# TRIUMPHS AND PROMISES OF ELECTRO - CHEMISTRY.

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Fred Willis Haselwood.

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#### OUTLINE.

1. Introduction.

2. Historical facts.

a. Volta's pile.

b. Faraday.

3. Electrolysis.

a. Laws of Electrolysis.

b. Theory of Electrolysis.

4. Practical Phases of Electro Chemistry.

a. Electro plating. - - Deposition of metals.

b. Preparation of alkalies.

6. Preparation of aluminum.

Hall Process - - Advantages.

5. Electric Furnace, - - Moissan.

Applications of heat of arc.

References. Solution and Electrolysis. Whetham.

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The glowing light of science, that has for ages past been sending out its radient gleams into the darkest corners of the unknown realms, revealing to the eager and inquisitive mind of man the simple truths that lie awaiting only these illuminating rays to dispell the enslaving bonds of superstition, ignorance and other shades darker than the darkest night that holds them captive, has through all the long lapse of time since when its first faint glimmer came as a stimulus to the mind's eye, been increasing in brilliancy and lustre until the gloom that so long hung over the broad field of natural science is largely dispelled. At first a mere glow-worm barely showing itself next increasing to a candle-power giving a faint delusive light to minds unaccustomed to the rays, it has constantly increased until like the marvelous X ray of today, its gleams shoot out as from a magnificent search-light penetrating the most dense shade that hovers about the unknown with that ever imperative message, "Truth in the name of science". It is truth that man is searching for and as a means of revealing truth, science ever stands as a true hand-maid. Whether looking through a microscope at the infinitely small organisms that inhabit every minute particle of matter to be found, or gazing through a telescope at the stars - - the inhabitants of that infinite region called space - - it is all the same, truth is the end sought. No man can be a true scientist unless the desire for truth is the leading motive. A man is not a philanthropist who does a kind deed because he knows that the consequences will rebound heaping honor upon his own head. The alchemists who wore out their miserable lives in dingy laboratories living on little save their own delusive aircastles of the fabulous wealth they might produce when at last the mystic process was discovered by which otherosubstances might be converted into gold, were not scientists. Yet whatever we may think of them now, it was with these people that the germ of that great branch of natural science - - chemistry - - first felt the influence of those conditions under which it might begin to grow, and now the extent of the dependence of all other sciences upon chemistry is beyond calculation. The ripple that started with the alchemists has extended its circle far out over the unknown waters crossing with others as it spread. The blind and undirected hope that guided the alchemist has been superceded by a systematic and logical method of investigation when different motives rule.

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How far man had ascended or descended along the scale of evolution before the truth-laden rays, of science's light first roused his slumbering sensibilities, matters little in the practical comsideration of this subject, but a few suggestions here may tend to show what we may rightly consider as grounds for claiming great promises for the future of that recently developed branch of science known as electro-chemistry.

The first condition we notice in the growth of any science, is the crude development from a few facts perhaps of a more crude hypothesis and with this as a working basis the structure is soon outlined for a theory. This is in short the process, but there is something that lies at the bottom of this that requires great qualifications. The whole process of the development of any science may be included under the two following heads: (1), The discovery of facts and (2), the discovery of relations. The whole is a simple building up from the discovery of facts thru the process of combining them by some existing relations into a hypothesis from which by accretion of other facts the theory and then the general truth grow forth. The problem of science of today is what it ever has been, the discovery of new relations between the concepts we already have. The science of chemistry, delving as it does into the very infinite construction of matter and dealing with relations so delicate and so intricate, is a mere bundle of related concepts as is its sister science, physics. In recent years relations have been discovered between concepts in the realm of chemistry with those of physics which unite the two sciences more closely than ever before. Electric connections combine two branches of these sciences into a new one called electro-chemistry.

Electro-chemistry is a young branch of science, little more than a century old and yet time has shown that as in all other things there is an endless field for investigation and that far beyond the ever widening circle where the light dimly shines are fields where the grass sparkles with brighter dew-drops of truth than have ever yet been discovered. Side by side with physics has chemistry grown with many of the intricate relations between the two unknown until the blinding flash of lighten ng that leaps from cloud to cloud and darts to earth, controlled by man and named electricity, united the two sciences by living bond. A few of all the facts of the science have been gathered together and are accordingly written herein.

#### HISTORICAL FACTS.

Whatever may have been done in electro-chemical study and investigation the first real and conclusive work of any importance was the discovery of <u>Volta's pile</u> in 1800. This pile, which is in reality nothing more than a primative battery consists of a pile of plates of zinc and copper separated from each other by a piece of blotting paper moistened with brine or water. These plates were connected in series and furnished quite an appreciable electro motive force. Shortly after the discovery of this pile, Nicholson and Carlisle dis-

brass terminals of a battery were immersed in water, hydrogen was given off at one while the other was oxidized. If gold or platinum were used as terminals the gases given off were found to be liberated in the proportion of one volume of oxygen to two volumes of hydrogen and since that is the proportion of the respective gases in water the electro decomposition of water was thus explained and proven.

In the first part of the nineteenth century, Sir Humphrey Davy, did much work in electro chemical investigation. Among others whose investigations and researches have aided in establishing many important facts of the science in its early days are Hisinger, Berzelius and Cruickshank, but there is perhaps there is no name that stands out more prominently as the first in rank among the early investigators of this subject, than that of Faraday, whose laws of electrolysis are held as fundamental laws of the science of electro chemistry.

Faraday was a most thorough investigator, a man who prodeeded with greatest care and most accurately followed every minute detail of the operations. He gives complete descriptions of his work which was always progressive. He forms theories yet when any further investigation shows them to be in any degree erroneous, he does not hesitate to discard or re-model them. Besides being progressive, Faraday's work was entirely constructed. He introduced into the science a new and more appreciative nomenclature in the terms, electrode, kathode, anode, electrolyte, etc. Among the important things he showed was the difference in effects produced by a battery and a frictionalemachine was dependent upon the great difference of potential and small quanity of electricity supplied by the machine, and the much larger supply of electricity with less difference of potential supplied by the battery.

### ELECTROLYSIS.

It was early discovered that liquids were capable of conducting electricity, but the manner in which they did it was not definitely known. The many mysterious effects of the action of electricity upon the liquid that conducts it have by much work, patience, and study, been traced to a few fundamental laws that govern all such reactions. Much work along this line was done by Faraday who discovered the two most importanthand fundimental laws of the science of electrolysis. When electricity is passed through a liquid or a solution, it may be transferred in one of two ways; 1. The liquid may act as a solid dielectric and thus induces a charge at the other pole - - - - turpentine, pretroleum, etc., act in this way; 2. it may be transferred p by atomic convection between the poles - - acids, alkalies and salts act in this way. The second method has been called electrolysis. It was observed that when electricity is transferred by means of atomic convection the different atoms or atomic groups collected at the poles, the acid -forming being eletro negative appear at the positive pole the base-forming elements being electro positive appear at the negative pole.

Before speaking in detail of the process of electro-decomposition of solutions it will be advisable first to consider the terminology and general nature of the apparatus and material employed. The terms that are now employed are those supplied by Faraday. The process of transferring the electricity through the solution is called <u>electrolysis</u>. The solution through which the current passes is called electrolyte. The <u>electrodes</u> furnish an entrance and an exit for the current which enters at the <u>anode</u> or positive electrode and goes out at the kathode or negative electrode. The electricity is transferred

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by atoms or small atomic groups called ions. When a current is passed through an electrolyte it is observed that some of the ions collect at the anode and some at the kathode. Those gathering at the anode are <u>anions</u> or the ions of acid forming elements; those gathering at the kathode are <u>kathions</u> or the ions of base-forming elements. The electrode may be of any conducting material but in order to prevent decomposition of the electrodes themselves, platinum is most commonly used. Carbon is used in many or most cases where the current is used for metalurgical purposes.

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### LAWS OF ELECTROLYSIS.

The two following laws which lie at the basis of electrolytic processes were established by Faraday in 1833.

1. The amount of chemical change that takes place in any electrolytic circuit is directly proportion to the quality of electrification transferred through the circuit.

2. For the same quanity of electrification transferred through any circuit, the amounts of the different electrolytes decomposed in that circuit - - and therefore the amounts of the ions - - are proportional to the chemical equivalents of those ions.

From the first law we see simply the relation between the amount of the electrolyte decomposed and the strength of the current. For example a current of three amperes for three seconds would produce the same effect as a current of nine amperes for one second. The amount of the electrolyte decomposed by unit current in unit time is called the <u>electro-chemical equivalent</u> of that substance. By this: we see, that in order to obtain the quantity of any electrolyte decomposed, it is necessary on to multiply together the time, the current strength, and the electro-chemical equivalent. It is evident that the truth of this law is necessary for

the maintenance of the theory of convection-transference. The charge carried by each ionic atom of any electrolyte is considered as constant, hence the amount of electricity must be proportional to the number of atomic groups concerned in the transference or in other words to the number of ions liberated.

The second and perhaps the more important law from a chemical point of view asserts that for different electrolytes, the amount of each decomposed by the same quantity of electrification will be proportional to their respective chemical equivalents. The chemical equivalent of an ion is defined as the smallest quantity of a compound that enters into combination with er replaces one atom of hydrogen; i.e. the quantity of an ion which is chemically equivalent to an atom of hydrogen. Thus in any univalent element, the chemical equivalent would correspond to the atomic weight, or taking any element into consideration, the chemical equivalent corresponds to the atomic weight divided by the valence. This law also bears a close relation to the theory of convection-transference. Considering that each atom conveys the same charge and that the relative masses of the ionic atoms are proportion to the chemical equivalents, then it follows that when equal quantities of electrification are passed through different electrolytes they require for tranportation equivalent quantities of these ions.

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#### THEORY OF ELECTROLYSIS.

In regard to an explanation of the phenomena taking place in the process of electrolysis there is in reality no explanation that goes further than a theory. In dealing with the peculiar activities of molecules, atoms, and ionic groups which are themselves theoretical units, much use must, indeed, be made of the theory. And theories

here as in all cases are useful merely as they serve as a tool by means of which we may gather the facts and build up the structure of our knowledge of any branch of science. Perhaps the present theories of electrolysis are wrong but so long as the tool has a keen edge, it will be used and when it becomes dull and inefficient at last it may be laid aside with the inscription "Well done thou good and faithful servant." The theory that is now generally accepted as the most reasonable explanation is the theory of dissociation. Ostwald and others who have done much In solving the mysteries of solution are supporters of this theory. When any salt is dissolved in water there is a diffusion or separating of the molecules and the former solid is lost to view, swallowed up as it were by the liquid. When two dry salts are mixed together no reaction takes place. In order for any interchange of ions or double- decomposition to take place, the salts must first be in solution. In the solution, not only are the molecules separated and diffused throughout the liquid allowing freer molecular activity, but there is a dissociation of the atoms or ions in the . molecular which allows more immediate contact offering greater opportunity for an interchange of ions between the two compounds. There is in thensolution a separating of the ions or a weakening of the power of chemical affinity, the extent of which depends upon the concentration of the solution. The forces that hold the ions together in the molecule are considered as electrical in their nature, i. e. one ion is charged negatively and the other positively, and when the substance is dissolved in a liquid of such high specific inductive capacity as water, this electrical power holding them together is much weakened. It has been stated above that when a current is passed through a solution there is a separation of the ions which collects at the poles. The electricity is transferred by these ions

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some of which carry the positive, some the negative. The action of the ion in the transference has been called the migration of ions. There are various theories of the transference by the ions. One holds that the individual ions pass from one pole to the other. Another and a more probable one holds that an ion set free at a pole reacts on the next molecule, etc., until the ion of the opposite sign is freed at the other pole.

## PRACTICAL PHASES OF ELECTRO CHEMISTRY.

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There is always a great pleasure to be derived from the study of any science even if studied only in a theoretical way, or rather studied with the intention of merely following the development of theories and facts. But beyond the excellent opportunity for a study in theories, electro chemistry has a practical side which is fast increasing in importance. The value of electro chemical decomposition goes far beyond the simple breaking down of compounds and the power is of vast importance not only in the production but in the comtinuance of electrical phenomena. It has been a most interesting means of determining the nature of many chemical compounds, has been used in compounding substances, and has given some new compounds. The fundamental facts of electro chemical decompositions are, (1), Separation of a decomposible substance into its proximate principles is which (2), gather at the poles, (3). The elements set free go to different poles according to certain laws.

Among the most practical applications of the current is the process of electro-plating. The object to be plated is used as the negative electrode and placed in the solution of a salt of the metal of which the plating is to be made. The strength of the current may influence the physical state of the deposited metal, therefore the current density must be carefully adjusted to prevent a crystaline deposit, or too loose a deposit caused by depositing a metal too fast. By virtue of the fact the least oxidizable metals are deposited, first it is possible by proper adjustment of the current to separate the metals from a solution of the salts of various metals. The current is perhaps of as much importance as a factor in metallurgy as in any other office. Many metals that have not been separated by other means have yielded to the current. The process of the separation of aluminum has been so cheapened by the use of the electric current in its preparation that its use is fast becoming universal. Another important application of the process is in the preparation of alkalies

Alkalies and zinc are prepared at the same time. The electrolytic vessel is divided by two diaphragms into three compartments. The anode compartment comtains Na SO , the kathode an alkaline solu-2 4 tion of zinc. The center contains Na SO , a solution of alkaline electrodes or dilute lye. On passing the current through the zinc, is deposited in the kathode compartment and at the same time the alkali which is formed passes into the center. The acid set free at the anode is neutralized by stirring lime in the electrolyte. The solution in the center is drawn off regularily.

The first pure aluminum that was obtained was made by electrolysis. The Hall process of aluminum manufacture that is now in use, is the simplest and perhaps the cheapest that will ever be devised. By the Hall process, the alumina is electrolyzed in a fused mixture of the fluorides of aluminum, sodium or potassium or with a fused bath of the fluirides of any metal more electro-positive than aluminum. this process is used extensively by the Pittsburg Reduction Company.

lined, iron tanks whatch with reduced metal in the bottom form the

The mechanical arrangement consists of a series of carbon

negative-electrodes. A series of carbon cylinders three inches in diameter form the positive-electrodes. These are attached to copper conductors by copper rods three-eights of an inch in diameter. A current of 5000 amperes and 50 volts is turned on in one series, and 2000 amperes with 20 bolts into the other. The heat generated by the resistance offered by the fluorides causes them to melt. The mixture is melted in less than two hours after which the alumina is added. It is claimed by some that the oxide is decomposed and the aluminum sinks to the bottom while the oxygen goes to the opposite pole and unites with the carbon escaping as carbon dioxide. Others claim that the fluoride is decomposed and thethree fluorine breaks, up with the oxide forming aluminum and oxygen which goes off as explained above. Most metallurgists hold to the former view of the case. Among the reasons for this belief is the fact that fluorine will replace oxygen in alumina, therefore aluminum fluoride is a more stable compound and less easily decomposed. In order to retain the heat in the molten bath powdered by carbon is spread over the top of the molten mass. When a rising resistance is indicated by a volt meter attached to the top of the pot, more of the ore is stirred in. The metal is dipped out with cast iron ladles, the electrolytebeing skimmed back into the pot with iron rods.

## ADVANTAGES OOF THIS PROCESS.

1. Purity of the metal. After the first run which removes the reducible impurities of the electrolyte, the only other impurities must be in the alumina or in the ash of the positive carbon electrode.

2. Saving of Material. There is no loss of ore in the finely divided state. There is no slag and no waste product except

All the aluminum in the ore comes out in ingot metal. 3. Economy. The heat in the electrolyte being constantly maintained the only other necessities are the constant current, the ore, and fresh carbon electrodes occasionally, with sometimes a small addition electrolyte as some is taken out with the metal. There is little expense in furnishing the electrical energy for heat. This process may be carried on with the use of copper electrodes instead of carbons.

Whatever new process may be invented for the preparation of aluminum, it is generally believed that no more simple inexpensive ore will be found. The greatest item of expense is the ore and alumina is certainly the richest and cheapest of aluminum compounds from which the metal may be extracted. The alumina is obtained from beauxite.

#### ELECTRIC FURNACE.

Another and final item will complete the triumphs of electro chemistry enumerated and the wast fields that have been opened by recent discoveries are fraught with promises of future possibilities. Henri Moissan, who wished to obtain a greater heat than any existing means afforded, invented what has been called the electric furnace. In order to describe the furnace accurately his own words are used.

"This new furnace is formed of two bricks of quick-lime, carefully placed one above the other. The lower brick has a longitudinal groove which receives the two electrodesand in the middle is a small cavity which serves as a crucible. This cavity may be more or less deep, and contains a layer some centimeters in thickness of the substance on which the thermic energy of the arc is to act. Or we may also arrange a crucible of charcoal containing the substance to be

ignited. Or for the reduction of oxides and subsequent fusion of the metals, we use larger crucibles, and a cylindrical (aperature made in the upper brick allows of throwing from time to time of small packets formed of a compressed mixture of the oxide and carbon. The furnace therefore receives merely a single arc and the diameter of the carbons which serve as conductors will, of course, vary with the intensitybof the current. After each experiment, the ends of the carbons are entirely converted into graphite." By means of this furnace a much higher temperature may be obtained than is possible by any other known means, and many interesting as well as valuable phenomena were discovered. The first attempt with the furnace gave a temperature of 2250 degrees for 30 amperes and 55 voltes. Later with 450 amperes and 70 volts, a temperature of about 3000 degrees was reached. When the temperature reaches the 300 degrees mark; the material of the furnace melts and flows like water. Carbon redness, calcium oxide at the same temperature and calcium is set free which combines with the. electrode forming calcium carbide. Uranium oxide which cannot be reduced by the heat obtained by ordinary means, yields readily to the heat of the arc. Many substances that are entirely insusceptible to other temperatures are changed easily by the electro furnace.

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Moissan applied the heat of the electric arc to diamonds, which turned to graphite. The diamond at first seemed to sprout without melting and soon turned entirely to graphite, the stable form of carbon. When boron or silicon is placed between the electrodes, they will be found to combine with the carbon forming a boride or silicide. Many metals may be entirely vaporized by the heat of the arc.

Electro chemistry has a much wider application than has been indicated here but it has been impossible to treat the entire subject. The conversion of chemical energy into electricity is an important phase of the subject for consideration. The field is broad and is ever growing broader. The end is not nor ever will be in sight. Both theoretically and practically, electro chemistry has in the past hundred years taken an enviable stand among the branches of physical science.

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