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THE PATHWAY TO THE LAWS OF ELECTROLYSIS

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Michael Faraday has a massive physical monument - the vast number of books, papers, and general articles that have surveyed virtually every aspect of his life and work. This paper is the result of looking at a limited but important aspect of this monument.

As a life member of the Royal Institution of Great Britain, I spent part of a sabbatical leave under the direction of Professor Ronald King. At that time, he was planning the Faraday Museum in the basement of the Institution. I had the opportunity of reading some of Faraday's manuscripts, giving me a feeling of looking over his shoulder as he planned his next experiment. To mark the 150th anniversary of the 1834 publication of the Second Law of Electrolysis, I set up a commemorative exhibit in one of our departmental wall cases. Included was a display that cyclically highlighted some of Faraday's contributions to chemistry (1).

Although the histories of both chemistry and electricity go back to ancient times, electrochemistry as we know it today did

Christian von Grotthuss

not begin until 1800, when Volta's account of the so-called "pile" was published (2). This device, and developments that rapidly followed, provided for the first time a source of continuous, reasonably steady, and comparatively large amounts of electricity. As Faraday was to point out later, the then well-known static or "common" electricity is characterized by high intensity but very little quantity. Nicholson read Volta's communication before its publication, with the result that a pile was constructed and used to prepare hydrogen and oxygen by the electro-decomposition of water (3). From this deceptively simple experiment sprang the vast and diverse field of electrochemistry (4).

Although the fact of the electro-decomposition of water was obvious, a satisfactory explanation of the mechanism involved was not, despite various efforts over several decades. In the long-studied area of "common" electricity, beliefs were in the existence of two forms of electricity, positive and negative; "like signs repel, unlike, attract"; and "action at a distance", governed by an inverse square law. These beliefs were the inheritance of early workers concerned with voltaic electricity. In attempting to explain electro-decomposition, this inheritance was largely a handicap.

In 1801, Johnann Wilhelm Ritter (1776-1810), a German physician, used V-shaped tubes to re-examine the electro-decomposition of water (5). This shape prevented transfer of matter from one pole to the other by convection or agitation. To
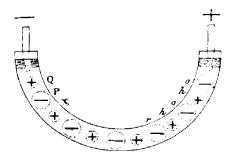
explain the fact that gases appear only at the poles, he theorized that water plus positive electricity gives oxygen, whereas water plus negative electricity gives hydrogen.

Christian von Grotthuss (1785-1822) suggested that water molecules are polarized, becoming centers of attractive and repulsive forces which vary inversely as the squares of the distances from the respective poles (6). Thus the hydrogen and oxygen in a given molecule will be subject to attractive and repulsive forces, acting in opposite directions. Hydrogen and oxygen produced by the breakdown of this molecule would not escape, but would attack adjacent molecules. The production of the gases only at the poles could be explained by a chain-like abstraction mechanism.

The 1806 Bakerian Lecture, given to the Royal Society by Humphry Davy (1778-1829), was based on his own electro-chemical experiments and ideas (7). His great contribution was to connect chemical affinity with electrical forces. Two of his experiments are shown in figure 1. Potassium sulfate solution was placed in each of two cups, with a moistened strip of asbestos as connector, as shown in (a) of figure 1 (8). A current was passed through the system for three days, then the contents of the cups were analyzed. The left cup contained sulfuric acid, the right, potash; Davy had achieved the complete separation of the components of the salt. The Grotthuss mechanism was obviously inadequate here; the "chain of molecules" must break for such completeness to be possible.

If the component acid and base existed even briefly in the solution rather than being generated at the electrodes, their detection in transit should be possible. Davy therefore set up the arrangement shown in (b) of figure1, the contents of the three vessels being as indicated (9). Moistened litmus paper strips X and Y were placed in contact with the asbestos connectors. On passing a current, the sulfuric acid moving towards the positive pole should redden strip X. This did not occur; instead, Y began to redden, and this effect slowly diffused into the central vessel. Apparently, ordinary chemical affinity had been suspended by the flow of electricity; acids could be passed through bases, and vice versa!

Although he had shown that the Grotthuss mechanism could not account for the complete decomposition of potassium sulfate, Davy wrote "In the cases of the separation of the
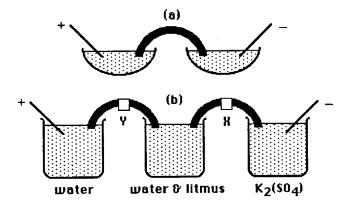

Figure 1. Davy's experiments with potassium sulfate solution: (a) the complete separation of acid and alkali (b) an attempt to detect the transit of sulfuric acid.

constituents of water, and of neutral salts forming the whole of the chain, there may possibly be a succession of decompositions throughout the fluid" (10). When Faraday surveyed the suggestions of others as part of his own attack on the elucidation of the mechanism of electro-decomposition, he noted the lack of specificity of Davy's theory.

In 1814, during the European tour with Davy, Faraday met Auguste de la Rive (1801-1873), Professor of Physics at Geneva. Faraday corresponded with him for many years. De la Rive reconsidered electrochemical action during the 1820s (11-13). He postulated that the current flowing from the positive pole attacks the nearby molecules, grasping their hydrogen if water, or their base, if the molecules are salts. The oxygen or acid is left behind, while the positive current carries the substance with which it is united to the negative pole. This metal conductor cannot admit the transported substance, so hydrogen or base is released as the electricity enters the negative pole. The reverse current acts analogously on the oxygen or acid in the molecules near the negative pole. De la Rive did not accept a chain-type mechanism, believing the bulk of the liquid acted merely as a conductor. With the concept of positive and negative currents, only portions of which were involved in transporting matter, De la Rive's theory became very complicated (13).

When Faraday began his work on electro-decomposition, he was faced with theories which had about one real or implied common view: the poles acted at a distance upon the constituents of the substances being decomposed. Another problem was the apparent existence of various forms of electricity. Faraday was convinced that all forms were manifestations of a single identity. By exhaustive examination of the literature and his own extensive experiments, he was able to prove his conviction that electricity, "whatever may be its source, is identical in its nature" (14).

Decompositions could be brought about by the use of a

Grotthuss' chain mechanism for electroytic conduction.

voltaic pile. Faraday therefore examined claims that common electricity could produce similar decompositions. This form of electricity is noted for its ability to produce sparks. By a litmus-paper version of Cavendish's production of nitric acid by sparking in air, Faraday showed that the mere heat of an electric discharge could bring about a chemical reaction. He was therefore very careful to use spark-free conditions in his own experiments.

The arrangement for one of these is shown in figure 2. Three pieces each of litmus paper *ppp* and turmeric paper *nnn* were moistened with sodium sulfate solution and placed on a glass plate as litmus-turmeric pairs (turmeric is reddened by alkalis, litmus by acids) (15). Platinum wire conductors were bent so that they made point contact with the papers, as shown. Wire *m* was connected to a large frictional electrical machine, while wire *t* went to the "discharging train." This was a wire connected to a gas pipe or water pipe. Nowadays, we would say the wire *t* was grounded. Brief operation of the machine caused formation of acid at all point contacts on litmus and of alkali on turmeric paper.

Apart from demonstrating that common electricity and voltaic electricity produced the same chemical effects, this finding assured Faraday that he could use the high-intensity output of his machine whenever poor conductance of a system under investigation prevented the use of a battery. He had already begun to suspect that the poles in an electrochemical system have no mutual decomposing dependence. On occasion, he used his finger as one of the poles! Then came the prescient remark (16):

When electro-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.

Incidental to his attempts to demonstrate the reality of this belief, Faraday commented on the value of the galvanometer for measuring what we would now term the current strength in a circuit (17). The development of this instrument has a long and interesting history (18). Faraday mentions one advance, the introduction by Ritchie of a fine glass thread as the torsion element (19). More than half a century was to pass before C. V. Boys demonstrated the superiority of quartz threads over
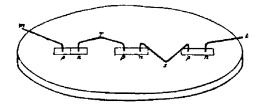

Figure 2. Multiple formation of acid and alkali by "common" electricity.

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

those of glass (20).

Faraday took four thicknesses of paper, equally moistened with a standard solution of potassium iodide, and placed them on a platinum spatula. A vertical platinum wire, 1/12 of an inch in diameter with a squared-off end, pressed on the paper sandwich, thus defining a definite area of contact. With a single platinum-zinc-dilute nitric acid cell as a source of electricity, the galvanometer in the circuit gave a steady deflection. By shifting the end of the wire from place to place on the test paper, the effect of varying the time of passage of the current could be observed as the extent of colorization due to the liberation of iodine. Faraday counted the beats of his watch as a means of timing. One finding was that, to match the effect produced by only an eight-beat period of voltaic current, he needed 30 turns of his frictional machine! A finding that 28 turns were insufficient probably indicates the attainable level of precision. Then comes the statement (21):

It also follows that for this case of electrochemical decomposition, and it is probable for all cases, that the *chemical power, like the magnetic force, is in direct proportion to the absolute quantity of electricity which passes.*

Here we have a statement of the First Law of Electrolysis, with a demonstrated precision of possibly about ten percent! An extensive treatment of the factors that led to the formulation of this law has been given by James (22).

Faraday had noted that "... the effects of decomposition would seem rather to depend upon a relief of the chemical

affinity in one direction and an exaltation of it in the other"
(23). Then the elements of a compound should separate and
then combine with neighbouring particles, on the lines of the
mechanism suggested by Grotthuss (6). Faraday thought that
if a current could decompose a solid, then structural informa-
tion might be obtained. He began to freeze solutions, aiming
to trace and catch certain elements in their transit. He was
surprised to find that even a thin film of ice interposed in the
circuit stopped the flow of electricity even from a very power-
ful battery. However, a gold-leaf electrometer could be dis-
charged through ice, which must therefore possess some small
conducting power (24).

Realizing that the change in conducting power exhibited by
the ice-water transition might also apply to other solid-liquid
pairs, he began to study the electrochemistry of fused salts.
Actually, Davy knew as early as 1801 that potassium nitrate,
caustic potash and soda conduct electricity when melted,
although, as Faraday indicated, he appeared to have forgotten
this 11 years later (25).

Faraday began by fusing lead chloride and silver chloride
on pieces of glass. He found that the melt conducted and
electro-decomposition could be achieved. He then used a
small V-shaped glass vessel, so that the decomposition prod-
ucts could be observed. The two compounds mentioned gave
chlorine at the positive pole, metals at the other. Molten
potassium nitrate or chlorate gave alkali, or even potassium at
the negative pole, and gases such as oxygen at the other pole.
Faraday used fusion on platinum when temperatures higher
than possible with glass were required. He showed that many
salts, oxides and sulfides became conductors when melted; in
general, the liquids were much better conductors than water.
The effect was not universal - sulfur, phosphorus, naphtha-
lene, etc., remained non-conducting when fused.

At the end of his paper, dated 15 April 15 1833, Faraday
summarized his results "... not without fearing that I may have
omitted some important points" (26). Before he continued his
fused-salt experiments, he returned to his suspicion that elec-
tro-decomposition did not necessarily depend upon the means
by which the electricity entered or left the substance under
investigation. He again used litmus and turmeric papers that
were moistened with sodium sulfate solution. However, the
papers, along with their point-contact wires, were placed on
separate glass plates. String wetted with the same solution
provided electrical connection between the two test papers. On
turning the electrical machine, the production of acid and of
alkali occurred, just as if the papers were in direct contact. This
occured even if the string was 70 feet long! The supposition by
others that both poles mutually "act at a distance" thus hardly
seemed plausible; for a fixed quantity of electricity, the dis-
tance between the poles had no effect upon the amount of
decomposition.

After several other experiments, Faraday used the arrange-
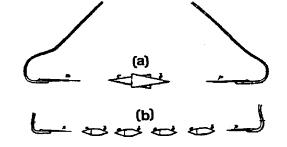ment shown at in (a) of figure 3 to produce decomposition

Figure 3. Electro-decomposition without contact with metallic
poles: (a) single effect, (b) multiple effect.

when there was *no contact* with any metal poles (27). A
triangular piece of litmus paper *a* was moistened with sodium
sulfate solution and partially overlapped by a similarly mois-
tened triangle of turmeric paper *b*. Needles *n* and *p* were
supported on wax so that the gaps between the points and the
tips of the papers were about half an inch. Needle *n* was
grounded, while *p* joined to the electrical machine. On work-
ing this, the tips of both papers became reddened, indicating the
evolution of both acid (litmus) and alkali (turmeric), despite
the absence of any real poles. Faraday extended the demon-
stration by using four isolated pairs of strips, as shown in (b) of
figure 3. All litmus tips indicated free acid, the turmeric tips,
free alkali. Faraday concluded that the power which causes
electrochemical decomposition appears to be exerted in the
solution, and not at the poles (28).

Having shown that electrochemical decomposition could
occur at an air-solution interface, Faraday demonstrated that
such a decomposition could also occur at a water-solution
junction (29). He had by now reached some important conclu-
sions (30):

* Not a single fact supports the concept of "two electrici-
ties", i.e., positive and negative.

* There is no reason to consider the influence of the
electric current as compound or complicated. This influence
has not been resolved into simpler influences, and is best
conceived as an "axis of power having contrary forces, exactly
equal in amount, in contrary directions".

* The concept of rectilinear action between the poles is
not necessary. Lines of action would be expected to diverge
rapidly from point-contact poles in a liquid.

* Electrochemical decomposition is due to a weakening
of the ordinary chemical affinity in one direction, and a
strengthening of it in the opposite direction. Particles of
opposite kinds will tend to pass in opposing courses. This
effect is essentially dependent upon the "mutual chemical
affinity" of these opposite species.

Like his predecessors, Faraday believed that the decompo-
sition into oppositely-charged particles was caused by the
passage of the electric current. The Arrhenius ionic theory,
postulating the production of mobile ions by the mere act of

dissolution of an electrolyte, introduced another way of think-
ing. However, the general acceptance of this theory, published
in full in 1887 (31), was by no means instantaneous.

Faraday had accounted for the major effects of electro-
chemical decomposition:

* The products appear only at the poles, and are expelled,
not drawn out by attraction.

* The transfer of elements is accounted for. Thus, in the
passage of current between silver wires in fused silver chlo-
ride, the positive wire is eaten away, while the negative wire
grows.

* The more the constituents of a substance have opposing
chemical affinities, the more readily they separate in electro-
decomposition. Davy's astonishing finding that acids could
pass through alkalis, and the reverse, is actually the essential
condition for the decomposition of a salt.

Planning to work quantitatively, Faraday began to con-
struct a device that he termed a volta-electrometer. This was
to be able to measure the "total amount" of electricity used in
an experiment. (A galvanometer merely measures the current
strength, or flow rate, at any given instant.) The idea was
simple; let the current decompose acidulated water and meas-
ure the volume of hydrogen plus oxygen thus evolved.

He first used a graduated tube with long platinum poles
sealed through the closed end. After filling with dilute acid, the
tube was inverted in a cup of the same liquid and the poles were
connected to a battery (32). Gas evolution occurred but, when
the battery was disconnected, the volume of gas began to
diminish and finally vanished. Faraday found that platinum
that had been used as the positive pole in the decomposition of
water could cause quite vigorous destruction of a previously-
prepared 2:1 hydrogen-oxygen mixture. Platinum that had
been used as the negative pole was inactive. At this stage,
Faraday sidetracked to investigate this induced chemical reac-
tion - what we would now term the heterogeneously catalyzed
reaction of the two gases to form water.

Returning to the design of the volta-electrometer (Faraday
later shortened the term to voltameter; the present-day term is
coulometer), Faraday now knew that he must keep the positive
pole out of any mixed-gas space (33). In one approach, hydro-
gen and oxygen are collected in separate graduated tubes. In
another version, only one of the gases is collected, while the
other escapes.

He then thought of a simple double-plate configuration,
diagrammed in figure 4; the plates remain totally submerged
and cannot affect the collected mixed gases. The plates can be
close together, thus lessening the electrical resistance of the
device. Faraday described three versions of this design.

He then carefully examined the variables that might control
the performance. For absolute measurements the collection of
hydrogen only, and correction of its volume to standard condi-
tions, are recommended.

Now beginning to use his new (our present) terminology,

Faraday defined "primary
products" of electro-decom-
position as those which re-
main unaltered when they are
evolved. Examples are hydro-
gen and oxygen from water,
or acid and alkali (both com-
pounds!) from sodium sulfate
solution. "Secondary prod-
ucts" occur when the separat-
ing substances are changed at
the "electrodes". Thus evolv-
ing oxygen can attack a car-
bon "anode", giving rise to
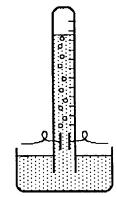carbon dioxide. At this junc-
ture Faraday came to a con-

Figure 4. A double-plate
volta-electrometer.

clusion that would have important consequences for the rest of
his experimental program (33):

... when aqueous metallic salts are decomposed by the current, the
metals evolved at the *cathode*, though elements, are *always* secondary
results, and not immediate consequences of the decomposing power
of the electric current.

It was for this reason that Faraday decided to use fused salts as
"electrolytes" in his quantitative studies, thus avoiding any
ambiguities that might arise from the use of aqueous systems
(34).

Figure 5 shows the arrangement used to investigate tin
protochloride (tin(II) chloride). The cathode, a platinum wire
coiled into a knob at one end, was weighed and then sealed into
a glass tube so that the knob was at the bottom. The salt was
then introduced and heated to melt it. After the introduction of
a platinum wire anode, the cathode was connected to a volta-
electrometer and battery power was applied. Volatile "bichlo-
ride of tin" (tin(IV) chloride) was produced at the anode, while
the tin liberated at the cathode formed an alloy with platinum
that was liquid at the fusion temperature. After collection of a
suitable volume of gas in the volta-electrometer, the anode was
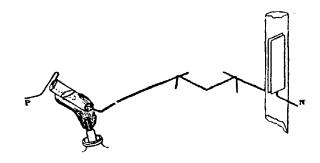removed from the melt, which was then allowed to solidify.

Figure 5. Determination of the electrochemical equivalent of tin.

The vessel was broken open and, after removal of salt and glass from the cathode, this was reweighed to obtain the weight of tin deposited.

From the results of four experiments, Faraday found an average value of 58.53 for the electrochemical equivalent of tin. The value of the chemical equivalent that he accepted was 57.9. Faraday gives the data concerning one of his experiments on tin protochloride, as well as the method of calculation. It is strange that the many glowing accounts concerning Faraday's work on the laws of electrolysis say little about his apparent lack of appreciation of "significant figures". However, a teacher in a grammar school has made the comment: "It is not only our pupils who claim five figure accuracy from three figure measurements" (35).

In the electrolysis of fused lead chloride, Faraday found that some platinum, dissolved from the anode, was cathodically deposited along with the lead. He therefore changed to a graphite anode. The mean of three experiments gave 100.85 as the electrochemical equivalent of lead. A similar experiment with lead borate gave 101.29, "which is so near to 103.5 (the "chemical" value) as to show that the action of the current had been definite."

Having passed the same current through protochloride of tin, lead chloride, and water, Faraday remarked (34):

It is needless to say that the results were comparable, the tin, lead, chlorine, oxygen, and hydrogen being *definite in quantity* and electrochemical equivalents to each other.
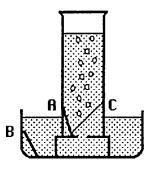
Here is an implied statement of the Second Law of Electrolysis. No data are given; if the accuracy was much the same as in the separate measurements for tin and lead, Faraday had proved experimentally that this law holds to within a few percent.

In the electrolysis of fused silver chloride between silver electrodes, the anode dissolves and silver is deposited on the cathode. When attempts were made to perform this experiment quantitatively, the crystalline nature of the deposit gave problems. Faraday was more successful with fused lead chloride, finding that the loss in weight at the lead anode was equal to the gain at the cathode. The experiment gave 101.5 as the electrochemical equivalent of lead. Similar "metal transference" experiments with lead iodide and tin protochloride gave values of 103.5 and 59 for lead and tin, respectively.

Faraday, actually determined the electrochemical equivalent of zinc by use of aqueous media (36). However, it seems that his principal aim was to show that "the electricity which decomposes, and that which is evolved by the decomposition of a certain quantity of matter, are alike". The method involved the spontaneous anodic dissolution of zinc to cause displacement of hydrogen at the cathode.

The apparatus is diagrammed in figure 6. Dilute sulfuric acid was left overnight after the addition of a small piece of zinc. In this preconditioning step, dissolved air was expelled by liberated hydrogen. A gas jar was entirely filled with this acid and inverted in a basin containing the same liquid. Amalgamated zinc plates A and B (amalgamation inhibits direct attack by the acid), were weighed and introduced as shown. Then platinum plate C was introduced, so that it touched plate A. Hydrogen rose only from the platinum plate. After 10 to 12 minutes, plates A and B were

Figure 6. Determination of the electrochemical equivalent of zinc by internal electrolysis.

withdrawn, rinsed, dried, and reweighed. The hydrogen was transferred to a water trough for volume measurement. Faraday turned his measured volume of hydrogen, 12.5 cu. in., into a corrected volume of 12.15453 cu. in. With logic so devastating in other respects, it is indeed surprising that Faraday did not sense the implication of his "expansion of figures." However, the value, 32.31, that he found for the electrochemical equivalent of zinc agrees closely with the then accepted chemical equivalent, 32.5.

By 1834, Faraday had placed electrolysis on a sound quantitative basis. He then turned to a consideration of the absolute quantity of electricity associated with an atom of matter and to an examination of the rival "metal contact" and "chemical" theories of the action of the voltaic pile. These stories are beyond the scope of the present paper.

With the advantage of hindsight, we can see that Faraday paid a high price for his belief that metal deposition from aqueous solutions is a secondary process, and therefore possibly subject to ambiguity. He turned to the much more difficult fused-compound electrolyses, becoming a pioneer in this important field. It is ironic that deposition of silver from aqueous silver nitrate solution was later shown to be so precise that the procedure was used for many years to define the international ampere.

Faraday is unique in having two units named for him. These are the "farad", the unit of capacitance, and the "Faraday", the unit of electrochemical action. No doubt Faraday would have been pleased to learn that, when the latter unit was redetermined at the National Bureau of Standards, the value, precise to about 1 part in 50,000, depended upon the loss in weight of a silver anode when a known amount of electricity was passed through the perchloric acid electrolyte (37).

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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):

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

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

F $= 9.6485309(29) \times 10^4$ 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