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

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.	9. Lead.
2. Zinc.	10. Quicksilver.
3. Copper.	11. Palladium.
4. Cadmium.	12. Bismuth.
5. Tin.	13. Iron.
6. Silver.	14. Platinum.
7. Nickel.	15. Cast Iron.
8. Antimony.	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 in-

creases 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 semipervious 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 evapora-