated, that oxygen is less soluble in strong than in weak cyanide solutions. The following results for the solubility-coefficient of oxygen in KCy are plotted from his curves by interpolation.

TABLE XVII.—*Solubility of Oxygen in Solutions of KCy at* 18° *C.* (*Maclaurin*).

Strength KCy, per cent...	1	5	10	20	30	40	50
Solubility, per cent........	0.0295	0.0235	0.019	0.014	0.0103		
Solubility, per cent.*.....	0.0290	0.022	0.018	0.013	0.008	0.005	0.003

I have replotted the results of the above experiments of Maclaurin so as to make them more comparable with my own results. I have replotted both the gold losses of Maclaurin and the second of his oxygen solubility coefficients in Fig. 21; and

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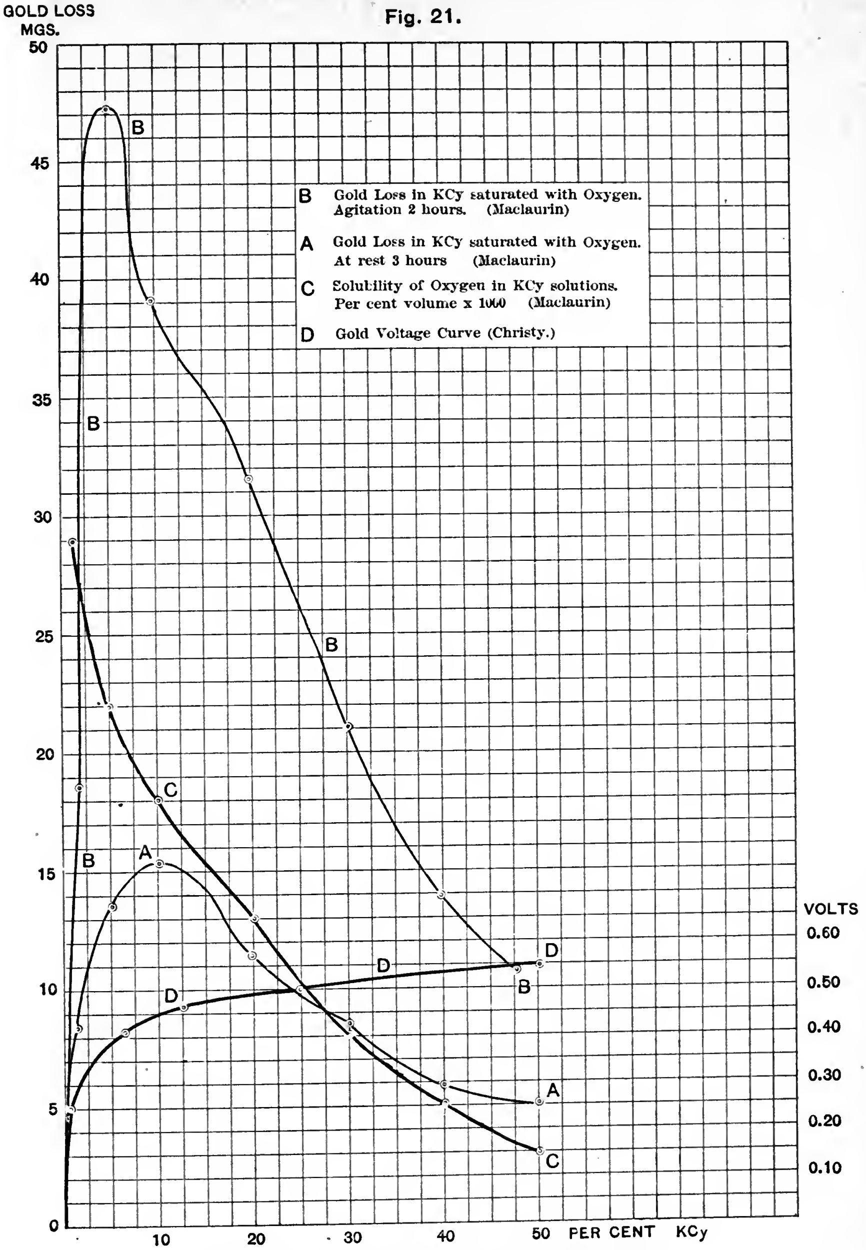
* Curve C, Fig. 21.

Fig. 21.



SOLUBILITY OF GOLD AND OXYGEN IN KCy,

From experiments of Maclaurin. (J. Chem. Soc. 1893, pg. 724.)
Replotted, and Gold Voltage - Curve Added.

I have also added the voltage-curve for gold from my own experiments.

It is plain now, for the first time, why there should be a maximum solubility somewhere between 5 and 10 per cent. There are two causes at work tending to dissolve the gold. First, the electromotive force of the gold itself, which alone is insufficient for the purpose; and second, that of the hydroxyl ions. If we suppose the latter proportional to the solubility of the oxygen, we see that the two forces operating to cause the solution of the gold tend to increase in inverse relation. Further, that the electromotive force of the gold rises very rapidly till it gets to between 5 and 10 per cent. and then rises very slowly after that, so that it has little effect on the solubility beyond that point. The solubility of the oxygen (and, as we have assumed, of the hydroxyl ions) is a maximum for pure water, and sinks as the gold-voltage rises. It is at between 5 and 10 per cent. that these two factors give their maximum effect. Beyond that point, the solubility-curves of the solution for oxygen and for gold run along nearly parallel.

Neither of these two factors alone is able to account for the maximum point in the solubility-curve. If the presence of oxygen were the only cause, the maximum solubility would be with dilute solutions. If it were alone due to the electromotive force of the gold, it would be greatest in strong solutions. As both act together, the maximum effect lies between these extremes.

As far as I am aware, this inverse relation between the electromotive force of gold, and that of oxygen in cyanide solutions of· varying strength as a controlling factor in determining the solubility of gold in such solutions has never been brought out before. In a certain sense it is a turning-point in this discussion, and hence merits a little close attention.

The ionizing tendency of oxygen has been measured by a cell containing a platinum electrode made absorbent for oxygen by coating it with platinum sponge.* When this is immersed in oxygen at atmospheric pressure, and the end of the wire is immersed in $\frac{M}{1}$ sulphuric acid, and the latter is connected with the normal electrode, the mercury dissolves, and a positive current flows through the solution from the mercury to the platinum with a potential of + 0.75 volt.

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* Le Blanc, *Electro-chemistry*, p. 221.

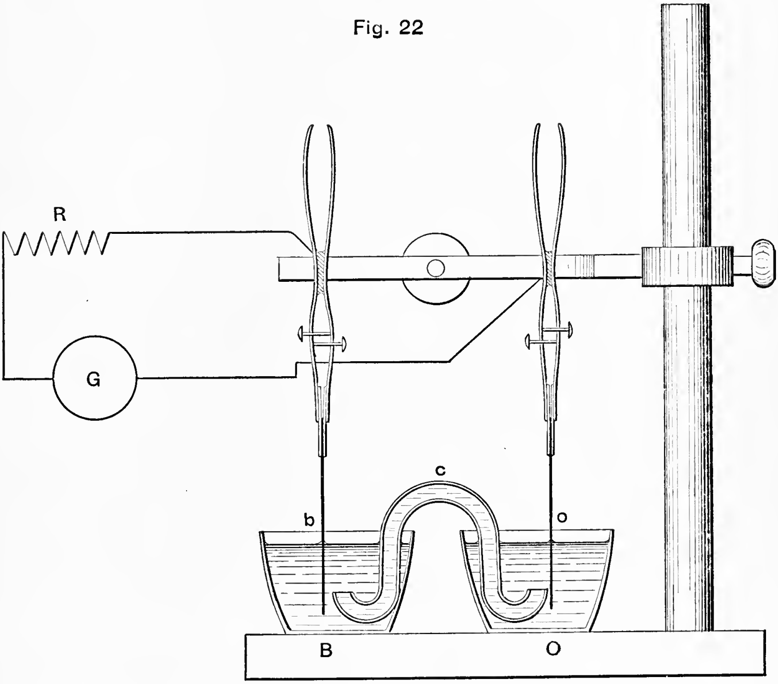
This current moves in the opposite direction to that due to the electromotive force of the mercury, viz.: —0.560 volt; consequently the electromotive force of the oxygen at atmospheric pressure in contact with platinum sponge in $\frac{M}{1}$ sulphuric acid is equal to the sum of these, or 1.31 volts. It is negative, or —1.31 volts, since negative ions are produced, and the solution is negatively electrified by them.

If the above determination is correct, it follows that if, instead of the normal electrode in the above combination, we place a vessel containing a gold electrode and a solution of cyanide of potassium so weak that the potential of the gold is not merely zero, but as low as that of the mercury, viz.: —0.560, it is plain that a similar voltage of + 0.75 should exist; but in this case the gold would dissolve instead of the mercury, and the positive current would flow through the solution from the gold to the platinum as before. In this case it would be, of course, necessary to interpose an $\frac{M}{1}$ solution of K_2SO_4, KCl, or some other neutral salt, between H_2SO_4 and the KCy, to prevent their direct action with each other from interfering with the mere transfer of electromotive forces at the end of the line which we wish to effect.

Now gold does not absorb and ionize oxygen as readily as platinum does, but it acts similarly, though to a much less extent. In order to test the correctness of these views, I took two small porcelain cups, B and O, Fig. 22, in which were immersed the two electrodes *b* and *o*. These were gold strips held in platinum-tipped forceps, connected in series with a reflecting galvanometer G of 3000 ohms resistance, including that of the cell, and a resistance R of 30,000 ohms. The solution in either vessel is connected electrically by the liquid in the siphon C.

It is very difficult to prepare, and impossible to keep, a cyanide solution entirely free from oxygen, unless it is hermetically sealed. But the following method was selected as giving an approximation to it. A liter of distilled water was boiled under a filter-pump, and when most of the dissolved oxygen had been removed, cyanide of potassium was added, and the boiling was continued a few minutes, to drive out the air absorbed during the solution of the cyanide. A cork was provided with two tubes like those of an ordinary wash-bottle; and after inserting the long tube below the surface, a layer of paraffine oil was floated on to the surface to exclude the air. The tip of the discharge-tube was kept closed by a cork when not in use. It was easy, by blowing in through the short tube above the surface of the oil, to discharge any required amount of the solution as required, but of course each time this was done a small amount of air entered the solution. After cooling, the liquid was titrated and found to contain 0.62 per cent. KCy. A similar 0.621 per cent. KCy solution was prepared and nearly saturated with oxygen. Through the galvanometer G and the resistance R, a Latimer-Clark cell gave a deflection of 7 scale-divisions. In vessel B were placed 12 c.c. of boiled 0.62 per cent. KCy solution and in O an equal volume of 0.621 per cent. KCy solution containing oxygen. On immersing the gold strips, the strip in B became negative, that is, the positive

Fig. 22



APPARATUS FOR SHOWING THE
LOCAL ELECTROLYTIC ACTION
INVOLVED IN THE
SOLUTION OF GOLD IN
AERATED CYANIDE SOLUTION

current flowed from B through the solution to O, with an EMF = +0.02 volt. When the liquid in both B and O was covered with paraffine oil to exclude the air, the EMF rose to +0.108 volt. On gently shaking electrode *o*, the EMF rose to +0.185 volt; on gently shaking B it fell to +0.08 volt (owing to absorbed oxygen). On cutting out the 30,000 ohms resistance, leaving that of the galvanometer (3000 ohms), the deflection rose to 6.5 scale-divisions, coming back again on inserting the resistance R to 0.6 scale-divisions or +0.12 volt. This gradually fell to 0.2 scale-division or +0.04 volt, where it remained for two hours. At the end of that time the resistance was cut out and the deflection rose to 2.5 scale-divisions; then, on shaking, to 12 divisions; and then sank again to 2.7, where it remained fairly steady for two hours longer. At the end of this time, four hours in all, the electrodes were removed and cleaned with gasoline and ether from the oil and solution; and it was found that the electrodes had lost weight as follows:

b lost 1.28 mg. *o* lost 1.73 mg.

The solutions contained in the vessels B and O and in the siphon C were also assayed with the following results:

B contained 1.25 mg., O contained 1.68 mg., and C contained 0.06 mg. of gold.

The total loss of the electrodes was 3.01 mg., and that found was 2.99 mg. The difference of 0.02 mg. was probably lost in the washings of the electrodes, which were not saved.

This experiment, corroborated by many others, shows clearly that the positive current flows from the deoxygenated to the oxygenated cyanide, just as theory would indicate. The fact that more gold has dissolved in the oxygenated than in the deoxygenated cyanide does not militate against the indication of the galvanometer.

The solution of the gold in the vessel O is evidently due to the well-known phenomenon of "local action." The current that flows through the siphon has to overcome a resistance of from 3000 to 33,000 ohms, while local action can go on in the vessel O wherever an OH (—) ion comes in contact with gold and KCy. Here it forms a "short circuit," and it completes itself on the gold strip *o* at any point free from oxygen, without having to pass through the entire external circuit.

It might be objected that the fact that 1.73 mg. of gold had dissolved in O as against 1.28 in B only went to prove that some oxygen had been contained in B, though less than in O, and that the solution in each had been simply in proportion to the oxygen present. But this does not account for the absolute verdict of the galvanometer, which shows that the positive current flows during the entire experiment from strip *b* through the solution to the strip *o*. The only explanation that remains is the one which I have suggested. There is no doubt that considerable local action went on in cell O. That this was the case is also evidenced by the fact that the action was more uniformly distributed over the surface of *b*, while the strip *o* was not uniformly acted on, but was eaten into in a remarkable manner. These strips, and particularly some of those to be described later (with peroxide of hydrogen), were not corroded most upon the edges where one would naturally expect it, but along vertical lines running up and down the middle of the strip. In some cases they were eaten through along these lines in such a manner that nothing remained but a thin film like gold lace. It appeared that local action started in along these lines rather than at the edges, owing to differences of potential due to the distribution of the oxygen, and that when it had once set in, it was able to maintain itself.

It is probable that in all cases of the solution of gold in aerated cyanide solutions the process, as in the above case, is one of local electrolytic action, though, as it is impossible in such a case to apply the galvanometer, it would be difficult to prove this proposition except by inference.

In all such experiments it is important to be certain that the gold strips are in the same physical state, since the existence of microscopic films or unweighable traces of occluded gas cause an appreciable difference of potential in apparently similar gold strips. This is best tested by comparing the strips in the same solution. They react similarly if they are carefully cleaned with boiling acid, and are then washed with distilled water and ignited to redness side by side in the muffle or over a Bunsen flame in a small porcelain dish. But if they are heated in different parts of the same Bunsen flame, they frequently show quite appreciable differences of potential due to occluded gases.

The Effect of Hydrogen Peroxide.

The peroxide of hydrogen used was Marchand's medicinal, containing 3.3 per cent. of available peroxide, as determined by titration with permanganate of potassium. According to the new theory, the H_2O_2 (±) takes up from the gold strip *o*, which becomes positive, two units of negative electricity and dissociates into 2 (OH) (—).

In the first experiment a $\frac{M}{1}$ KCy solution containing the usual amount of absorbed oxygen was used, and 10 c.c. of this solution was placed both in B and in O. Gold strips *b* and *o* were then placed in B and O, and the siphon was inserted. Both strips showed themselves of the same potential. The siphon was removed and 5 c.c. of water was added to B and 5 c.c. of hydrogen peroxide to O. On inserting the siphon and the electrodes, *b* proved to be electronegative, that is, the solution in B was electropositive by + 0.66 volt; in other words, the positive current flowed through the solution from *b* to *o*.

Another experiment was made with boiled water with 0.62 per cent. KCy that had been kept under $\frac{1}{8}$ in. of oil for a week. B and O were each filled with 10 c.c. of this solution, and the gold strips and siphon were inserted. The strips proved to be of the same potential. The siphon was then removed, and to B was added 2 c.c. of distilled water, and to O two c.c. of peroxide of hydrogen. After mixing, on replacing the siphon, the voltage rose to + 0.57 volt. That is, the positive current flowed through the solution from *b* to *o*. To exclude the air, a layer of paraffine oil about $\frac{1}{8}$-in. thick was floated over each solution before inserting the siphon.

The resistance of 30,000 ohms was then cut out, leaving only that of the galvanometer (3000 ohms), and the needle which had previously shown a deflection of 2.6 scale-divisions was thrown out of sight. (The limits of the scale used were 21.0 scale-divisions.) After being thus short-circuited for an hour and a half, on throwing in again the 30,000 ohms resistance, the voltage of the combination showed itself to be still in the same direction, + 0.63 volt. The 30,000 ohms were again cut out and the combination was again short-circuited overnight. In the morning some bubbles of gas from the action of the peroxide had collected in the upper part of the siphon, and had nearly cut off the current. But on removing and refilling the siphon the voltage still showed itself to be in the same direction, + 0.55 volt. The resistance of 30,000 ohms was again cut out and that of the galvanometer only left in, and after 5½ hours more the electrodes were taken out and cleaned and weighed. Total time, 23 hours.

The strip contained in B had lost 13.25 mg., while that in O had lost only 9.20 mg. *Evidently, in spite of the local action that had taken place in the vessel* O, *more gold had dissolved in the vessel* B *in the absence of the oxidizing agent, than in* O *where the oxidizing agent was present.*

In order to determine how much of the loss in B might be due to dissolved oxygen which had leaked through, or by, the oil-cover into the cyanide solution since it had been made, a week previously, 10 c.c. of the same solution as that used in B was placed in a similar vessel, and a gold strip was immersed in it half-way, and the liquid was then covered with the paraffine oil just as had been done in B and O. After 19¼ hours it had lost 4.28 mg. A similar strip entirely submerged below solution and oil lost, in 24 hours, 2.64 mg. These experiments prove that some air had leaked through, or by, the oil cover. It had been previously proved that if a thicker layer were used, it was possible practically to prevent altogether the ingress of oxygen and the solution of the gold. In this case it was inconvenient to use a layer thicker than ⅛-in. But the experiment also clearly shows that the amount of gold thus dissolved by absorbed oxygen is so much less than that shown by the *b* strip, that the solution must have been caused by the electromotive forces of the combination in the manner I have explained.

The same experiment was repeated exactly as before, except that to 10 c.c. of 0.62 per cent. KCy in B was added 1 c.c. of water and to 10 c.c. in O was added 1 c.c. of peroxide of hydrogen. At first the voltage was + 0.652 volt, rapidly falling to + 0.63 volt. After cutting out all but 3000 ohms resistance for 21 hours, the voltage, on adding the 30,000 ohms, proved to be still + 0.63 volt. After again cutting out the 30,000 ohms for 27 hours, it still showed, on inserting it again, + 0.434, rising after resting a few minutes to + 0.456 volt. At this point, after a total of 47 hours, the electrodes were cleaned and weighed, and *b* was found to have lost 24.06 mg. and *o* to have lost only 13.25 mg. *Here, again, the positive current has moved through the solution from* b *to* o, *and more gold has dissolved in the vessel containing no oxidizer, than in the one containing the oxidizer.*

In some other experiments with peroxide of hydrogen, there was more local action in O, and the *o* strip lost as much, and in some cases even twice as much, as the *b* strip. The exact conditions governing this local action are still under investigation. *But in these cases, also, the galvanometer showed that the positive current was still flowing through the solution from the strip* b *to the strip* o *in contact with the cyanide containing the oxidizer, and thence back through the gold strip* o *back again to* b, *the place of beginning.*

The course of the negative current may be traced from the gold strip *o* immersed in the oxygenated cyanide to the strip *b* immersed in the unoxygenated cyanide in two ways, as follows:

1. According to Ostwald* the reaction $O_2 + H_2 = 4OH$ produces 4 × 21,100 calories. Assuming this to be true, the oxygen molecule O_2 forms with the water four negative hydroxyl ions, 4 (OH) (—); these, assuming a negative charge from the electrode *o*, cause that end of the gold electrode to be positively electrified. Now these negative ions travel through the solution, displacing at the other end of the line four negatively electrified cyanogen ions, 4 (Cy) (—), which give up their negative charge at the other gold electrode *b*, and thus enable four positive gold ions, 4 Au (+), to go into solution there, forming with eight cyanogen ions four complex negative ions, 4 $(AuCy_2)$ (—).

The water present may be regarded as not dissociated appreciably, and the dilute solution of cyanide of potassium as entirely so. Making these assumptions, the principal reactions may be expressed as follows:

$$O_2(\pm) + 2H_2O(\pm) + 4Au(\pm) + 8K(+) + 8(Cy)(-) = 8K(+) + 4OH(-) + 4(AuCy_2)(-).$$

But this is equivalent to the so-called Ellsner reaction:

$$O_2 + 2H_2O + 4Au + 8KCy = 4KAuCy_2 + 4KOH,$$

which Maclaurin† has proved to be quantitatively correct.

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* *Chemische Energie*, p. 956.

† *Jour. Chem. Soc.*, vol. lxiii., p. 728.

2. The other view, following Traube, has been urged by Bodlaender, of the Clausthal *Bergakademie*.* He shows first, in agreement with Maclaurin and myself, that the reaction

$$H_2O + 2Au + 4KCy = 2KAuCy_2 + 2KHO + H_2,$$

proposed by Macarthur to explain the solution of cyanide of gold in cyanide solutions, is incorrect. Next, he claims that the so-called Ellsner reaction really proceeds in two stages:

(*a*) The hydrogen, which is not formed according to Macarthur's reaction, is, in the presence of cyanide of potassium, water, gold and oxygen, potentially nascent; and a molecule of oxygen combines directly with two atoms of nascent hydrogen, forming hydrogen-peroxide, while two atoms of gold dissolve; —thus:

$$O_2 + 2H_2O + 2Au + 4KCy = 2KAuCy_2 + 2KHO + H_2O_2.$$

(*b*) Next, the hydrogen peroxide gradually dissociates into hydroxyl, and causes the solution of two more atoms of gold thus:

$$H_2O_2 + 2Au + 4KCy = 2KAuCy_2 + 2KHO.$$

The sum of these two reactions is, of course, the same as that of the Ellsner reaction, which correctly expresses the end-result.

When gold was rapidly dissolved in an aerated cyanide solution, Bodlaender was able to detect as much as 72.3 per cent. of the hydrogen-peroxide required by reaction (*a*); and, as reaction (*b*) had probably already set in, this renders his explanation extremely probable.

Expressed in terms of the ions, reactions (*a*) and (*b*) become:

$$(a)\ O_2(\pm) + 2H_2O(\pm) + 2Au(\pm) + 4K(+) + 4Cy(-) = 4K(+) + 2AuCy_2(-) + 2OH(-) + H_2O_2(\pm).$$

$$(b)\ H_2O_2(\pm) + 2Au(\pm) + 4K(+) + 4Cy(-) = 4K(+) + 2AuCy_2(-) + 2OH(-).$$

The flow of ions through the solution is the same as in the

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* *Zeitschr. f. angewandte Chemie*, 1896, p. 583.

first case. On the whole, the second seems the more probable explanation, though either agrees with most of the facts.*

According to either of these views the new theory agrees quantitatively with the results of experiment, but offers for the first time a consistent explanation of its occurrence. *It is due to the superior electromotive force of the oxygen (or, in case they are present, to some other electronegative ions, as $(OH)\,(-)$, $Cl\,(-)$ $Br\,(-)$, etc.), together with the capacity of the gold for forming complex ions with cyanogen.*

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* While this paper was in press, a paper on "Freiwillige Oxydation" (Auto-oxidation), by Dr. Manchot, of Goettingen, has appeared, in which he has examined the oxidation of a large number of phenol-derivatives, such as those used as developers in photography. One of these derivatives, oxanthranol, was particularly well adapted to give quantitative results, and he was able to prove that for every molecule of oxygen absorbed a molecule of hydrogen in the oxanthranol was oxidized, and a molecule of hydrogen-peroxide was formed.

Representing the organic radical by R, and the oxanthranol by RH_2, he assumes that the reaction takes place as follows:

$$RH_2 + O_2 = R + H_2O_2.$$

The organic radical, if unstable, is frequently still further oxidized in a second reaction by the hydrogen-peroxide thus formed.

It would appear that similar reactions ensue in the rusting of metals in damp air. The rusting of iron, zinc, etc., is worthy of thorough study in the light of these new ideas.

It would seem that the modern electrochemical views necessitate a return, in part at least, to the ideas of Berzelius and Schoenbein. They supposed that the same element was at times positively, and at other times negatively, electrified. This appears to be a consequence of the new view also. For if we regard the oxygen molecule $O_2(\pm)$ as electrically neutral, this can only be the case when one of its atoms has a double positive and the other an equal negative charge. By the attraction of these charges the molecule may be regarded as being held together. Its real composition then would be $O(--) + O(++)$. On the other hand, two atoms of oxygen in the elemental state would be similarly electrified with negative electricity, thus: $O(--)$, $O(--)$, and would consequently repel each other. Hence, to change an oxygen molecule into two oxygen atoms would require *four* units of negative electricity.

On the other hand, the hydrogen molecule would be composed as follows: $H(+) + H(-)$; and to change it into two hydrogen atoms $H(+)$ and $H(+)$ would require *two* units of positive electricity.

It would also seem necessary to assume that there is an inherent tendency in the oxygen molecule (due, perhaps, to some peculiarity of shape or volume) to assume negative, and in the hydrogen molecule to assume positive, electricity in dissociating.

It would also appear as if a different result ought to be produced when neutral hydrogen molecules combine with a neutral oxygen molecule, from that which results from the combination of positively electrified hydrogen atoms with a neutral oxygen molecule. This may be the key to the formation of water in the one case and hydrogen-peroxide in the other.

If instead of having the two ends of the gold strip immersed in two separate cyanide solutions, the strip is immersed in the same solution containing some dissolved oxygen, the same electrolytic action can still go on as a case of "local action;" for the couple

$$\frac{\text{Au} : \text{KCy}}{(\text{OH}) : \text{Au}}$$

is still possible if we regard the gold to be short-circuited on itself, and the explanation given above still applies.

When I began this investigation in 1896, I marked out for myself a much wider range of investigation than here outlined, and the course of its partial execution has suggested many other interesting questions, some of which are still under investigation; but the constant and pressing interruptions of routine-work have made it impossible to carry the work further at the present time.

IV.—Conclusions.

Whatever may be the nature of the objections that may be raised against the final acceptance of the modern electrolytic theory in its present form, it will, I think, be conceded that the following conclusions may be fairly drawn from the foregoing:

1. That the new electrolytic theory explains in a remarkably complete manner the reason for the departure of metals immersed in cyanide solutions from the sequence of electromotive force which they present in acid solutions.
2. That it is the only theory ever presented that gives any clue to the remarkable aberration of cyanide solutions from all the usual chemical analogies.
3. That it explains in an entirely adequate manner the reason for the reactions that go on when gold, silver and other metals are dissolved and precipitated from cyanide solutions.
4. That the determination of the electromotive force of the metals in cyanide solutions under different conditions offers a means of research that is likely to be of great practical utility in determining the direction and intensity of chemical reactions, under fixed conditions, or in following them under changing conditions, just as they occur.
5. That the differences of electromotive force of metals in dilute cyanide solutions do not give much support to the so-called

"selective affinity of dilute cyanide solutions for gold," the only common metal that shows any indication of such favorable action being copper.

6. It is probable that, in the absence of external electromotive forces, an aerated cyanide solution less than $\frac{M}{10,000}$ or 0.00065 per cent. is without action on metallic gold.

7. That for all practical purposes, an aerated cyanide solution of less than 0.001 per cent. is without action on metallic gold.

This study has led apparently far afield from the practical side of the cyanide process; yet I hope that it may be of service in at least calling attention to the work of others who have toiled for many years in attempting to clear up some of the most subtle questions that have ever taxed the human mind. For I am firmly convinced that, in the long run, such work is always of the greatest practical service. In these days, the words of Ostwald have certainly come true:

"The science of to-day is the practice of to-morrow."