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FROM ELECTROCHEMICAL EQUIVALENCY TO A MOLE OF ELECTRONS: THE EVOLUTION OF THE FARADAY

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In the 1988 edition of *Quantities, Units and Symbols in Physical Chemistry*, (1) we find the following recommended values for the Avogadro constant (L or N_A), the elementary charge (e), and the Faraday constant (F):

$$N_A = 6.0221367(36) \times 10^{23} \text{ mol}^{-1}$$

$$e = 1.60217733(49) \times 10^{-19} \text{ C}$$

$$F = 9.6485309(29) \times 10^4 \text{ C mol}^{-1}$$

Simple multiplication of the first two of these yields, with suitably arcane adjustments of limits of error, the third, i.e.

$$N_A e = F$$

Further examination reveals that the recommended values for both N_A and e are independent of any electrochemical measurement (2). It would seem that the long and fruitful marriage of electrochemistry and the Faraday has come to an amicable parting of the ways, a parting endorsed by the units of C mol^{-1} . A brief history of the "Faraday" will be given in terms of a concept (however named), a value (however measured) and a name (by whomever dubbed).

Faraday's establishment of the law(s) of electrolysis - "electrochemical equivalents coincide, and are the same with ordinary chemical equivalents" - has been widely studied (3-8). What has seldom been remarked is the sparsity of examples and the semiquantitative nature of much of the data upon which

his great quantitative generalization was based. In Faraday's table of relative electrochemical equivalents of some 60 anions and cations (including "quinia", "cinchona" and "morphea"!) less than ten were substantiated by direct electrochemical means; the remainder are "chemical results of other philosophers in whom I could repose more confidence, as to these points, than in myself" (9). He adds:

I may be allowed to express a hope, that the endeavour will always be to make it a table of *real*, and not *hypothetical*, electrochemical equivalents; for we shall else overrun the facts, and lose all sight and consciousness of the knowledge lying directly in our path.

In the prefiguring of this passage in the *Diary* we find the more admonitory: "I must keep my researches really *Experimental* and not let them deserve any where the character of *hypothetical imaginations*" (10).

As to precision, the *Diary* gives the values 59.805, 56.833, 57.9 and 59.57 for the relative electrochemical equivalent of tin (11). (Faraday was charmingly cavalier when it came to significant figures.) In the published paper he states (12):

It is not often I have obtained an accordance in numbers [with the accepted chemical equivalent] so near as that I have just quoted ... The average of the four experiments gave 58.53 as the electrochemical equivalent of tin.

Similarly for lead one finds such varied values as 105.11, 97.26, 101.29, 93.17 and 80.51 (13). Admittedly the experimental difficulties of working with molten salts were large but as a later worker in the field somewhat ruefully remarked (14):

The experiments upon which he based his law of electrolysis are an interesting illustration of the keen insight which led Faraday to enunciate a general law upon what seems today to be very meagre and inaccurate data.

"On the Absolute Quantity of Electricity Associated with the Particles or Atoms of Matter" - so runs the heading for the concluding section of Faraday's magisterial Seventh Series of *Experimental Researches in Electricity*. The opening paragraph might seem to raise our Whiggish hopes (15):

The theory of definite electrolytical or electrochemical action appears to me to touch immediately upon the *absolute quantity* of electricity or electric power belonging to different bodies. It is impossible, perhaps, to speak on this point without committing oneself beyond what present facts will sustain: and yet it is equally impossible, and perhaps would be impolitic, not to reason upon the subject. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere



John Frederick Daniell (left) and Michael Faraday (right), circa 1843.

motion of ordinary matter, or some third kind of power or agent, yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity.

However, Faraday, like many of his contemporaries, was at best a reluctant atomist, a view he passionately believed to be fraught with hypothetical, if not quite horrible, imaginings. One wonders what he would make of recent work on "electrochemistry at single-molecule sites" (16). A later passage finds him turning aside atomistic temptation (17):

The harmony which this theory of the definite evolution and the equivalent definite action of electricity introduces into the associated theories of definite proportions and electro-chemical affinity, is very great. According to it, the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity, or have naturally equal electric powers; it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them. 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.

Faraday's electrochemical researches, with their accompanying nomenclature, quickly found their way into some of the

more adventurous textbooks of the time (18, 19) but for over 30 years no one probed much more deeply into their ultimate significance than had Faraday himself.

The closest, and incomparably the most rewarding, reading of Faraday's *Experimental Researches in Electricity* was that of James Clerk Maxwell. As befits one of the founding fathers of kinetic molecular theory Maxwell was reasonably comfortable with the concept of a molecule while remaining something of an agnostic on the reality of Daltonian atoms. In 1873 (the year that saw the publication of his *A Treatise on Electricity and Magnetism*) Maxwell gave a lecture on "Molecules" at the Bradford meeting of the British Association for the Advancement of Science (20). After paying tribute to his predecessors - "The lecture in which Democritus explained the atomic theory to his fellow citizens of Abdera realized, not in golden opinions only, but in golden talents, a sum hardly equalled even in America" - Maxwell goes on to propound the conventional wisdom of physicists of his time (20):

Every substance, simple or compound, has its own molecule. If this molecule be divided, its parts are molecules of a different substance or substances from that of which the whole is a molecule. An atom, if there is such a thing, must be a molecule of an elementary substance. Since, therefore, every molecule is not an atom, but every atom is a molecule, I shall use the word molecule as the more general term.

Later in the lecture he turns to electrolysis but does not pursue the question of a molecular charge (20):

We have no time to do more than mention that most wonderful molecular motion which is called electrolysis. Here is an electric current passing through acidulated water, and causing oxygen to appear at one electrode and hydrogen at the other. In the space between, the water is perfectly calm, and yet two opposite currents of oxygen and of hydrogen must be passing through it ... Electrolysis, therefore, is a kind of diffusion assisted by electromotive force.

The reasons are not far to seek (20):

There is another set of quantities which we must place in the third rank, because our knowledge of them is neither precise, as in the first rank, nor approximate, as in the second, but is only as yet of the nature of a probable conjecture. These are the absolute mass of a molecule, its absolute diameter, and the number of molecules in a cubic centimeter.

In the *Treatise* Maxwell addresses the question of molecular charge directly in the short chapter on "Electrolysis" (21):

Of all electrical phenomena electrolysis appears the most likely to furnish us with a real insight into the true nature of the electric current, because we find currents of ordinary matter and currents of electricity forming essential parts of the same phenomenon. It is probably for

this very reason that, in the present imperfectly formed state of our ideas about electricity, the theories of electrolysis are so unsatisfactory.

Maxwell makes the characteristic point that:

... the ordinary chemical equivalents, however, are the *mere* numerical ratios in which the substances combine, whereas the electrochemical equivalents are quantities of matter of a determinate magnitude, depending on the definition of the unit of electricity.

Ah, the physicist's "mere"! He continues:

It is therefore extremely natural to suppose that the currents of the ions are convection currents of electricity, and, in particular, that every molecule of the cation is charged with a certain fixed quantity of positive electricity, which is the same for the molecules of all cations, and that every molecule of the anion is charged with an equal quantity of negative electricity.

Maxwell, still an adherent of the "two fluid" theory, then issues the caution (21):

But if we go on, and assume that the molecules of the ions within the electrolyte are actually charged with certain definite quantities of electricity, positive and negative, so that the electrolytic current is simply a current of convection, we find that this tempting hypothesis leads us into very difficult ground ... If, instead of a single molecule, we consider an assemblage of molecules constituting an electrochemical equivalent of the ion, then the total charge of all the molecules is, as we have seen, one unit of electricity, positive or negative.

We do not as yet know how many molecules there are in an electrochemical equivalent of any substance, but the molecular theory of chemistry, which is corroborated by many physical considerations, supposes that the number of molecules in an electrochemical equivalent is the same for all substances. We may therefore, in molecular speculations, assume that the number of molecules in an electrochemical equivalent is N , a number unknown at present, but which we may hereafter find means to determine.

Each molecule, therefore, on being liberated from the state of combination, parts with a charge whose magnitude is $1/N$, and is positive for the cation and negative for the anion. This definite quantity of electricity we shall call the molecular charge. If it were known it would be the most natural unit of electricity.

Maxwell's speculations are leading us close to macroscopic/microscopic concept of the Faraday.

G. Johnstone Stoney is today best remembered for suggesting the name "electron" for the elementary charge in 1894. Twenty years earlier he had read a paper "On the Physical Units of Nature" at the Belfast meeting of the British Association for the Advancement of Science. This rather idiosyncratic

paper was republished in 1881, the year of Helmholtz's famous Faraday Lecture (22). It provides an interesting historical background to the subject of SI units. Having first defined "lengthine", "massine", "timine", and "forcine" Stoney continues (22):

e_1 , the electromagnetic electrone, or the electromagnetic unit quantity of electricity in the metric series, is that quantity of each of the two kinds of electricity which must be discharged every second in opposite directions along a wire in order to maintain in it the metric unit current - this currentine or unit current being defined as the current which must exist in a wire a metre long in order that it may exert a force of a hyper-decigramme on ponderable matter at a metre distance charged with a unit of magnetism ...

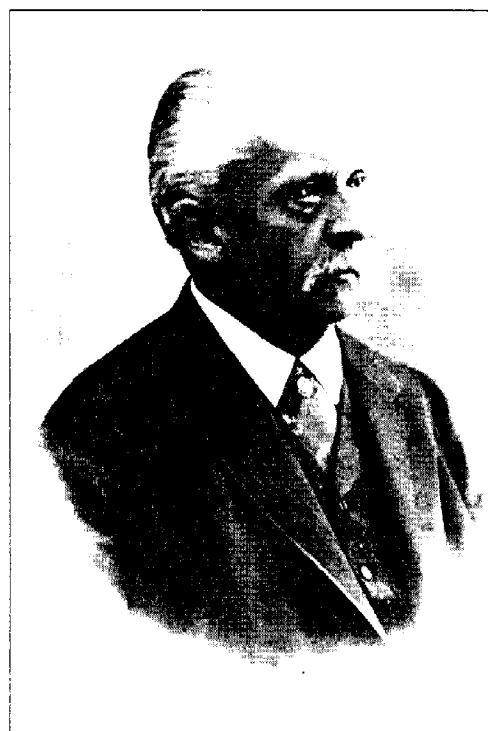
So far all rather academic but later we find (22):

And, finally, Nature presents us, in the phenomenon of electrolysis, with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear I shall express "Faraday's Law" in the following terms, which, as I shall show, will give it precision, viz.: *For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases.* This definite quantity of electricity I shall call E_1 . If we make this our unit quantity of electricity, we shall probably have made a very important step in our study of molecular phenomena.

Crucially, Stoney goes on to estimate E_1 using Loschmidt's, his own, and Thomson's estimates of the size of atoms/molecules and hence of the approximate number of atoms/molecules in a macroscopic "amount of substance". His estimate is within an order of magnitude of today's value. In short, Stoney was the first to interpret a macroscopic electrochemical equivalent (of hydrogen) in terms of a microscopic charge (positive or negative) carried by an approximately known number of microscopic particles. This seems to us the essence of the concept of the "Faraday".

In his 1894 paper "Of the 'Electron', or Atom of Electricity" (23) Stoney juxtaposes the second of the above quotations to the more famous statement by Helmholtz made in his Faraday Lecture of 1881. The circumstances of this lecture are well known. More so Helmholtz's statement (24):

Now the most startling result, perhaps, of Faraday's law is 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. As long as it moves about on the electrolytic liquid each atom remains united with its electric equivalent or equivalents. At the surface of the electrodes decomposition can take place if there is sufficient electromotive power, and then the atoms give off their electric charges and become electrically neutral.



Hermann von Helmholtz

For our purposes little need be added to what has already been written. Nowhere does Helmholtz estimate explicitly the elementary (later the electronic) charge. Sir Henry Roscoe was in the chair on the occasion of Helmholtz's lecture and his concluding remarks include the passage (25):

But our lecturer has gone further, for upon Faraday's well-known law of electrolysis he has founded a new electro-chemical theory, which reveals to us chemists, conclusions of the utmost importance. He tells us as the results of the application of the modern theory of electricity to Faraday's great experimental law, that the atom of every chemical element is always united with a definite invariable quantity of electricity. Moreover - and this is most important - that this definite amount of electricity attached to each atom stands in close connection with the combining power of the atom which modern chemistry terms quantivalence. For if the amount of electricity belonging to the monad atom be taken as the unit, then that of the dyad atom is two, of the triad atom three, and so on.

The future historian of the atomic theory was clearly pleased by this marriage of Dalton's atoms and Faraday's laws. Even though F was not yet the Faraday, N was not yet Avogadro's Constant, and the electron was not yet discovered, the macroscopic/microscopic essence of F was now established.

By its nature, the electrochemical equivalent is a charge-to-mass ratio and it is not surprising that it played a key role in Thomson's elucidation of the nature of the electron in 1897 and

in Rutherford's identification of the alpha particle in 1905. Thomson gave a Friday Evening Discourse at the Royal Institution on 30 April 1897. Its title was "Cathode Rays" (26). After establishing a value of 1.6×10^{-7} for the mass-to-charge ratio of the electron, Thomson concludes his lecture with the passage (26):

This is very small compared with the value 10^{-4} for the ratio of the mass of an atom of hydrogen to the charge carried by it. If the result stood by itself we might think that it was probable that e was greater than the atomic charge of [the] atom rather than that m was less than the mass of a hydrogen atom. Taken, however, in conjunction with Lenard's results for the absorption of the cathode rays, these numbers seem to favour the hypothesis that the carriers of the charges are smaller than the atoms of hydrogen.

It is interesting to notice that the value of e/m , which we have found from the cathode rays, is of the same order as the value 10^{-7} deduced by Zeeman from his experiments on the effect of a magnetic field on the period of the sodium light.

In Churchill's phrase, this was the electrochemical equivalent's finest hour. Mention of the Zeeman Effect brings to mind that an unsuccessful search for this effect was the subject of Faraday's last experiment (27).

Almost exactly four years later, in another Friday Evening Discourse, Thomson showed how the charge on a single electron and the value of the electrochemical equivalent yielded a satisfactory value for Loschmidt's Number (Avogadro's Constant had not yet been so named) without the "not entirely satisfactory" assumptions of Kelvin, Stoney and Loschmidt (28).

Shortly afterwards Rutherford was to use similar arguments in pinning down the nature of the alpha particle (29):

It is now necessary to consider what deductions can be drawn from the observed value of e/m found for the α particle. The value of e/m for the hydrogen ion in the electrolysis of water is known to be very nearly 10^4 . The hydrogen ion is supposed to be the hydrogen atom with a positive charge, so that the value of e/m for the hydrogen atom is 10^4 . The observed value of e/m for the α particle is 5.1×10^3 , or, in round numbers, one half of that of the hydrogen atom. The density of helium has been found to be 1.98 times that of hydrogen, and from observations of the velocity of sound in helium, it has been deduced that helium is a monatomic gas. From this it is concluded that the helium atom has an atomic weight 3.96. If a helium atom carries the same charge as the hydrogen ion, the value of e/m for the helium atom should consequently be about 2.5×10^3 . If we assume that the α particle carries the same charge as the hydrogen ion, the mass of the α particle is twice that of the hydrogen atom. We are here unfortunately confronted with several possibilities between which it is difficult to make a definite decision.

The value of e/m for the α particle may be explained on the assumptions that the α particle is (1) a molecule of hydrogen carrying

the ionic charge of hydrogen; (2) a helium atom carrying twice the ionic charge of hydrogen; or (3) one-half of the helium atom carrying a single ionic charge.

With typical aplomb, Rutherford comes out firmly for the second option.

We must now turn to a short history of the experimental determination of the numerical value of the electrochemical equivalent. Near the close of his life Faraday purchased the first one ohm wire-wound resistance standard offered for sale by the Committee of the British Association for Electrical Resistance Standards (30). For most of his active research life he had had to be content with relative effects, e.g., relative electrochemical equivalents, and with semi-quantitative measurements based on ingenious *ad hoc* standards. The problem is well-illustrated in one of Faraday's most memorable metaphors (31):

One grain of water, acidulated to facilitate conduction, will require an electric current to be continued for three minutes and three-quarters of time to effect its decomposition, which current must be powerful enough to retain a platina wire 1/104 of an inch in thickness, red-hot, in the air during the whole time; and if interrupted anywhere by charcoal points, will produce a very brilliant and constant star of light. If attention be paid to the instantaneous discharge of electricity of tension, as illustrated in the beautiful experiments of Mr. Wheatstone, and to what I have said elsewhere on the relation of common and voltaic electricity, it will not be too much to say that this necessary quantity of electricity is equal to a very powerful flash of lightning. Yet we have it under perfect command; can evolve, direct, and employ it at pleasure; and when it has performed its full work of electrolyzation, it has only separated the elements of a single grain of water.

The establishment of international units in electric science was effected by one of the earliest, greatest and most influential of international collaborations in science (32, 33). There were two essential components to the task: (a) relating the various electrical units to the more fundamental units of mass, length and time, e.g., resistance has the dimensions of a velocity, (b) developing practical and transportable standards incorporating these fundamental units. Following theoretical contributions of Gauss and of Weber and prompted by the "progress and extension of the electric telegraph", a particularly important role was played by the Committee of Electrical Standards of the British Association for the Advancement of Science. The original committee of 1861 consisted of Williamson, Wheatstone, Thomson (Kelvin) and Jenkin. They were shortly joined by Siemens, Maxwell and Joule. All of these illuminati were working members and it is scarcely surprising that progress was rapid. The choice of the (as yet un-named) ohm as the first target of opportunity was dictated partly by the importance of resistance measurements in telegraphy and partly by the realization that the unit could be manifested in a

simple material standard such as a specified column of mercury that could then be matched with conveniently transportable wire-wound resistors. International agreement was ratified in 1881.

The next step - the establishment of units and standards for current/quantity and/or for electromotive force - was more complex. As Rayleigh was later to state in his classic 1884 paper "On the Electrochemical Equivalent of Silver, and on the Absolute Electromotive Force of CLARK Cells" (34):

The complete solution of the problem of absolute electrical measurement involves, however, a second determination, similar in kind, but quite independent of the first. In addition to resistance, we require to know some other electrical quantity, such as current or electromotive force. So far as we are aware, all the methods employed for this purpose define, in the first instance, an electrical current; but as a current cannot, like a resistance, be embodied in any material standard for future use, the result of the measurement must be recorded in terms of some effect. Thus, several observers have determined the quantity of silver deposited, or the quantity of water decomposed, by the passage of a known current for a known time. In this case the definition relates not so much to electric current as to electric quantity.

Rayleigh had inherited a tradition (and even some requisite equipment) for advancing electrical standards from his predecessor as Cavendish Professor, James Clerk Maxwell. His experiments, in which he was aided by Mrs. Sidgwick, were carried out in the same room where, 15 years later, his successor, J. J. Thomson, was to discover the electron (35).

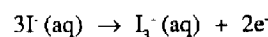
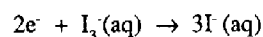
Rayleigh's was by no means the first determination of the electrochemical equivalent of silver but it set a standard (in several senses) for thoroughness and exquisite attention to detail that lasted until the middle of the 20th century. It is not difficult to recognize the experimental skills that were later to enable Rayleigh to sniff out the presence of argon in the atmosphere from a less than one half of one per cent discrepancy in the density of nitrogen (36). As R. J. Strutt proudly points out in his biography of his father, Rayleigh's value for the electrochemical equivalent of silver (0.00111794 g/ampere-second corresponding to $F = 96488$) stood the test of time extraordinarily well. In 1893 it was to become the basis of the international ampere.

Many others were to attempt to refine Rayleigh's value. In a paper titled "The Universally Exact Application of Faraday's Law", T. W. Richards showed that (37):

... a galvanic current deposits essentially the same amount of silver from a solution of argentic nitrate in other [sodium and potassium] nitrates at 250°C as it does from an aqueous solution at 25°C, within 0.005 per cent. Taken in connection with previous work of Richards, Collins, and Heimrod, this result shows that Faraday's law is not a mere approximation, but is rather to be ranked among the most precise and general of the laws of nature.

However, Richard's value for the electrochemical equivalent of silver differed significantly from that of Rayleigh.

In spite of all the experimental ingenuity subsequently expended on the silver voltameter (or silver coulometer as Richards preferred to call it), nagging discrepancies remained. As a consequence, alternate chemical systems were investigated. The first of these was the iodine coulometer perfected by Washburn and Bates (39). This obviates the weighing of silver deposits (possibly containing occluded liquid) and has the further advantage of internal referencing since the reactions at the anode and cathode can be monitored by identical analytical methods:



Differences of 0.02% in the value of the Faraday calculated from the iodine and the silver voltameter remained, though many years later it was shown that these differences could be largely reconciled (39). Other systems studied included benzoic and oxalic acids (40), and 4-aminopyridine (41) coulometers. A major advance in precision was also achieved when the silver coulometer was changed from the silver-deposition to the silver-dissolution mode.

As we shall see, the various electrochemical determinations of the Faraday gradually converged over the years. Increasingly, however, they were challenged by non-electrochemical methods. Given the simple identity $F = Ne$, it is obvious the knowledge of any two quantities can be used to calculate the third. This relationship was first implicitly employed as we have seen by Stoney and was later used by J. J. Thomson to show that it yielded a plausible value for N , or rather for the Loschmidt Number. With the progress of X-ray crystallography, increasingly accurate values for N became available and the presently accepted value cited at the beginning of this article is based on this method (42). Precision measurements of the absolute charge on the electron by Millikan and others followed a more chequered path (43,44). As a consequence, in 1949 Sommer and Hipple still felt justified in claiming (45):

The value of the Faraday has been determined by a physical method ... This measurement is particularly significant because this new method is entirely different from the usual electrochemical derivation.

The method measures the Faraday directly and involves determinations of the proton rest mass, the gyromagnetic ratio of the proton, and the proton magnetic moment in nuclear magnets. In a 1968 summary paper, Zielen gave the comparative values shown in Table 1 for the electrochemical Faraday (46).

Since then the electrochemical methods have been made

Table 1. Comparative values of the Faraday in coulombs/equivalent.

* Silver dissolution coulometer	96,486.82 ± 0.66
* Iodine coulometer (new or recalculated)	96,486.5 ± 2.3
* Iodine coulometer (old)	96,490.7 ± 1.9
* Oxalate	96,481.6 ± 3
* Electromagnetic	96,487.6 ± 1.3

vastly more precise to yield $96,486.00 \pm 0.10$ (47). In addition the 4-amino pyridine coulometer of Diehl *et alia* yields $96,486.05 \pm 0.72$ (48). Problems of interpretation and correlation still remain as is apparent from the following wry comment by Diehl (49):

The Craig silver dissolution value was the accepted value from 1960 on, as recalculated successively, for the shift of the atomic weight scale to carbon-12 for two changes in the definition of the ampere, for a determination of the isotope ratio in the silver used, for a change in the definition of the volt, and for a more generous statistical treatment than Craig gave his own data. The physicists interested in the values of the various fundamental constants, given successively better values for various physical quantities, obtained the significantly lower value. This discrepancy, some 20 ppm, is some four times greater than the estimated uncertainty in the electrochemical value and ten

times the estimated uncertainty in the calculated value. So confident had the physicists become by 1973 that they felt it necessary to reject the Craig electrochemical value outright as "being subject to some serious error". It came, then, as a source of astonishment to them when the Iowa State University (ISU) value based on coulometric titrations of 4-aminopyridine was advanced in 1974, agreeing in most pleasant and surprising fashion with the Craig value (49).

Today both physical and chemical methods seem to be ineluctably and asymptotically approaching the "true" value, a value that appears astonishingly close to that put forward by Rayleigh in 1884. One is reminded of T. S. Eliot's lines:

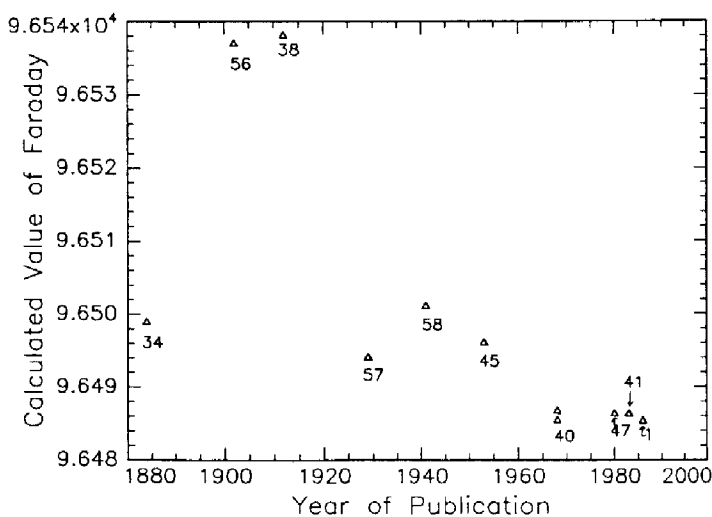
We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time.

When did the value for the electrochemical equivalent (of silver) become known as the Faraday? Later than one might expect it seems. The name "ohm" for the unit of electrical resistance was adopted in 1862. Five years later the unit of electrical capacitance was dubbed the "farad". "Volt", "coulomb", and "ampere" were adopted at the First International Electrical Congress held in Paris in 1881. Others had been quick to capitalize on the Faraday name. In *A Practical Treatise on the Medical and Surgical Uses of Electricity*, the second edition of which was published in 1875, we find index entries for: "Faradism", "Faradization", "Farado-contractility", "Farado-electrolyzation", "Farado-puncture or Electropuncture with the Faradic current (not much used)", and "Farado-susceptibility" (50). As is typical with that most faddish of professions, few of these pseudo-treatments and effects survive.

It is probably largely a coincidence that the words "mole", "Avogadro's Constant" and "Faraday" all entered the scientific literature during the ten years following the discovery of the electron. The term "mole" was introduced by Wilhelm Ostwald in the 1900 edition of his *Grundlinien der anorganischen Chemie* (51). The concept and name are introduced

almost in passing in a section titled "The Molar Weight of Hydrogen Peroxide". Understandably there is no mention of the associated (in our eyes) Avogadro Constant or Loschmidt number, for Ostwald was at that time the most visible apostate from atomic theory; indeed the suggestion has been made that the coinage of the word mole was a consequence of this apostasy (52). In this connection it is of interest to read Ostwald's Faraday Lecture to the Chemical Society (53) delivered "in the Theatre of the Royal Institution on Tuesday, April 19th 1904". It expresses a profound scepticism concerning the existence of atoms. One wonders if the ghost of Faraday murmured his approval.

The use of the term "Faraday" for the electrochemical



Values of the Faraday over the years. The year, value and reference number for the points on the graph are **1884**: 96,498.9 (34); **1902**: 96,536.9 (56); **1912**: 96,538 (38); **1929**: 96,494 (57); **1941**: 96,501 (58); **1953**: 96,496 (45); **1968**: 96,486.7 (40); **1968**: 96,485.4 (40); **1980**: 96,486.33 (47); **1983**: 96,486.05 (41), **1986**: 96,485.309 (1).

equivalent seems also to have arisen in Germany. In 1904 we find Lehfeldt writing in the opening chapter of his *Electrochemistry* (54):

This fundamental quantity of electricity, which occurs constantly in all writings on electro-chemistry, is called by the Germans a "faraday", a term which we in England may very well adopt.

The name soon took hold in England and elsewhere.

All threads of our story seem to come together in Jean Perrin's classic paper of 1909, "Mouvement Brownien et Réalité Moléculaire" (55):

Any two gram-molecules contain the same number of molecules. This invariable number N is a universal constant, which may appropriately be designated Avogadro's Constant.

... lastly, if the name faraday is given to the quantity F of electricity (96,550 coulombs) which passes in the decomposition of 1 gram-molecule of hydrochloric acid, it is known that the decomposition of any other gram-molecule is accompanied by the passage of a whole number of faradays, and, in consequence, that any ion carries a whole number of times the charge on the hydrogen ion. This charge e thus also appears as indivisible, and constitutes the atom of electricity or the electron (Helmholtz).

It is easy to obtain this universal constant if either of the constants, N or α [i.e., $3R/2N$], is known. Since the gram-atom of hydrogen in the ionic state, that is to say N atoms of hydrogen, carries one faraday, then necessarily, $Ne = F$...

All that remained was to improve the accuracy and precision with which N and/or e and/or F was known.

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A BIOGRAPHICAL CHECKLIST

The following is a checklist of biographies of Faraday. For teachers and students looking for a brief, accessible introduction, Thomas (1991) is highly recommended. For a more detailed biography, Williams (1965) is still the standard and is currently available in an inexpensive paperback reprint. Though long out of print, the volumes by Bence Jones (1869) and Thompson (1898) are also very worthwhile provided one is lucky enough to come across a copy.

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