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Faraday's Laws of Electrolysis

M. Aquinas

FARADAY'S LAWS OF ELECTROLYSIS

By

Sr. M. Aquinas S. M.

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PREFACE

Physics has no equal, perhaps, in bringing the student to an appreciation of the beauty, the order and the harmony of the universe, and thus drawing the heart and the mind to God whose unbounded powers executed the eternal and marvelous wonders that are all about us.

It is intensely fascinating to take peeps into the "laboratories of God" and wonder what will be the next secret that He will let man in on. It seems as the ages roll by He gradually allows us to share more and more in His secrets of nature; He appears to be slowly unraveling to man the mysteries of earth, sky and sea.

In this thesis, my farewell bow to Marquette, I wish to express my appreciation and gratitude for the "good things" received at Milwaukee's great university; my appreciation for the wisdom and truth of her philosophy, the conciseness and completeness of her science, the beauty and power of her art, the kindness and courtesy of the administration, and the scholarship and personality of her faculty.

I desire especially to thank Dr. Skinner, my major professor, for his kindly interest and his patient helpfulness. I also wish to acknowledge my indebtedness to Miss Dolores Mulrooney and Miss Eunice Schucht for valuable services in drawing and typing.

INTRODUCTION

Faraday was a prince among physical investigators and may well be called the father of electrical science. His intimate friend, Tyndall, compares his discoveries to a whole mountain range, with here and there a mighty peak. Two of these peaks are his two Laws of Electrolysis, now commonly known by his name.

These laws as originally given to the world in Faraday's own words are:

> "I. The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."
>
> "II. Compound bodies may be divided into two great classes, namely, those which are decomposable by electricity and those which are not. Of the latter some are conductors, others non-conductors of voltaic electricity. I propose to call bodies of the decomposable class, electrolytes. Then again the substances into which these divide under the influence of the electric current, form an exceedingly important general class. They are directly associated with the fundamental parts of the doctrine of chemical affinity and have each a definite proportion in which they are always envolved during the electrolytic action. I have proposed to call these bodies generally ions or particularly anions and cations according as they appear at the anode or cathode, and the numbers representing the proportions in which they are evolved, electro-chemical equivalents. Thus oxygen chlorine, iodine, hydrogen, lead, tin are ions; the three former are anions, hydrogen and the two metals are cations, and 8, 36, 125, 1, 104, 58, are their electro-chemical equivalents nearly."[1]

These laws are given very concisely in our college text books as:

> "I. The mass on any ion deposited from an electrolyte by an electric current is proportional to the quantity of electricity passed through the electrolyte."
>
> "II. If the same quantity of electricity is

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[1]Wm. Tilden: Scientific Chemistry p. 212.

> passed through a number of electrolytic cells, each containing a different electrolyte, the mass of each substance deposited is proportional to its chemical equivalent."
>
> "The chemical equivalent may be defined as the weight of an element which is necessary to combine with, or displace, one part by weight of hydrogen."
>
> "The electro chemical equivalent of any substance is the mass of that substance which is deposited by unit current in unit time."[1]

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[1]Spinney, Louis: A Text Book of Physics p. 273.

CHAPTER I

HISTORICAL DEVELOPMENT

The well known English writer, Father Faber, at this time wrote, "It would seem as if we were getting down into the primeval caves and laboratories of creation and might expect any moment to come upon God at work." Faraday, the most gifted of experimenters and the self-educated son of a poor London blacksmith, was one of those who took intense peeps into the "laboratories of God." He had a genius for seeing relations between the different phenomena of nature, a "divine spark" that he fed with great patience and unremitting toil.

After he had given to the world his discovery of the laws of electromagnetic induction and had made the first dynamo, there seems to have been some doubt in the minds of the scientists of that time, regarding the identity of the electricity excited by different means; it remained still to be proved that electricity, whether frictional, chemical, thermal or electro magnetic is identical in nature.

F. K. Richtmyer: Introduction to Modern Physics p. 67.

Faraday, to whom doubtful knowledge, as he called it, was most repugnant, undertook to prove by a series of beautiful and well chosen experiments, that the same effects could be produced whatever the method used to excite the power.

One of his proofs of identity of electricity from different sources was the decomposition of certain chemical compounds to their elements. By many ingenious experiments Faraday began to unravel the mystery of the relation between electricity and chemical attraction; that mysterious force that holds together the atoms of a compound into such an intimate and close union.

It had been known for some time that an electric current was able to dissolve this chemical union. Nicholson and Carlisle in 1800 had accidently discovered the decomposition of water by an electric current. They had used a drop of water in order to make contact in an electric circuit, and when the current passed, noticed the odor of hydrogen. Davy had made use of an electrical current in his researches that lead to the discovery of potassium and the alkali metals, also Davy's Electro-chemical theory of affinity and Berzelius' theory of atomic polarization brought electro-chemistry into the domain of theoretical chemistry, but very little was known of its laws or the mechanism of the action involved.

F. K. Richtmyer: Introduction to Modern Physics p. 63.

It was then erroneously believed that the wires, by which the current entered and left the decomposing substance, acted like positively and negatively charged conductors, tore the reluctant atoms from the molecules of the compound. Faraday saw that this hypothesis was scientifically unsound, for he had by careful experiments, broken up the strongest chemical compounds by the weakest of currents, and besides he had proved that provided a current passed, the decomposition took place as well with as without metal poles, and that the amount of substance decomposed was entirely independent of the size of these conductors, or their distance apart, factors most important if they were exerting force on the substance.

Faraday then asked himself what was the work of the current and upon what did it depend. Does the same current always produce the same decomposition? If so, could not the amount of decomposition be used as an easy and valuable means of measuring voltaic electricity? He answered all these questions, as was his wont, by a number of ingenious experiments.

For months he worked in his laboratory giving the subject his usual exhaustive treatment. He first took some cells, fitted them up with electrodes of various sizes, shapes and materials, filled them with slightly acidified water and connected them in series. He collected the gases at the different electrodes and found that the same quantities were liberated at all the anodes and the same at all the cathodes. Then he changed the strength of the acid in the batteries by adding different amounts of dilute water to the cells. The results were the same. He was convinced that the amount of chemical decomposition depends not on the size of the electrodes, not upon their distance apart, not upon the strength of the solution; but solely upon the quantity of electricity that passed through the cell. He saw that the "poles" were only the doors by which electricity enters into or passes out of the decomposing substance.

When he had given his discovery to the world, he wished to erase from the minds of the people the wrong conception regarding the "attraction" of the "poles." Faraday appreciated the tyranny of a name and with the advice of his friend, Dr. Whenwell, he decided to supplant the old names, tainted with wrong ideas, with a new nomenclature. The metal plates by which the current entered and left the liquid he called "electrodes", (amber and, a way) distinguishing between the two by calling the positive pole by which the current entered, the "anode" (upwards) and the negative by which the current left, the "cathode." The substances that were deposited on them he named "ions" or wanderers. Those that moved toward the anode he called "anions" (that which goes up, i.e. up stream with the positive current), while those that migrated toward the cathode he called "cations" (that which goes down.) The decomposing and conducting substance he called "electrolytes" (I loose) and the process itself "electrolysis." The names proved to be most apt and now form an important part of scientific vocabulary.

Crowthers, J. A.: Michael Faraday p. 40.

By this discovery Faraday was able to realize his hope of using the amount of chemical decomposition as a measure of the quantity of electricity flowing during a given period of time. His voltameter was similar to the cells used in the discovery of his law, except that the tubes for collecting the gases given off at the electrodes were graduated so that the amount liberated by the current could be read easily.

Faraday now set about testing the soundness of this method by using cells containing electrolytes other than acidified water. He first used tin chloride as an electrolyte, connecting the cells in the circuit with his new voltameter to see what relation there was between the different substances liberated when the same current was used. When a considerable amount of gas had been liberated in the voltameter, he broke the circuit, found the amount by reading the graduated scale and weighed the tin deposited on the cathode immersed in the tin chloride. By easy calculations he was able to ascertain the amount of water decomposed and also the weight of tin that would be liberated by the current needed to decompose the equivalent weight of water. Let us suppose, to make it easy, that the amount of hydrogen liberated was 1.008 gram. Then at the same time 8 grams of oxygen was given off, while 59.35 grams of tin was deposited from the stannous chloride, $SnCl_2$. Now 8 grams of oxygen is the exact weight of oxygen which is able to combine chemically with 1.008 gram of hydrogen. Similarly 59.35 grams of tin is the amount of tin that is capable of combining with 8 grams of oxygen to form stannous oxide, SnO. The three weights are then chemically equivalent.

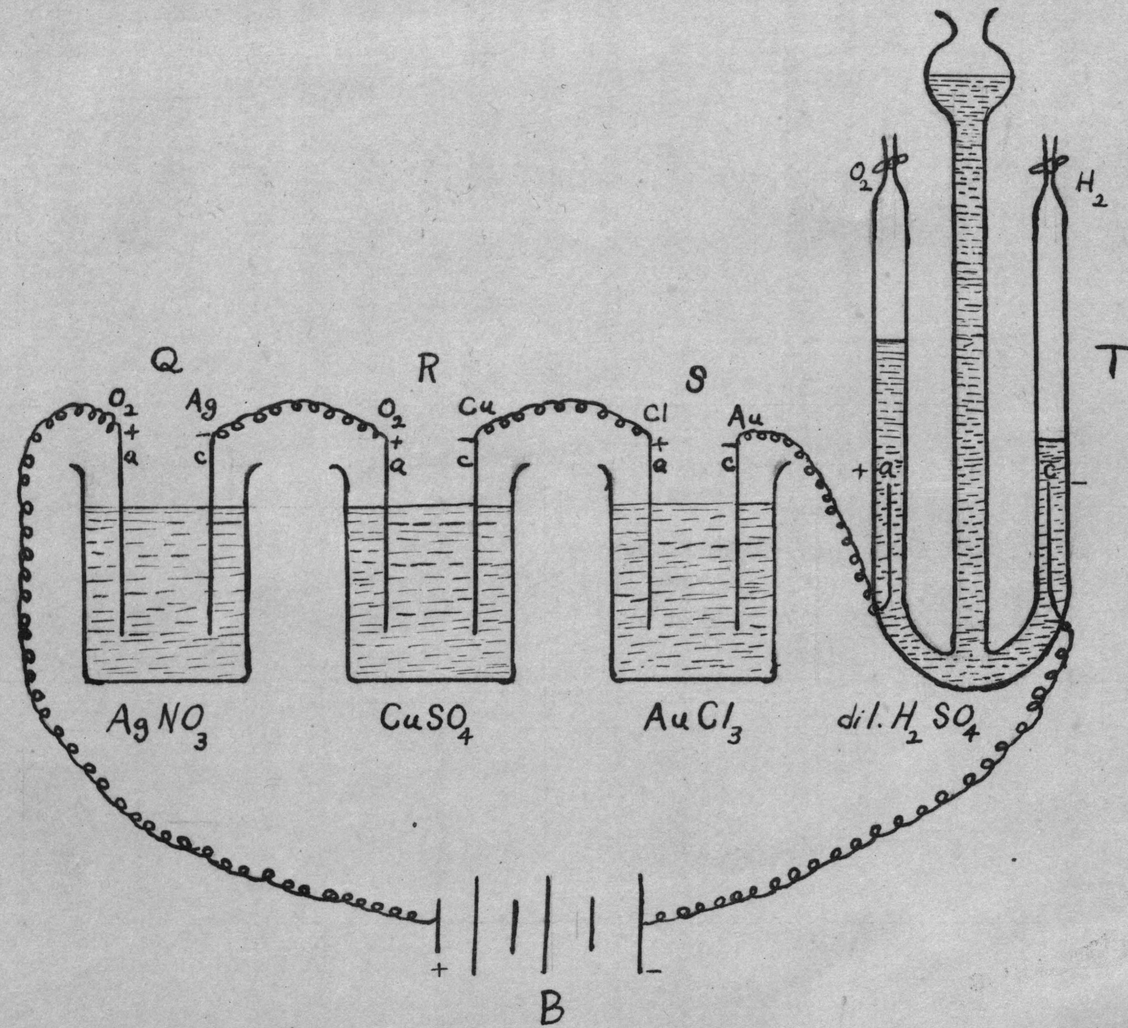
Faraday's mind was ready at once to reach to the generalization, but he held himself in check until he had subjected the matter to the most searching experiments. He would leave no uncertainty behind him and seemed to delight in inventing all kinds of strange combinations that included secondary action between the substances liberated and the electrodes, to test his theory. His discovery when given to the world would need no corrections or require any exceptions. When he was thoroughly convinced that there was the closest relationship amounting to identity, between electricity and chemical affinity, he proposed his second law;

"The amount of substances liberated at the electrodes when the same quantities of electricity passes through solutions of different electrolytes is proportional to their chemical equivalents."
Spenser James: Elementary Practical Chemistry p. 166.

In order to understand this second law better, let us suppose a number of electrolytes cells Q R S T as in figure I on the following page, having each two platinum electrodes, a and c, where a is the anode and c the cathode, connected in series with the battery B. The cells contain respectively solutions of silver nitrate, copper sulphate, gold chloride and dilute sulphuric acid. Then when a current is passed through the cells and the products of electrolysis carefully collected and accurately weighed, the quantities in every case will be proportional to the chemical equivalents, for the same current has passed through all the cells for the same length of time. If 1.008w is the weight of hydrogen liberated at the cathode in cell T, then 8w of oxygen will be liberated at the anode of that cell. 35.46w of chlorine will be liberated at the anode of S and 65.73w of gold will be deposited on the cathode of this cell. In the cell R 8w of oxygen will be liberated at the anode and 31.78w of copper will be found deposited on the cathode. And in the cell Q, 8w of oxygen will be liberated at the anode and 107.88w of silver will be deposited on the cathode. These quantities are proportional to the chemical equivalents of the elements liberated.

The two laws of Faraday may be combined by the formula:

PLATE I.



Dolores Mulrooney

$$Q = \frac{I\ e\ t}{96,500}$$

in which Q is the mass of the substance in grams deposited when a current of I amperes flows through the solution in t seconds if e is the chemical equivalent of the substance deposited.

Spenser James: Elementary Practical Chemistry p. 166.

This law holds true for the amount of secondary products formed at the electrodes. Thus when sodium sulphate is being electrolyzed, the amount of sodium deposited is given by the formula:

$$Q = \frac{It \times 23}{96,500}$$

where 23 is the chemical equivalent of sodium. Sodium, however, will not remain at the electrode but immediately react with the water.

$$Na \quad H_2O = NaOH \quad H.$$

From which it can be seen that 23 grams of sodium will combine with 16 grams of oxygen and 1.008 gram of hydrogen to give 40.008 grams of sodium hydroxide.

Spenser James: Elementary Practical Chemistry p. 167.

The charge of electricity carried by one gram equivalent of an ion; that is, for example by 107.88 grams of silver as ion or 35.46 gram ion of chlorine, is the electro chemical unit and has been named the "faraday" in honor of Michael Faraday.

Walker James: Introduction to Physical Chemistry p. 235.

Besides having discovered these two fundamental laws of electricity, Faraday had proved conclusively that the only difference between the effect produced by frictional and voltaic electricity was due to difference in quantity and intensity (potential). The frictional machine produces a very small quantity of electricity at a high intensity, while the battery produces a much greater quantity that has a much lower intensity.

Jones, H. S.: Elements of Physical Chemistry p. 486.

CHAPTER II

VERIFICATION

Faraday's laws at first met with great opposition from the scientists of his day due principally to the fact that they did not clearly understand them. Trouble arose because quantities of electricity were confounded with quantities of electrical energy. The law simply refers to the quantity of electricity and asserts the separation of chemical substances in quantities proportional to their chemical equivalents, in the passage of equal quantities of electricity, without referring at all to the quantity of energy necessary to accomplish this work.

Le Blanc, Max: Electro Chemistry p.41.

The laws, however, were soon subjected to the most searching experimental tests and were found to be among the most, if not the very most, exact of our scientific laws. Buff in 1853 tested the laws by the use of very large currents. Oswald and Nernst tested the laws for very small currents, and found that when .000008 coloumb is passed through a dilute solution of sulphuric acid, hydrogen is liberated at the cathode. They measured the amount and found the law of Faraday held for such an infinitesimal quantity of electricity.

Solutions of electrolytes were electrolyzed under high pressure and it was found that the amount of the electrolyte decomposed was less than it should be according to the law of Faraday. This however has since been satisfactorily explained. Under high pressure some gas dissolved in the water containing the electrolyte and then helped to conduct the current. More current therefore passed than corresponded to the amount of electrolyte decomposed.

Jones, H. S.: Elements of Physical Chemistry p. 340.

Nernst, Lorenz, Reynolds and Faraday himself, tested the laws for fused salts. The big difference between the salts and solutions is that in solutions there are mixtures of solute and practically non-conducting solvents involved while with fused salts only one substance is present or the components are conductors of the same class. In spite of this great difference, the ions deposited were found to be the same in both cases, showing that Faraday's laws hold good for fused salts. In the electrolysis of silver the accuracy was .005 per cent up to 260 C and .9 per cent up the 640 C, with lead the accuracy is about one per cent up to 1050 C.

Taylor, H. S.: Elementary Physical Chemistry p. 379.

A very drastic test of the laws as applied to the different conducting substances was performed by Richards, in which silver was deposited from a fused salt at 260 C and by the same current from a salt solution at 20 C. Four experiments showed an agreement in the deposits by one part in 22,500 or well within the limits of experimental errors.

Taylor, J.: Treatise on Physical Chemistry p. 380.

C. C. Davis has reported to the American Chemical Society that two of his students have performed a series of experiments in dilute H_2SO_4 and $CuSO_4$ solvent with free electrodes and without any connection with an outside source of current for the separation of the ions. They found that the fundamental laws of electrolysis by Faraday remained valid for the formation and separation of ions at these electrodes.

Chemical Abstracts Vol. 18 - 1924 pt. 2, p. 2457.

Another experiment by J. A. Almquist was reported on the electrolysis of LiH. Quantities of H_2 produced by dissociation and by electrolysis were pumped off and measured separately. In the best experiment the volume of H_2 produced at the anode was 99.5% of that calculated from Faraday's laws. The electrolysis was carried on between 550 C and 650 C with Li H in solid state. The liberation of the Li at the cathode was also demonstrated. The dissociation pressure of the Li H was abnormal because of the solution of some Li in the Li H.

American Chemical Abstracts: Vol. 18, 1924 p. 615.

Tubandt found Faraday's laws to hold within one per cent when using solid silver iodide, bromide and chlorides as electrolytes.

Taylor, H. S.: A Treatise on Physical Chemistry p. 500.

Admirable confirmation of Faraday's laws has been given recently by Vinal and Bates. They did a large amount of experimental work on the electrolysis of solutions of silver nitrate to determine precisely the electro-chemical equivalent of silver and the definition of the ampere. The value of the faraday has been determined with an experimental error not exceeding .01 per cent. In these investigations solutions of silver nitrate and potassium iodide were electrolyzed in the same circuit, and the weights of the silver and iodine liberated ascertained. The results of these experiments as shown by the following table furnish an excellent confirmation of Faraday's laws.

Getman, F. H.: Outlines of Theoretical Chemistry p. 461. Fourth Edition.

Faraday's Laws of Electrolysis after having been subjected to the most exhaustive and accurate investigations of eminent scientists since 1833 may justly be proclaimed to be among our most exact scientific generalizations.

TABLE I

Determination of the Faraday

Mean Silver Deposit	Mean Iodine Deposit	From Ag. Voltameter	From Cell and Res.	Ratio Silver: Iodine	Electrochemical Equivalent of Iodine	Value of the Faraday (I=126.92)
mg	mg					
4105.82	4829.59	3672.47	......	0.85013_8	1.31508	96 511
4104.69	4828.62	3671.45	3671.53	07_5	518	504
4099.03	4822.24	3666.39	3666.55	02_6	526	498
4397.11	5172.73	3933.01	......	05_6	521	502
4105.23	4828.51	3671.94	3671.84	20_5	498	518
4123.10	4849.42	3687.92	......	22_6	495	521
4104.75	4828.60	3671.51	3671.61	09_1	515	506
4184.24	4921.30	3742.61	......	23_0	494	521
4100.27	4822.47	3667.50	3667.65	24_2	492	523
4105.16	4828.44	3671.88	3671.82	20_4	498	519
				0.85016	1.31505	96 514
Weighted mean (all observations)				0.85017	1.31502	96 515

CHAPTER III

VALUE

Before Faraday's time the different sciences were like so many foreign countries, with impassible barriers, different languages and different laws, but after Faraday's extensive tours, accompanied by profound study and diligent work, these interesting countries have become under his master mind a confederation of states linked together by a union of interests, common laws and common language. Faraday's Laws of Electrolysis were the first links in the chain of common interests that unite electricity, chemistry, and physics in one great branch of Natural Science.

By these two laws atoms and electricity were intimately associated. Helmholtz in his Faraday Lecture at the Royal Institute in London said,

> "Now the most startling results of Faraday's laws is perhaps this: If we accept the hypothesis that the elementary substances are composed of atoms we cannot avoid concluding that electricity also, positive as well as negative is divided into definite elementary portions which behave like atoms of electricity."[1]

Faraday, himself, seems to have realized fully the significance of his discoveries and had he been able to dtermine the number of atoms in unit mass of any substance, he would have anticipated by sixty years the determination of the fundamental charge. In 1834 he wrote,

> "If the electrical power that holds the elements of a grain of water in combination or which makes a grain of oxygen or hydrogen unite in the right proportions in a grain of water, when they are made to combine, could be thrown into the condition of a current, it would exactly equal the current required for the separation of that grain of water into its elements again."[2]

The first real foundation upon which our modern theories of atomic structure with its electrons and protons, was laid when Faraday by his

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[1]Muir, M. M. Pattison: Chemical Theories and Laws p. 337.
[2]Thompson, Silvanus: Michael Faraday p. 138.

laws of electrolysis made it clear that with each univalent atom taking part in electrolysis is associated a definite electric charge or a multiple of it for a multivalent atom and that this charge is the same for all atoms having the same valence.

It was the researches of Faraday that gave Maxwell the material for the crowning achievement of our age, the electro-magnetic theory. Before Maxwell began his work he said he carefully read and studiously pondered on all of Faraday's scientific writings.

Faraday's Laws are a valuable aid to research. A new weapon of attack upon the mysteries of the atom was placed in the hands of the investigator. Reliability of many chemical calculations, both of theoretical and industrial importance depend on the accuracy of which atomic weights have been calculated. Knowing the chemical equivalents that an element should have as shown by electrolysis, it was possible now to check up atomic weights of metallic elements, impossible by other methods. Several new elements have been discovered by this method and added to our stock of scientific knowledge.

Scientific curiosity was aroused by the publication of Faraday's successes; curiosity that led to countless research experiments. Research workers now had a new and most helpful constant to aid them in their calculations. This constant may be compared in its usefulness in all problems involving electrolysis, with the usefulness of the quantity 22.4 liters in problems involving change from weight to volumes of gases.

> "The exact laws of electrolysis enable engineers to design electrolytic apparatus and plant equipment in accordance with exact requirements of the undertaking.
>
> "Faraday's laws furnish us with an almost bewildering choice of methods for determining the quantity of electrical energy that has passed through a circuit. We have only to insert an electrolytic cell in the circuit, at the close

> of the experiment determine by analytic methods the quantity of chemical change, and calculate from this indirectly the quantity of electrical energy that has passed."[1]

On reading the life of Faraday and the account of his discoveries one is impressed by the beautiful simplicity, the Christian charity, the deep faith, the orderly industry that characterized his life and concludes that Tyndall was right when he said, "Faraday was a just and faithful Knight of God."

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[1]Bigelow, S. Law: Theoretical and Physical Chemistry.

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TABLE II

Products of Electrolysis

Electrolyte	Cathode Product	Anode Product
H Cl (concd)	H_2	Cl_2
H_2 SO_4	H_2	O_2
NaOH, KOH	H_2	O_2
Na NO_3	H_2 and Na OH	O_2 and H NO_3
K_2 SO_4	H_2 and KOH	O_2 and H_2 SO_4
Cu SO_4	Cu	O_2 and H_2 SO_4
Ni SO_4	Ni	O_2 and H_2 SO_4
Cu Cl_2	Cu	Cl_2
Ag NO_3	Ag	O_2 and H NO_3

TABLE III

Element	Atomic weight	Valency	Equivalent weight	Output per coulomb amp/sec. Milligrams	Output per 3600 coulombs i.e. amp/hrs. gms.
Aluminum (Al)	27	3	9	0.0933	.3356
Chlorine (Cl)	35.5	1	35.5	.368	1.3237
Copper (Cupric)	63.5	2	31.75	.329	1.1837
Copper Cuprous	63.5	1	63.5	.658	2.3674
Hydrogen H.	1	1	1	.01035	.0372
Iron ⨍Fe	56	2	28	.290	1.0441
Lead Pb.	207	2	103.5	1.072	3.8595
Lead (anion)	207	4	51.75	.536	1.9297
Nickel Ni.	58.5	2	29.25	.303	1.0907
Oxygen O	16	2	8	.083	.2983
Silver Ag	108	1	108	1.119	4.0273
Sodium Na.	23	1	23	.238	.8577
Zinc Zn.	65	2	32.5	.337	1.2119

Approved

Charles H. Skinner,
Major Professor

W. J. Grace, S.J.
Dean

Date April 15, 1930