

# Faraday's Laws or Faraday's Law?

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## Question

I have noticed that some textbooks refer to Faraday's laws of electrolysis whereas others refer just to Faraday's law. Which is correct and why?

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## Answer

In sharp contrast to the approach taken in earlier columns, this question is best answered mathematically, rather than historically, by first providing a rigorous derivation of Faraday's law(s) using the notational system introduced by the Belgian physicist, Théophile De Donder, (1872-1957), in the 1920s (1). Thus, for a generalized chemical reaction:



the change in the amount or extent of reaction,  $d\xi$ , measured in units of moles of reaction events, is defined as the change in the moles,  $dn_s$ , of any of the various species,  $s$ , in the reaction, weighted by its stoichiometric coefficient,  $\nu_s$ , in the balanced equation:

$$d\xi = dn_s/\nu_s = dn_A/a = dn_B/b = dn_C/c = dn_D/d \quad [2]$$

where  $\nu_s$  is assumed to have the units of moles of species  $s$  per mole of reaction and to be inherently negative for reactants and inherently positive for products. Using these conventions, De Donder was also able to express the rate of a reaction in terms of the change in its extent of reaction per unit time (2):

$$d\xi/dt = (dn_s/dt)/\nu_s \quad [3]$$

Applying this notation to the equation for a typical electrochemical reduction:

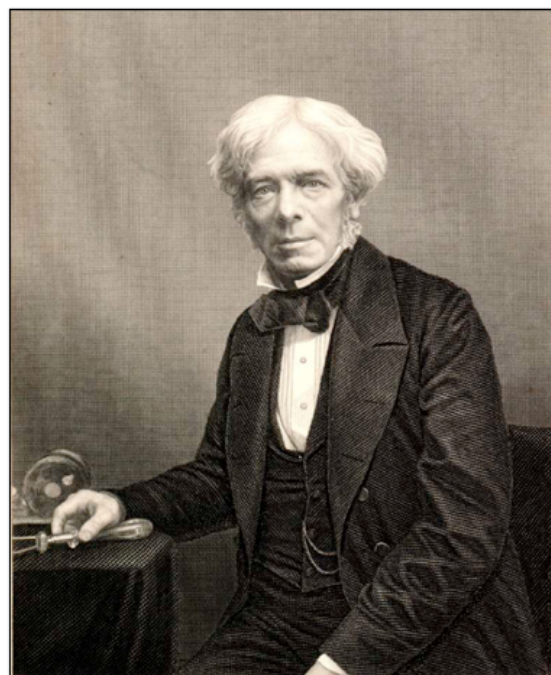


Figure 1. Michael Faraday (1791-1867).

we can express its rate of reaction,  $d\xi/dt$ , in terms of either the weighted change in the moles of electrons consumed per unit time,  $(dn_e/dt)/\nu_e$ , or the weighted change in the moles of any one of the various chemical species generated or consumed per unit time  $(dn_s/dt)/\nu_s$ :

$$(dn_e/dt)/\nu_e = (dn_s/dt)/\nu_s \quad [5]$$

Multiplying both sides of this equation by Faraday's constant,  $F$ , having the units of coulombs per mole electrons, and using the fact that the product,  $Fdn_e$ , is equal to the change in the number of coulombs,  $dQ$ , and its time derivative,  $dQ/dt$ , is, in turn, equal to the electric current,  $i$ , gives us:

$$F(dn_e/dt)/\nu_e = (dQ_e/dt)/\nu_e = i/\nu_e = F(dn_s/dt)/\nu_s \quad [6]$$

Regrouping the terms and defining the ratio  $(\nu_e/\nu_s)$  as  $z_s$ , with the units of moles of electrons per mole of species  $s$ , we obtain the differential form of Faraday's law:

$$idt = (v_e/v_s)Fdn_s = z_s Fdn_s \quad [7]$$

In an introductory chemistry course we usually further assume that the current,  $i$ , is constant over time, thus allowing us to use a simple integrated form of equation 7 instead:

$$it = z_s F n_s \quad [8]$$

in which the two most important electrical variables ( $i$  and  $t$ ) are segregated on the left and the two most important chemical variables ( $z_s$  and  $n_s$ ) are segregated the right.

Textbooks have traditionally summarized Faraday's original work on electrolysis, which dates from the 1830s, in the form of two verbal statements known collectively as Faraday's laws of electrolysis (3):

*a. The mass of any substance deposited or dissolved is proportional to the absolute quantity of electricity that passes through the cell.*

*b. The masses of different substances deposited or dissolved by the same quantity of electricity are proportional to their electrochemical equivalent weights.*

It should be noted that, although these textbook statements accurately summarize his results, Faraday himself never clearly distinguished between these two statements but rather combined them into a single verbal law which he called the "doctrine of definite electrochemical action" (4):

*... the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes ... the results obtained for any one substance do not merely agree among themselves, but also with those obtained from other substances, the whole combining together into one series of definite electrochemical actions.*

By the term "definite" Faraday meant that the results were in keeping with the law of definite proportions or equivalents.

In order to recover these two laws from equation 8, we need to make use of the fact that the moles,  $n_s$ , of species  $s$  is equal to its mass,  $m_s$ , divided by its molar weight  $MW_s$ , which, upon substitution into equation 8, gives the result:

$$it = z_s F (m_s / MW_s) \quad [9]$$

Solving this for  $m_s$  and recognizing both that the terms in parentheses on the right side of the resulting equa-

tion are a constant,  $k_s$ , for a given species and that the  $it$  term is equal to the total charge  $Q$ , we obtain the mathematical equivalent of Faraday's first law of electrolysis:

$$m_s = (MW_s / z_s F) it \quad \text{or} \quad m_s = k_s Q \quad [10]$$

Regrouping the terms again and recognizing that  $MW_s / z_s$  for a given species,  $s$  is equal to its electrochemical equivalent weight,  $EW_s$ , we obtain, provided that  $Q$  is kept constant, the mathematical equivalent of Faraday's second law:

$$m_s = (Q/F)(MW_s / z_s) \quad \text{or} \quad m_s = k'(EW_s)Q \quad [11]$$

Based on these derivations, we can draw a number of important conclusions:

1. Since the two traditional verbal laws can be combined into a single mathematical equation (equation 8), it is more appropriate to talk of Faraday's law rather than Faraday's laws (5).

2. As demonstrated by the Italian chemist, Carlo Matteucci (1811-1868), in 1839, the relationship embodied in equation 8 is equally applicable to both an electrolysis cell and to a voltaic cell (in which case it correlates the current generated by the cell with the amount of reaction within the cell, rather than the amount reaction in the cell with the applied current) (6). Hence, it is no longer appropriate to talk of Faraday's law of electrolysis. Rather it should be called, following Faraday's original suggestion, Faraday's law of electrochemical action, in which the concluding qualifier is necessary in order to distinguish it from "Faraday's law of magnetic induction," as used in the field of electromagnetism.

3. Our derivation clearly shows that, in contrast to the Nernst equation, which is thermodynamic in nature, Faraday's law of electrochemical action is kinetic in nature (7).

Though I was taught equation 8 as an undergraduate, I was rather surprised to recently discover that the author of the Freshman textbook used at Cincinnati seems to be unaware of it and that the entire subject is essentially missing from the textbook currently being used in our undergraduate physical chemistry course. A quick review of additional Freshman and physical chemistry textbooks yielded similar results. In many cases only the verbal equivalent of the first law was given or a series of special-case relationships similar to equations 10 and 11, thus suggesting that it is time that we finally update our textbook coverage of this subject.

## Literature Cited

1. The most accessible English-language account of De Donder's original work is found in T. De Donder, P. van Rysselberghe, *Thermodynamic Theory of Affinity*, Stanford University Press: Stanford, CA, 1936.
2. For homogeneous reactions, the reaction rate is usually expressed as the rate per unit volume,  $d\xi/Vdt$ , whereas for heterogeneous reactions, it is usually expressed as the rate per unit area,  $d\xi/Adt$ . If Faraday's law is derived using the latter, rather than just the simple rate, then it must be restated in terms of current densities,  $i/A$ , which is not normally done in an introductory course.
3. See, for example, S. Glasstone, *The Elements of Physical Chemistry*, Van Nostrand: New York, NY, 1946, p. 401.
4. M. Faraday, "Experimental Researches in Electricity VII," *Phil. Trans. Roy. Soc.*, **1834**, 124, 77-122, Reprinted in M. Faraday, *Experimental Researches in Electricity*, Vol. 1, Quaritch: London, 1839, pp. 195-258, and in abridged form in M. Faraday, *Experimental Researches in Electricity*, Dent: London, 1914, pp. 145, 148, 152, 156.
5. An earlier attempt to reduce Faraday's laws to a single equation, in which several of the variables in equation 8 are implicit, rather than explicit, may be found in F. C. Strong, "Faraday's Laws in One Equation," *J. Chem. Educ.*, **1961**, 38, 98.
6. C. Matteucci, "Sur la force électro-chimique de la pile," *Ann. chim. phys.*, **1835**, 58, 75-80. See also R. E. Ehl, A. J. Ihde, "Faraday's Electrochemical Laws and the Determination of Equivalent Weights," *J. Chem. Educ.*, **1954**, 31, 226-232.
7. Both reference 1 and G. W. Castellan, *Physical Chemistry*, 3rd ed., Addison-Wesley: Reading MA, 1983, pp. 874-875 are among the few sources that explicitly acknowledge the kinetic nature of Faraday's law.

*Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to [jensenwb@ucmail.uc.edu](mailto:jensenwb@ucmail.uc.edu)*