Faraday and Electrochemical Decomposition

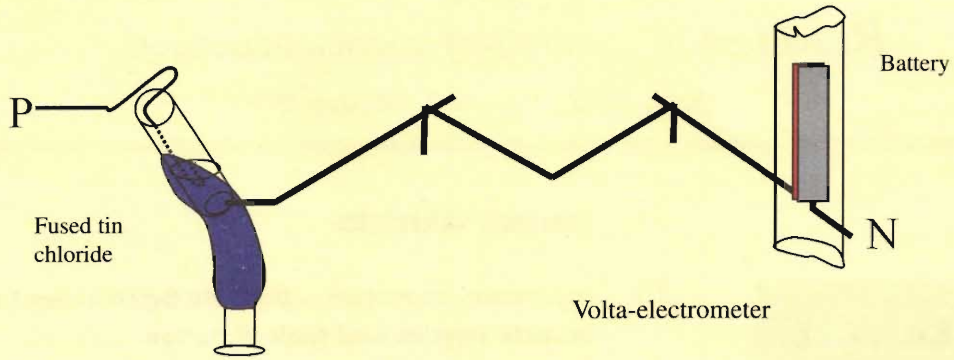
Among the many areas of science where Michael Faraday has left his mark, electrochemistry is most recognizably associated with his name through the universal constant, F, named after him. Sir Humphry Davy, who introduced Faraday to the world of science, had been working for sometime on electrolysis and had carried out electrodeposition of potassium from solid potassium hydroxide in 1807. Faraday was fascinated by the effect of various forms of energy ('force' as he called it) on chemical/mechanical systems (matter). Thus he studied the effects of solar heat and 'terrestrial' heat on heating and cooling of bodies, a comparison of 'static' and 'dynamic' electricity, interconversion of chemical/electrical/mechanical/magnetic 'force'. From his studies of the electrolysis of many chemical systems, he came to the following conclusion, "The chemical power of a current of electricity is in direct proportion of the absolute quantity of electricity which passes." At that time (1833) the distinction between the quantity of electricity (now measured in *coulomb*) and electrical energy (measured in *joule*) was not clearly understood. As a result Faraday's law was severely criticized by some of his contemporaries, especially by Berzelius, who could not believe that the same quantity of electricity would separate the constituents of different compounds having different amounts of energy associated with their formation. Now as we know, the energy changes associated with different electrochemical reactions can have very different magnitudes, even though the same quantity of electricity is involved, since the electrical energy depends on the potential difference as well as on the quantity of electricity (*volt* × *coulomb* = *joule*). If one mole of a univalent ion is deposited (e.g., silver deposited from a solution of silver nitrate) the charge consumed (quantity of electricity) is,

$$F = N \times e,$$

where N is the Avogadro number and e is the electronic charge. The charge, F, according to Faraday's law is a constant and is known as *Faraday* (equal to 96,485 coulomb). As is obvious, F is a product of two fundamental constants and provides an alternative basis for the determination of the value of these constants. Faraday's law also provides the basis for the fundamental unit of current, ampere. The ampere is defined as the steady current which, when passed through a solution of silver nitrate in water, deposits silver at the rate of 0.00111800 g s^{-1}. It is ironic that Faraday's law is, indirectly, a manifestation of the atomic theory proposed by Dalton because Faraday himself was highly skeptical of the atomic theory. One gets a glimpse of how Faraday himself introduced the law to a lay audience, from a lecture given as part of the Christmas Lecture Series in 1859. His description after the electrolysis of water was as follows:

Now, when water is opened out in this way by means of the battery, which adds nothing to it materially, which takes nothing from it materially (I mean no matter; I am not speaking of force), which adds no matter to the water, it is changed in this way – the gas which you saw burning a little while ago, called hydrogen, is evolved in large quantity, and the other gas, oxygen, is evolved in only half the quantity; so that these two areas represent water, and these are always the proportions between the two gases.

Oxygen ... 88.9 Hydrogen ... 11.1
Water ... 100.0



Apparatus used for the determination of chemical equivalent of tin. Fused tin choride is electrolyzed using an electrolysis cell with two electrodes. The difference in weight of the cathode before and after the deposition of the metal is used to determine the chemical equivalent. The electricity passed through the cell is determined using a volta-electrometer.

But oxygen is sixteen times the weight of the other – eight times as heavy as the particles of hydrogen in the water; and you therefore know that water is composed of nine parts by weight – one of hydrogen and eight of oxygen; thus:

Hydrogen	46.2 cubic inches	= 1 grain
Oxygen	23.1 cubic inches	= 8 grains
Water (steam)	69.3 cubic inches	= 9 grains.

Faraday's researches required that he develop appropriate terms to describe his work and this led him to coin, with help from his polymathic Cambridge friend Whewell, the terms that are now commonly used in electrochemistry. The electrochemical terms, *anode* (from the Greek, *ana* for *up* and *hodos* for *road*), *cathode* (from *kata* for *down*), *ion* (for *wanderer*), and consequently *anion* or *cation*, were first used by Faraday.

In electrochemical literature, there are two electrical units named after Faraday, one is Farad (F) and the other is Faraday (Fd). The first is the SI unit of electric capacitance. One Farad is defined as the ability to store one coulomb of charge per one volt of potential difference between two conducting surfaces. Faraday is, on the other hand, the unit of charge that is equivalent to 96,485 coulombs.

Faraday was a true pioneer of scientific discoveries. His discoveries have had an immense effect on successive scientific and technological development. It is appropriate to finish the article with a quote by his successor Tyndall, "Taking him for all and all, I think it will be conceded that Michael Faraday was the greatest experimental philosopher the world has ever seen; and I will add the opinion, that the progress of future research will tend, not to dim or to diminish, but to enhance and glorify the labours of this mighty investigator".

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