

FARADAY'S ELECTROCHEMICAL LAWS AND THE DETERMINATION OF EQUIVALENT WEIGHTS¹

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Jöns Jakob Berzelius

As soon as the atomic theory was announced by Dalton it became apparent to those who accepted atoms as the fundamental units of matter that the determination of relative atomic weights was an activity of primary importance. The well-meant but pitifully inaccurate analyses made by Dalton produced the first table of relative atomic weights. There were others who made analyses, but it was Berzelius who shouldered the burden of making systematic determinations of atomic weights of the known elements. Before atomic weights could be assigned, however, it was essential that combining or equivalent weights be determined as accurately as possible, and it is here

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that the great experimental genius of Berzelius is especially well illustrated. He devoted ten years of his life to the determination of over 2000 combining weights of elements. With relatively crude balances, impure chemicals, and very little equipment at his disposal, Berzelius labored at this gigantic task under conditions which most present-day chemists would describe as completely unbearable. Yet his results were excellent and his equivalent weights are not far removed from modern values.

During his lifetime a uniquely simple and accurate method of determining equivalent weights became available to Berzelius. In January, 1834, Michael Faraday announced the discovery of the electrochemical laws. Subsequent researches led him to the investigation of the electrochemical equivalents of several elements and finally to the conclusion that the electrochemical equivalents are identical with the ordinary chemical equivalents. Here was a method devoid of the endless and tedious precipitations, filtrations, and weighings of the purely chemical procedures used by Berzelius. Here, too, was a method supported by what proved to be one of the most accurate laws known to science.

It is strange that Berzelius did not grasp at this approach, if not to replace his chemical methods, at least to provide a check on them. He was not unfamiliar with electrochemical manipulations, for he was an expert in the field, having begun his brilliant scientific career with investigations on the effects of the voltaic pile soon after its development in 1800. Yet there is only one shred of evidence that Berzelius ever determined chemical equivalents by use of the method outlined by Faraday, and even this evidence is questionable (see footnote 26). On the other hand, there is considerable evidence that Berzelius chose to neglect this discovery by the greatest scientist in England.

Although the "law of definite electrochemical action," as he named it, was not formally announced by Faraday until January, 1834, the notion that chemical effects in electrolysis are dependent on the quantity of electricity passed seems to have occurred to him much earlier. In his third series of researches published in January, 1833, Faraday remarked:²

When electrochemical decomposition takes place, there is great reason to believe that the quantity of matter decomposed is not proportionate to the intensity, but to the quantity of electricity passed.

² *Trans. Roy. Soc. London*, 123, 39 (1833).

Faraday took great pains to distinguish between quantity and intensity of the electric current. He used the words carefully and correctly and was seemingly well aware of the distinguishing characteristics and effects of each. This is a matter of no small importance, for it was precisely confusion on this point which helped to lead Berzelius astray.

The seventh series of researches published in January, 1834, is devoted to the work on electrochemistry and represents the final report of work which was referred to months earlier. Faraday found the prevailing electrochemical nomenclature unnecessarily confusing and proposed the use of the term "electrode" in place of "pole." He also suggested use of the terms anode, cathode, electrolyte, electrolyze, ion, cation, and anion.³

Faraday first tested the law of definite electrolytic action on water under a variety of conditions.⁴ When investigating the effect of variation in the size of electrodes, variation in current intensity, and variation in the concentration of the sulfuric acid solution used, he found that none of these three factors affected the amount of chemical action if the quantity of electricity remained the same. He also found that the law of definite electrochemical action was valid for aqueous solutions other than those of sulfuric acid. Faraday stated his final conclusions thus:⁵

...that when subjected to the influence of the electric current, a quantity of it (water) is decomposed exactly proportionate to the quantity of electricity which has passed...

These first experiments were all performed as preliminary steps in justifying the use of a current-measuring instrument which Faraday had invented and called a "volta-electrometer." The name was changed to "voltmeter" in 1838 and then to "coulometer" about 1902. Faraday's instrument consisted of two graduated glass tubes provided with electrodes and containing acidulated water. Mixed hydrogen and oxygen or the hydrogen alone was collected, the amount of gas collected giving a measure of the current which had passed. Faraday planned on using this device rather extensively in his future work in electrochemistry.

Upon considering the law of definite electrochemical action fully proved for the electrolysis of water, Faraday proceeded to apply it to other substances. He electrolyzed the fused protochloride of tin (SnCl_2) and by means of the gas volume in the volta-electrometer determined the electrochemical equivalent. The average of four experiments gave 58.53 as the value for the equivalent as compared with 57.9 which was quoted as the chemical equivalent. Faraday could not but conclude:⁶

...that the numbers leave little doubt of the applicability of the law of definite action in this and all similar cases of electro-decomposition...

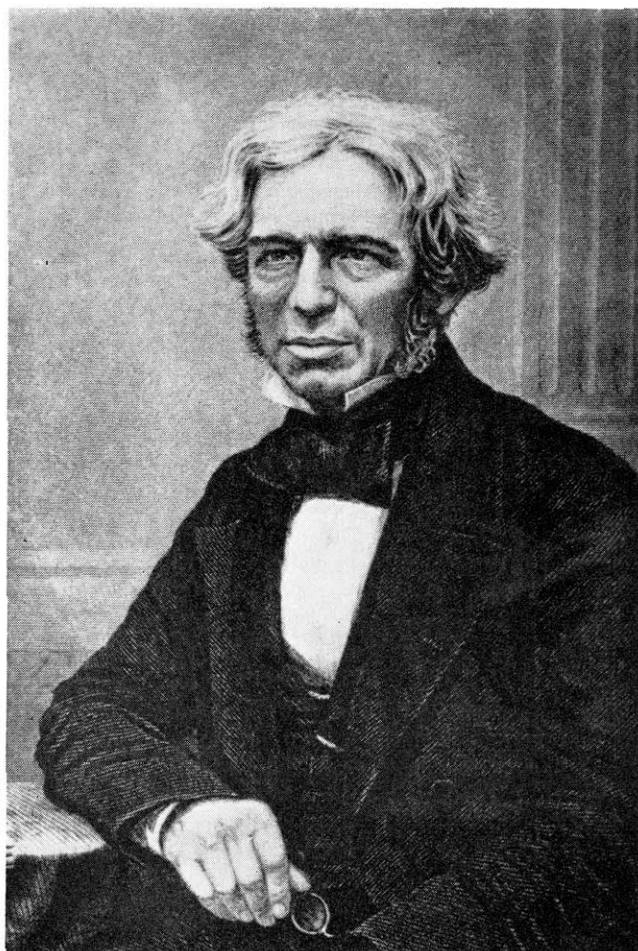
It is not often I have obtained an accordance in numbers so near as that I have just quoted.

Faraday electrolyzed many other substances, among them the chloride of lead, for which he again obtained results approximately equal to the chemical equivalent. To further establish the validity of the electrochemical law, Faraday resorted to using electrodes of different substances as well as using arrangements in which the metal under investigation was employed as the positive electrode so that there would be a direct transfer of metal from one electrode to the other. From these latter experiments Faraday happily found that the positive electrode lost as much weight as the negative electrode gained and all in equivalent proportion to the water decomposed in the voltameter.⁷

All these facts combine into, I think, an irresistible mass of evidence, proving the truth of the important proposition which I at first laid down, namely, *that the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.* They prove, too, that this is not merely true with one substance, as water, but generally with all electrolytic bodies...

That Faraday considered the electrochemical equivalent

⁷ *Ibid.*, p. 110.



Michael Faraday

³ *Ibid.*, 124, 77-9 (1834).

⁴ *Ibid.*, pp. 87-91.

⁵ *Ibid.*, p. 91.

⁶ *Ibid.*, p. 104.

lents and the chemical equivalents as identical is brought out by the following remarks in his paper:⁸

After the first experimental investigation to establish the definite chemical action of electricity, I have not hesitated to apply the more strict results of chemical analysis to correct the numbers obtained as electrolytic results....

The equivalent numbers do not profess to be exact, and are taken almost entirely from the chemical results of other philosophers in whom I could repose more confidence, as to these points, than in myself.

At this point Faraday inserted a "Table of Ions" which might more properly be considered a table of equivalents. It is of interest to note the method by which Faraday arrived at this table. What he apparently did was to determine the electrochemical equivalents for a number of substances by electrolytic methods. These results were then used to give an idea of the magnitude of the value, and then the chemical equivalents taken from other sources (probably Berzelius) were adjusted to fit this value. The values for tin and lead, for instance, are not those which Faraday had found by experiment, but are the chemical equivalents which his electrochemical results had closely approximated. The table itself gives the impression of being rather hastily put together, with the idea, as Faraday indicated, of showing the way rather than of providing accurate information.

Faraday was careful to point out that:⁹

A very valuable use of electrochemical equivalents will be to decide, in cases of doubt, what is the true chemical equivalent, or definite proportional, or atomic number of a body.... I can have no doubt that, assuming hydrogen as 1, and dismissing small fractions for the simplicity of expression, the equivalent number or atomic weight¹⁰ of oxygen is 8, of chlorine 36, of bromine 78.4, of lead 103.5, of tin 59, etc., notwithstanding that a very high authority doubles several of these numbers.

While no names are mentioned, the "high authority"

⁸ *Ibid.*, p. 114.

⁹ *Ibid.*, pp. 115-16.

¹⁰ Note Faraday's misuse of the term "atomic weight."

847. TABLE OF IONS.

<i>Anions.</i>			
Oxygen.....	8	Selenic acid 64	
Chlorine.....	35.5	Nitric acid 54	
Iodine.....	126	Chloric acid 75.5	
Bromine.....	78.3	Phosphoric acid.....	35.7
Fluorine.....	18.7	Carbonic acid.....	22
Cyanogen 26		Boracic acid.....	24
Sulphuric acid.....	40	Acetic acid 51	
<i>Cations.</i>			
Hydrogen 1		Cadmium 55.8	Soda..... 31.3
Potassium 39.2		Cerium..... 46	Lithia..... 18
Sodium..... 23.3		Cobalt..... 29.5	Baryta..... 76.7
Lithium..... 10		Nickel..... 29.5	Strontia..... 51.8
Barium..... 68.7		Antimony 64.6?	Lime..... 28
Strontium 43.8		Bismuth..... 71	Magnesia... 20.7
Calcium..... 20.5		Mercury..... 200	Alumina.... (?)
Magnesium 12.7		Silver..... 108	Protoxides generally
Manganese 27.7		Platina..... 98.6?	Quinia..... 171.6
Zinc..... 32.5		Gold..... (?)	Cinchona... 160
Tin..... 57.9			Morphia.... 290
Lead..... 103.5		Ammonia... 17	Vegeto-alkalies generally.
Iron..... 28		Potassa.... 47.2	
Copper..... 31.6			

Faraday's Table of Equivalents

undoubtedly refers to Berzelius. Berzelius considered the true equivalent of hydrogen to be a double atom, H₂, and considered this equivalent to K, Zn, etc. Thus he was inclined to write KO, AgO, KCl₂, NaSO₄, etc., and the atomic weights of potassium, sodium, lithium, and silver were doubled. Faraday showed how the electrochemical equivalents could be used to decide matters of this kind, for the table which he offered is essentially correct as regards equivalents.

Faraday's position is clear. He discovered the laws of electrochemistry and suggested methods for their use, but this was as far as he cared to take the problem. Further work on equivalents would have led him into the field of atomic weight determinations and Faraday had not yet convinced himself of the existence of atoms. Faraday, the experimental genius, like many great experimenters, was not fond of theories or speculation in any form. Rather, he chose to trust the concrete facts which he could collect as a result of researches in his laboratory. In this respect he was like his teacher, Davy, from whom he perhaps acquired much of his dislike of theoretical speculation.

In the very same paper in which he announced the electrochemical laws he showed his distaste for the atomic theory by making the following statement:¹¹

...but I must confess I am jealous of the term *atom*; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

The reluctance to carry the study of equivalents further than he had already done was no doubt a result, at least in part, of this aversion to the particulate theory of matter.

Other people were, at this time, substantiating the validity of the electrochemical laws. In a letter to Faraday, John Frederic Daniell, inventor of the Daniell constant cell and obviously a great admirer of Faraday, had remarked:¹²

One result, I know will gratify you; namely, that amongst the almost innumerable tests to which I have exposed your great discovery of the *definite chemical action of electricity*, I have found no fact to militate against it....

In Italy the electrochemical laws apparently underwent an independent discovery soon after Faraday had announced them. The discoverer was Carlo Matteucci, a man of whom little is written in the English language, and who is seemingly almost unknown to the historians of science, although in 1848 he received the Copley medal in London and is considered the originator of modern electrophysiology.

Matteucci, chemist, physiologist, and physicist, was born at Forlì in 1811 and died at Ardenza, near Leghorn, in 1868. He received his doctor's degree in mathematics at the University of Bologna in 1828, and then continued his studies in Paris, where he had the opportunity to meet the great men who associated

¹¹ *Trans. Roy. Soc. London*, 124, 121 (1834).

¹² *Ibid.*, 126, 107 (1836).

themselves with Arago. Although he was mainly interested in electrophysiology, he conducted researches in many other fields of science.^{13, 14}

It was after his return from Paris in 1831 that he continued, in Florence, the research he had started in Forlì on the action of electric current upon chemical combination. The short biography in the "Enciclopedia Italiana" makes this statement:

As a result, he was able to demonstrate the law of proportionality between the quantity of deposited electrolyte and the quantity of electricity passed through the voltameter, and this he did independently of the well known experiments by Faraday. Furthermore, he was able to draw conclusions of such an importance that Faraday himself said that they had given the young Italian scientist—at that time in his early twenties—a European fame.

Matteucci's paper containing the work on the law of definite electrochemical action bears the date October, 1834, and is published in the French *Annales* for January, 1835.¹⁵ Matteucci measured the quantity of current by using a silver coulometer. With this instrument in the circuit he conducted experiments in which zinc was destroyed with acid. Despite conditions in which he varied the concentration of acid, the temperature, and the surface area of the zinc, he always obtained the same current from the same weight of metal. Through other experiments Matteucci came to two additional conclusions:¹⁶

In causing the electric current developed by a certain chemical action to pass through different metallic solutions, the quantities of metals reduced and separated in these different solutions are variable, and whatever may be their relative densities, they are always in the same ratio as the chemical equivalents of these same metals.

There is finally the third and last result at which I have arrived, and which can well be regarded as the necessary consequence of the other two: *in disposing of different metals in the form of a pile, so that their decomposed quantities are in the same ratio as their chemical equivalents, one obtains a uniform electrochemical action.*

Matteucci seems to have arrived at the same conclusions as Faraday. The question of whether the discovery was independent is an interesting one. The "Enciclopedia Italiana" says that it was, but this source might be expected to favor Matteucci's position.

In the *Annales* for 1839,¹⁷ Matteucci published another article in which he commented on his previous discovery. In this comment he claimed independent discovery of the electrochemical laws but gave Faraday credit for the original discovery and for the establishment of the law of definite electrochemical action. This notion apparently did not prevail among certain other European scientists. In the *Philosophical Magazine* Poggendorff affirmed Faraday's priority to the discovery of definite electrolytic action.¹⁸ Poggendorff felt that Faraday had been greatly wronged. He

admitted that since news traveled slowly to Italy Matteucci might not have known of Faraday's discovery. However, Poggendorff felt that Gay-Lussac and Arago, editors of the *Annales*, surely were aware of Faraday's discovery and therefore should not have published Matteucci's article in the form in which it appeared.

While it is possible that Matteucci was aware of Faraday's work when he did his own, we must give him credit for a certain amount of originality. In the first place he used a silver coulometer to measure current quantity, an instrument which Faraday does not mention. Second, he had arrived at the law by experiments very different from Faraday's. Faraday had used current from a pile to cause the deposition of certain substances which he could weigh. Matteucci measured the amount of current which a known amount of metal furnished as it underwent chemical action. These two facts strengthen Matteucci's position as the independent discoverer of the electrochemical laws.

While the law of definite electrochemical action was accepted by many scientists as a well established fact, there was one who questioned its validity. This was Berzelius, who first learned of Faraday's discovery from Poggendorff's *Annalen*,¹⁹ in which Faraday's seventh series of researches was reprinted in complete translation. Berzelius' comments on the law of definite electrochemical action made their appearance in the 1836²⁰ volume of his *Jahres-Bericht*. These comments begin with a brief summary of the conclusions which Faraday had drawn from his experiments. Berzelius registers his first complaint against the conclusion that the concentration of sulfuric acid had no effect on the amount of hydrogen and oxygen evolved during the electrolysis of water if the current quantity remained the same:

Hereby, however, it seems to me that an error of observation could have been made. With the passage of the electric current through the acidic liquid, acid collects in excess amount at the positive pole and water at the negative pole, and the amount must vary with the unequal amount of the acid. But if a fixed quantity of electricity is used for this division with water and concentrated acid, then, so it seems, variations must take place in the quantity of water which is decomposed into its constituents. Even if the sum of both decompositions is the same each time, then surely both types can vary among themselves in relative quantity.

Considering Faraday's reputation as an experimenter, the suggestion that Faraday had made an error in observation was a bold step. Berzelius, however, was not one to hesitate! The fallacy in Berzelius' argument results from his failure to see that the quantity of electricity is related only to those substances actually separated at the electrode even though it is true that acid does collect around the anode. The irregularities which Faraday did find he attributed to solubility

¹³ "Enciclopedia Italiana," Rome, 1934, p. 596.

¹⁴ BIANCHI, N., "Carlo Matteucci e l'Italia del suo tempo," Turin, 1874. The portrait is taken from this work.

¹⁵ *Ann. chim. et phys.*, **58**, 75 (1835).

¹⁶ *Ibid.*, pp. 78-80.

¹⁷ *Ibid.*, **71**, 90 (1839).

¹⁸ *Phil. Mag.*, [3] **7**, 421-2 (1835).

¹⁹ *Ann. Phys. Chem.*, **33**, 301, 433, 481 (1834).

²⁰ *Jahres-Bericht*, **15**, 30-9 (1836). The two-year lag in the material published in the *Jahres-Bericht* was not unusual since Berzelius was outside the main center of scientific activity in Europe. The Berzelius quotations which follow are all translations from this reference. The translations are the authors'.



Carlo Matteucci

effects of the gases and not to the failure of the law of definite electrolytic action. Berzelius continues his comments and objections:

He declares further to have found that the same number of couples in the pile, charged stronger or weaker (what is to be understood by this is not indicated for certain. It would be entirely wrong, however, if it meant "built up with fluids of unequal electromotive force"), gave the same quantity of hydrogen gas, and also showed the same ratio, when at one time the pile consisted of 5 couples and at another time consisted of 10 couples, provided plates of the same size had been used.

Here we see that Berzelius has hopelessly confused the concepts of current quantity and current intensity. He cannot see that "strongly and weakly charged" and the number of couples in the pile refer to variations in current intensity which need not affect the current quantity, on which chemical effects are dependent.

Berzelius continues with a statement of Faraday's conclusions on the decomposition of water and the use of the volta-electrometer as a current measure. Then he comments on the electrochemical equivalents:

In this way Faraday comes to the third and principal result of his experiments, namely "*that those things which the same quantity of electricity decomposes are chemical equivalents.*" The proofs for this principle are not many, to be sure. They surely seem, however, to show this behavior for the cases mentioned. Thus he found that with hydrochloric acid and hydriodic acid dissolved in water each gave the same quantity of hydrogen gas at the negative pole which he had obtained in the quantity measured with dilute sulfuric acid. . . . When silver chloride, and especially lead chloride in molten condition, was decomposed between platinum wires, of which the negative was weighed, then it became apparent that the weight of the reduced metal adhering to

the negative wire corresponded to the volume of the hydrogen gas collected in the quantity measured, in such a manner, that both were chemical equivalents. . . .

In the evaluation of these experiments it appears as if the theorem stating that the same quantity of electricity always gives the same amount in decomposition has not been proved as completely as one could wish. The fact is perhaps correct. This must not keep us from a closer criticism of the proof.

The skepticism of Berzelius is quite evident at this point but he has some other more important objections:

In the results of these experiments I find nothing that would be decisive enough to prove more than that if water and melted lead chloride²¹ are decomposed one after the other by the same electric current the quantities of the reduced lead and hydrogen are equivalents. But also here the presence of sulfuric acid²² in the water causes an uncertainty, as I mentioned before. It must cause a variation, which is perhaps too small to show up, when the experiment must be carried out on such a small scale. Still another question can be asked here: is the same quantity of electricity necessary to separate one atom of silver and one atom of oxygen from each other, as to separate one atom of potassium from one atom of oxygen,²³ that is, to neutralize forces of such an immense difference in magnitude? Can the intensity in strength compensate, as it is to be assumed, for the overcoming of a great force? Would not the condition be conceivable that affinities of the same amount are equally overcome by the same current and affinities of a little different degree with such a small difference in their amounts that in a small-scale experiment it falls into the errors of observation? It is known that lead separates chlorine from hydrogen only with difficulty and on boiling and that therefore these affinities lie very close. One sees from this that this investigation must be taken from a much broader viewpoint, before the result which Faraday has inferred from it can be considered as valid.

That Berzelius is confusing the roles of current intensity and current quantity is evident, for he suggests that it would take more *current* to separate the atoms in a stable compound than in a less stable one. It also happens, says Berzelius, that lead and hydrogen possess about the same combining tendency or affinity for chlorine, since it is hard for lead to replace hydrogen in hydrochloric acid. Hence it ought to take almost the same *current* to separate lead from chlorine as hydrogen from oxygen and this then explains why Faraday gets consistent results, with the provision, of course, that there be a difference in the current quantity, but this is so small in this instance that Faraday has missed it.

There is at least one respect in which Faraday's work can be genuinely criticized. Faraday was under the false impression that only compounds composed of single equivalents of each element could be decomposed by the electric current. He was led to this hypothesis as a result of testing various substances for conductivity and decomposition. He found, for instance, that SnCl_2 was decomposed but SnCl_4 was not. If substances which were known not to consist of single equivalents were decomposed, Faraday thought this

²¹ Of all Faraday's experiments, Berzelius seems to be most favorably impressed with the results obtained with lead chloride.

²² That is, the acid used to make the water in the volta-electrometer conducting.

²³ Note the Berzelian formulas AgO and KO .

was the result of some secondary action at the electrodes and was not the primary decomposition caused by the electric current. Ammonia was one of these substances. When Faraday attempted to decompose Sb_2O_3 and SbCl_3 he found that he got decomposition although he knew these substances did not consist of single equivalents. He was so convinced of the correctness of his single equivalent theory, however, that he proposed the existence of an oxide and a chloride of antimony containing the proportions of 1:1 which had up to this time been unknown. These alleged compounds were assumed to be present in the ordinary antimony compounds and were responsible for the conducting power of these compounds. By some experiments which he himself described as rough, he thought he had prepared the true antimony compounds SbCl and SbO . His experiments were done hastily and were, from an analytical point of view, rather incomplete.

Berzelius objected to these new compounds described by Faraday and repeated Faraday's experiments more carefully. He found Faraday to be completely mistaken regarding the existence of the new compounds. Faraday later admitted his error in regard to the antimony compounds but he did not offer to retract his theory on single equivalents or the electrochemical laws, both of which he still believed to be correct.

Berzelius concludes his remarks with a rather violent attack upon Faraday's new electrochemical nomenclature:

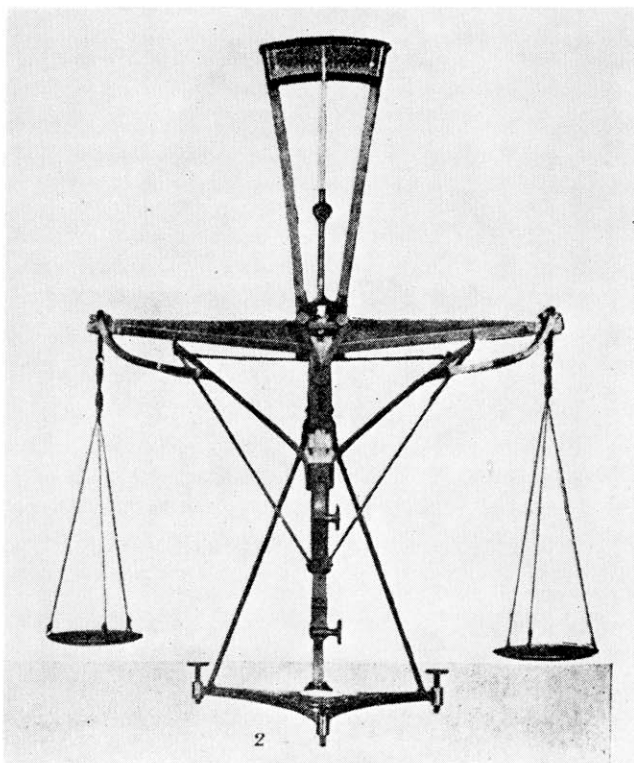
Faraday believes, for reasons which I do not consider valid, that his experiments lead to such changed views in the theory of science that our usual scientific nomenclature is inadequate for a correct expression of the ideas to which the results lead; therefore he has introduced others of which I do not think either that they were necessary in any respect, or that they deserve to be followed....

It is obvious to everyone that a new nomenclature established on the idea of only one electricity has never been more superfluous than in the moment when the electrochemical theory,²⁴ which without two opposite electrical forces would make no sense, is on the way to winning such strong support, as from the electrical quantitative relations which Faraday has sought to establish.

One must conclude from Berzelius' remarks that he was not convinced of the correctness of the law of definite electrochemical action. To the extent that Faraday's work supports his own electrochemical theory he is willing to accept Faraday's results. It is quite obvious, however, that he does not approve at all of the electrochemical nomenclature introduced by Faraday.

A word must be said about the confusion concerning the meaning of the words "equivalent weight" and "atomic weight." Among the chemists of this period the definitions for these terms were a matter of personal preference and no one agreed on the meaning of "equivalent," "atom," or "atomic weight." The word "molecule" was literally unknown, having been re-

²⁴ This refers to Berzelius' own electrochemical or dualistic theory which explained chemical combination and electrodecomposition on the basis of two oppositely charged forces.



A Berzelius Balance

jected along with Avogadro's hypothesis about 1811. "Atom" or "compound atom" was often used where "molecule" was meant. Some used equivalent and atomic weight synonymously. Even Faraday himself had done this. Berzelius seems to have been one of the few who had a clear concept of the difference between an equivalent weight and an atomic weight. The trouble over equivalents arose, however, not so much over incorrect ideas as over the multiplicity of points of view and lack of a generally accepted standard. The electrolytic equivalents could have been used most effectively as a standard but the idea was not consistently carried out.

Lothar Meyer, in his "Outlines of Theoretical Chemistry,"²⁵ mentions that there were two main difficulties in determining equivalent (not atomic) weights by use of Faraday's law. One of these was the fact that several metals such as copper displayed different values for their equivalents, depending on the nature of the compound investigated. The problem of which equivalent to select as the true equivalent which the symbol would represent was one which beset almost every chemist of the period. Some elements had only two equivalents but there were others, manganese, for instance, that had six equivalents. The smallest one was often used as the true equivalent. Faraday had been troubled by this too. He believed that there could be only one electrolytic equivalent for an element.

²⁵ MEYER, L., "Outlines of Theoretical Chemistry," Longmans, Green and Co., London, 1892, pp. 16-17 (1st German edition, 1890).

The second difficulty in the use of electrolytic equivalents was the fact that compounds of many elements would not conduct electricity and the determination of equivalents by electrolysis could not be systematically carried out.

One might suppose after a study of Berzelius' attitude toward Faraday's electrochemical laws that he would have nothing to do with them as regards the determination of equivalents. There is one bit of evidence that he did use electrolytic equivalents. This evidence appears in the form of one sentence in Meyer's book:²⁶

After the discovery of the law of isomorphism Berzelius regarded the crystallographic equivalent weights as identical with the atomic weights, except in the case of K, Na, Li, Ag, of which he determined the atomic weights by use of their electrolytic equivalents.

This evidence has never been substantiated in any other way. A very reliable source, Becker's "Atomic Weight Determinations,"²⁷ is a digest of atomic weight investigations published between the years 1814-80. This work makes no mention of any atomic weight determination by Berzelius in which he made use of electrolytic equivalents. As a matter of fact, this source mentions only two instances in which electrolytic procedures were used and both of these occurred after 1873.

The most important point which emerges at this time is the fact that the electrochemical laws of Faraday were almost completely neglected between 1834 and 1880. Some recognized them as a great discovery but the almost immediate opposition on the part of Berzelius dealt a telling blow to their complete acceptance. Berzelius, the "law-giver of chemistry" and the undeniable "first authority" in chemical matters, had to give his stamp of approval before a matter as important as this could be said to be accepted. This approval was unquestionably lacking and may be said to be the most important single factor in the neglect of Faraday's laws.

Berzelius apparently maintained this opposition to

the end of his life.²⁸ In the fifth edition of his "Lehrbuch der Chemie"²⁹ he mentions the laws and seems even more convinced of their incorrectness:³⁰

It is absolutely too early, indeed only conjectural, to accept the admission of these results for a general valid natural law. . . there occurs no comparison between the quantity of that which is separated in unlike substances and the quantity of the current.

As far as Faraday's theory of single equivalents and secondary action was concerned, Berzelius classified them as "...conclusions which require only a small application of logic in order to be rejected."³¹

Besides the objections of Berzelius there were some other factors which accounted for the neglect of the electrochemical laws. Faraday's own distrust of the atomic theory and his reluctance to carry his work on equivalents beyond the publication of his "Table of Ions" were undoubtedly contributing factors. His false interpretations of certain parts of his work, especially on the theory of single equivalents, certainly hurt his position, since the law of definite electrochemical action was intimately connected with this false hypothesis. The confusion over the meaning of "equivalent" and the existence of several equivalents for one element, as well as the fact that not all substances could be electrolyzed to give their electrochemical equivalents, were of importance also.

With all these factors operating toward the defeat of Faraday's electrochemical laws it is not surprising that as late as 1900 Louis Kahlenberg³² and T. W. Richards and his associates³³ were conducting studies to determine whether Faraday's law was universally applicable and valid under such simple conditions as, for example, for nonaqueous solutions and at different temperatures.

²⁸ Berzelius died in 1848.

²⁹ BERZELIUS, J., "Lehrbuch der Chemie," 5th ed., Arnoldische Buchhandlung, Leipzig, 1856, pp. 99-101. (Forward to the book bears the date 1842.)

³⁰ *Op. cit.*, pp. 100-1.

³¹ *Ibid.*

³² *J. Phys. Chem.*, **4**, 349 (1900).

³³ *Proc. Am. Acad. Arts Sci.*, **38**, 409-13 (1902).

²⁶ *Ibid.*, p. 20.

²⁷ BECKER, G. F., "The Constants of Nature. IV: Atomic Weight Determinations," Smithsonian Misc. Coll. 358 (1880).