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Resumé of Values of the Faraday

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A resumé is given of the determinations of the value of the Faraday. Values obtained by silver deposition, iodide oxidation, oxalate oxidation, the omegatron, and silver dissolution are reviewed. All values are converted to the unified ^{12}C international scale of atomic weights using the international atomic weights of 1967. Values of the Faraday are given in terms of both the NBS (legal) and absolute units of electrical measure. In the latter the new value for the acceleration due to gravity is used in computing the absolute value of electric current. On this basis and using the atomic weight of silver determined by Shields, Craig, and Dibeler, and converting to the ^{12}C scale, the value of the Faraday is 96,486.9 ± 1.6 absolute coulombs per gram-equivalent which differs by only 1 part per million from the value recommended by the National Academy of Sciences—National Research Council. If the atomic weight of silver recommended in 1967 by the International Atomic Weight Commission is used, the Faraday on the new gravity value is 96,486.5 ± 1.6 absolute coulombs per gram-equivalent which differs by 5 parts per million from that recommended by the National Academy of Sciences—National Research Council. No change in the value of the Faraday adopted by the NAS—NRC Committee is recommended.

Key Words: Coulometers; Faraday; inclusions in silver coulometers; values of Faraday.

In 1962, Remy [1] [1] in a review article converted all published values of the Faraday to the 1961 unified ^{12}C scale of atomic weights. In so doing, he used the international atomic weights of 1961 and several inappropriate conversion factors. It is the purpose of this resumé to clarify this matter and to bring the values of the Faraday as determined by various experimenters, up to date. International atomic weights of 1967 are used.

1. Silver Deposition Method

The classical method for the determination of the Faraday involves the electrolytic deposition of silver on platinum from an aqueous solution of silver nitrate. This method has been extensively studied and under closely specified conditions was used for many years in defining the international ampere. The international ampere was defined as that steady or unvarying current which when passed through a solution of silver nitrate in water deposits 1.11800 mg of silver per second [2]. This definition became the definition of the international ampere in the United States by Public Law 105 passed by the 53rd U.S. Congress [3]. The value of the Faraday on this basis, using the 1967 international atomic weight of silver [4],[2] is then:

$$F=\frac{107.868\pm 0.001}{0.00111800}=96{,}483.0\pm 0.9 \text{ int C g-equiv}^{-1},$$

where the ±0.001 represents the "experimental uncertainty" in the atomic weight of silver.

At the time the above definition was formulated it was realized that additional and more accurate measurements were needed to place the electrical units more closely on the theoretical MKSA electromagnetic units. By 1948, after interruptions caused by the two World Wars and after improvements in techniques, an accurate determination of the electrical quantities in centimeter-gram-second electromagnetic units was achieved and on January 1, 1948, changes from international to absolute units were officially made internationally. These conversion factors for the volt, ohm, ampere, and coulomb were as follows:

1 mean international volt
= 1.00034 absolute volts

1 mean international ohm
= 1.00049 absolute ohms

1 mean international ampere
= 0.99985 absolute ampere

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] This value is based on the mass spectrometer measurements of Shields, Craig, and Dibeler [5]. On the ^{16}O physical scale of atomic weights they obtained 107.9028 ± 0.0013 which on the ^{12}C scale becomes 107.8685 ± 0.0013 using $1.000317917 \pm 17 \times 10^{-9}$ to convert from the physical to the ^{12}C unified scale of atomic weights. The International Atomic Weight Commission rounded this value to 107.868 in 1965 and proposed the same value in 1967 [4]. See also footnote i of table 2.

1 mean international coulomb
= 0.99985 absolute coulomb

These factors were based on the conversion factors found by the various national laboratories and would be applied only by an international laboratory such as the Bureau International des Poids et Mesures (BIPM), Sèvres, France. The factors for the various countries differed from the means given above and for the United States were [6]:

1 international volt (USA)
= 1.00033 absolute volts

1 international ohm (USA)
= 1.000495 absolute ohms

1 international ampere (USA)
= 0.999835 absolute ampere

1 international coulomb (USA)
= 0.999835 absolute coulomb

Accordingly, the Faraday as given by silver deposition, in absolute units in the USA is:

$$F=\frac{(107.868\pm 0.001)(0.999835)}{0.00111800}$$

$$=96467.1\pm 0.9 \text{ abs C g-equiv}^{-1}.$$

Since the measurements were made in the USA the USA conversion factor given above must be used.

During the decades that the international ampere was defined as above, it became generally recognized that the value 1.11800 mg for the *electrochemical equivalent of silver* was too high owing to inclusions present in the silver deposited in the silver coulometer. Extensive work was carried out to ascertain the exact magnitude of these inclusions using various types of silver coulometers. Three methods were employed: (1) determination of the loss in weight of the deposit on heating to redness, (2) direct analysis of volatile material of the deposit on heating, and (3) direct analysis of the deposited silver for its silver content.

In method No. (2) Duschak and Hulett [7] detached the silver crystals from the platinum crucible and placed them in a glass tube provided with a manometer and a small side tube, after which the tube was evacuated and sealed. The crystals were heated and the pressure measured before and after the water vapor present was condensed in the side tube. Hulett later pointed out that the results of this method were uncertain because of the possibility that some of the gases expelled may have come from the glass container. Laird and Hulett [8] at a later time attempted to avoid this difficulty by dissolving the crystals in molten tin at 400 to 500 °C. As before, by working in an evacuated system, the volatile inclusions which were insoluble in the molten tin were measured by fractional condensation. In method No. (3) the crystals were dissolved in nitric acid and the silver precipitated as chloride or bromide.

A summary of the results obtained by these three methods is given in table 1. Scott [21] from a review of these results concluded that the amount of inclusions varies from 0.006 to 0.016 percent and like Richards and Anderegg [16] stated that there is "little prospect at this time of finding a universally applicable correction for inclusions in silver deposits." Although most of Richard's results are higher than those of others, they have been included in the mean value, given in table 1. An unequivocal value for the uncertainty of the mean is difficult to arrive at but an uncertainty based on the standard deviation of the mean of all the 176 experimental data is considered as good as any other choice.

TABLE 1. *Amounts of inclusions in silver deposits in silver coulometers*

Year	Experimenters	Method	Number of experiments	Results	
				Mean	Range
				Percent	*Percent*
1884	Rayleigh and Sidgwick [9]...........	[a] (1)	[b] 20	0.0108	0.028
1886	Gray [10].................................	[a] (1)	....	([c])	....
1902	Richards and Heimrod [11]...........	[a] (1)	12	0.018	0.027
1906	Van Dijk [12]...........................	[a] (1)	7	.000	.015
1908	Ayrton, Mather, and Smith [13]......	[a] (1)	[d] 11	.000	....
1912	Boltzmann [14].........................	[a] (1)	19	.024	.0113
1915	Jaeger and von Steinwehr [15]........	[a] (1)	18	.0008	.007
1915	Richards and Anderegg [16].........	[a] (1)	27	.0139	.0313
1916	Vinal and Bovard [17] [e]...............	[a] (1)	25	.0040	.0081
1905	Duschak and Hulett [7]...............	[a] (2)	[f] 8	0.0079	0.0052
1912	Laird and Hulett [8]...................	[a] (2)	[g] 15	.0051	.0055
1917	Bovard and Hulett [18]...............	[a] (2)	19	.0113	.0304
1899	Richards, Collins, and Heimrod [19]	[a] (3)	7	[h] 0.006	0.026
1915	Richards and Anderegg [16].........	[a] (3)	7	[i] .0141	.0070
	mean (weighted by number of experiments)[c, d, f] = 0.0102 ± 0.0014				

[a] Number refers to number of method given in text.

[b] Two additional experiments gave abnormally high results; the silver nitrate solution had been filtered through silver acetate. For two more experiments the deposit was not heated to redness.

[c] Gray gave no quantitative data and merely stated that "a plate will . . . be found to lose slightly in weight if heated to redness"; omitted from mean.

[d] Heated 8 deposits to 240 °C only and 3 only to 400 °C; omitted from mean.

[e] Rosa, Vinal, and McDaniel [20] previously made some experiments on inclusions, but considered their results inconclusive.

[f] As Hulett later pointed out this method gave uncertain results because of the possibility that some of the expelled gases may have come from the glass container; omitted from mean.

[g] Laird and Hulett made 20 measurements but determined only water in first five deposits.

[h] Richards, Collins, and Heimrod originally reported 0.007 percent but van Dijk [12] uncovered an error in their computations which when corrected gave 0.006 percent for the inclusions; see also, Laird and Hulett [8].

[i] This becomes 0.0119 on the presently (1967) accepted values for the atomic weights of silver and chlorine.

The mean of data in table 1 is 0.0102 ± 0.0014 percent. Accordingly, the denominator of the above equation must be multiplied by 1 − 0.000102 (± 0.000014) or 0.999898 ± 0.000014, hence:

$$F=\frac{(107.868\pm 0.001)(0.999835)}{(0.00111800)(0.999898\pm 0.000014)}$$

$$=96476.9\pm 2.3 \text{ abs C g-equiv}^{-1} \qquad (1)$$

Remy [1] used Richards and Anderegg's value of 0.0155 percent for the inclusions obtained with coulometers using roughened porous crucibles. Richards and Anderegg used the heating method to determine the amount of inclusions. Although this higher value for inclusions leads to better agreement with subsequent determinations of the Faraday by other methods its selection over the others cannot be justified, a posteriori. If a single group of determinations were to be selected that of Vinal and Bovard [17], namely, 0.0040 percent, should be chosen since it was arrived at by the same procedures and in the same laboratory where the Faraday was determined by silver deposition.

2. Iodide Oxidation Method

In 1916 Vinal and Bates [22, 23] made a direct comparison of the silver and iodine coulometers in the laboratories of NBS. The silver coulometer was used to establish the charge in international units and in 6 of 10 experiments the international coulombs were determined directly from the duration of the run and values of standard cells and standard resistors known in international units. A weighted mean of the 10 experiments gave 0.850176 ± 0.000009 for the ratio of the weight of silver deposited to the weight of iodine liberated. A weighted mean of the 6 experiments in which the coulombs were determined directly in terms of the duration of the run, the standard cells, and standard resistors gave 1.315008 ± 0.000014 for the electrochemical equivalent of iodine. In each case the uncertainty is based on a 95 percent confidence limit in terms of the standard deviation of the mean value. Using the 1967 international atomic weight of iodine, 126.9044, the Faraday in absolute units is, in each case:

$$F=\frac{(0.850176\pm 0.000009)(126.9044)(0.999835)}{.00111800}$$

$$=96487.7\pm 1.0 \text{ abs C g-equiv}^{-1}, \qquad (2)$$

$$F=\frac{(126.9044)(0.999835)}{1.315008\pm 0.000014}$$

$$=96488.7\pm 1.0 \text{ abs C g-equiv}^{-1}. \qquad (3)$$

3. Oxalate Oxidation Method

In 1953, Craig and Hoffman [24] determined the Faraday in absolute units by the electrolytic oxidation of oxalate ions in aqueous solutions of sulfuric acid using gold electrodes. They obtained 96492 ± 3 for the Faraday using 67.007 for the equivalent weight of sodium oxalate based on the international chemical atomic weights of 1950 [25] where the uncertainty is presumed to be a probable error. Using the 1967 atomic weights their value of the Faraday becomes:

$$F=(96492\pm 3)\left(\frac{66.99975}{67.007}\right)$$

$$=96{,}481.6\pm 3.0 \text{ abs C g-equiv}^{-1} \qquad (4)$$

where the second parenthesis encloses the ratio of the ^{12}C unified equivalent weight of $Na_2C_2O_4$ to that used by Craig and Hoffman. Remy [1] used an incorrect correction factor in converting Craig and Hoffman's equivalent weight of $Na_2C_2O_4$ based on the 1950 international atomic weights [25] to the ^{12}C unified scale. Furthermore, he converted the value from the NBS (legal)[3] scale to the absolute value using the relation 1 NBS ampere = 1.000010 ± 0.000005 absolute amperes [26]; more on this point is given later.

4. Omegatron Method

Also in 1953 Sommer and Hipple reported a value for the Faraday from measurements made with the omegatron, a special type of cyclotron [27], in which protons are accelerated to a maximum orbital radius of about one centimeter. In this method a knowledge of the values of the proton rest mass 1.00727663(8)u, the ratio of the proton magnetic moment and the nuclear magneton 2.79276(2), and the gyromagnetic ratio of the proton $2.675192(7)\times 10^8$ rad s^{-1} T^{-1} are needed. The latter two values include corrections for diamagnetic effects present in the original measurements [28]. The values listed above are the most recent ones [29], and the numbers in parentheses represent the uncertainty in the last decimal. Using these values the Faraday is:

$$F=\frac{1.00727663(8)\times 2.675192(7)\cdot 10^8}{2.79276(2)\cdot 10^3}$$

$$=96487.3\pm 0.9 \text{ abs C g-equiv}^{-1}. \qquad (5)^4$$

5. Silver Dissolution Method

Finally, in 1960, Craig, Hoffman, Law, and Hamer [30] reported a value for the Faraday based on the electrolytic dissolution of metallic silver in aqueous solutions of perchloric acid. Their value corrected to the ^{12}C unified scale of international atomic weights (107.868 for Ag, see footnote 2) is:

$$F=96485.4\pm 2.4 \text{ abs C g-equiv}^{-1} \qquad (6)$$

where the uncertainties are overall limits of error. (See footnote 6 given later.)

A summary of these six values for the Faraday are given in column 2 of table 2.

During the late 1950's Driscoll and Cutkosky [26] as a result of measurements with a current balance and a Pellat electrodynamometer reported that:

$$1 \text{ NBS ampere} = 1.000010$$

$$\pm 0.000005 \text{ absolute amperes.} \qquad (7)^5$$

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[3] The NBS (legal) ampere in the United States is maintained by the ratio of the values of standard cells and standard resistors as maintained by the National Bureau of Standards.

[4] Sommer and Hipple [27] in their original paper gave an uncertainty of 3.0 C g-equiv^{-1} which was "estimated to be several times the probable error"; the uncertainties given here are those cited by Cohen and DuMond [29]. Also see footnote [g] of table 2.

[5] The NBS ampere is also known in the United States as the legal ampere and the above relation is a final adjustment needed to bring the legal ampere to the theoretical or absolute MKSA units.

TABLE 2. *Summary of values for the Faraday*

Method	Values		
	U.S. legal basis	Absolute basis 1 [a]	Absolute basis 2 [b]
	(coulombs per gram-equivalent)		
Silver deposition	96476.9 ± 2.3 (eq 1)	96478.1 ± 2.3	96478.0 ± 2.3
Iodide oxidation [c]	96487.7 ± 1.0 (eq 2)	96488.9 ± 1.0	96488.8 ± 1.0
Iodide oxidation [d]	96488.7 ± 1.0 (eq 3)	96489.9 ± 1.0	96489.8 ± 1.0
Oxalate oxidation	96481.6 ± 3.0 (eq 4)	96482.8 ± 3.0	96482.7 ± 3.0
Omegatron	[g] 96487.3 ± 0.9 (eq 5)	96486.1 ± 0.9	96486.2 ± 0.9
Silver dissolution	96485.4 ± 2.4 (eq 6)	96486.6 ± 2.4	96486.5 ± 2.4
Silver dissolution [e]	96485.4 ± 1.6	96486.6 ± 1.6	96486.5 ± 1.6
Silver dissolution [e, f]	96485.8 ± 1.6	[h] $\underline{96487.0 \pm 1.6}$ [i]	96486.9 ± 1.6

[a] Based on the relation 1 NBS ampere = 1.000012 absolute ampere.

[b] Based on the relation 1 NBS ampere = 1.000011 absolute ampere.

[c] Based on the silver/iodine weight ratio.

[d] Based on coulombs used to liberate iodine.

[e] Based only on the vacuum values of Craig, Hoffman, Law, and Hamer [30].

[f] Using 107.8685 (see footnote 2) for the atomic weight of silver.

[g] The original value corrected for ^{12}C, ω_n/ω_c in water and for a new value for the gyromagnetic ratio of the proton is 1.1 greater than the value given here.

[h] Value recommended by the National Academy of Sciences—National Research Council [31].

[i] Cohen and DuMond [28] by using an atomic weight of 107.86827 ± 0.00030 obtained 96486.82 ± 0.66. They based their atomic weight on the nuclidic mass values for the two isotopes of silver given by Everling, König, Mattauch, and Wapstra [34], a weighted mean of the abundance ratios determined by Shields, Craig, and Dibeler [5], and Shields, Garner, and Dibeler [35], and a value of 1.1179722 ± 0.0000070 mg C^{-1} for the electrochemical equivalent of silver based on the NBS results.

The uncertainty, here given, is a "50 percent error" as cited by the authors. In these measurements they used a value for gravity 17 ppm lower than that derived from Potsdam. Later studies showed that −13 ppm was a better correction to the value derived from Potsdam. Using this correction:

$$1 \text{ NBS ampere} = 1.000012 \pm 0.000005 \text{ absolute amperes.} \qquad (8)$$

This was the correction accepted and used by the Committee of the National Academy of Sciences—National Research Council which in 1963 issued a consistent set of physical constants [31]. Using this factor, accepting the value of the Faraday as given by the silver-dissolution method (equation 6 above) and accepting the *unrounded* value of the atomic weight of silver as determined by Shields, Craig, and Dibeler [5], namely 107.8685 ± 0.0013 on ^{12}C scale, the NAS–NRC committee recommended:

$$F = 96487.0 \pm 1.6 \text{ abs C mol}^{-1} \qquad (9)$$

for the Faraday.[6]

If the internationally recommended value for the atomic weight of silver, namely, 107.868 ± 0.001 is used, the value in equation 9 becomes 96486.6 abs C mol^{-1}.

In column 3 of table 2 are listed the values all converted to the absolute base using the relation of equation 8. The conversion factor from NBS (legal) to absolute units is assumed to apply throughout. This assumption is consistent with the known stability of standard resistors [32, 3] and standard cells [33] used to define the NBS (legal) ampere. A value given by Cohen and DuMond is discussed in footnote i of table 2.

In 1966–68, Tate [36, 37] reported on a new determination of acceleration due to gravity at the National Bureau of Standards. He gave 980.1018 cm/s^2 for absolute gravity from which a value of 980.0834 cm/s^2 is derived for the pier site at the old location of NBS in Washington, D.C., where the absolute current measurements are performed. This value leads to

$$1 \text{ NBS ampere} = 1.000011 \pm 0.000005 \text{ absolute amperes.} \qquad (10)$$

The values in the last column of table 2 were obtained from this relation. This conversion factor is the same as the one given by Terrien [32] of the International Bureau on Weights and Measures.[7]

Since the apparent correction for the acceleration due to gravity and the uncertainty in the correction for the relation between the NBS and absolute ampere are of the order of 1 ppm, the value of the Faraday presently recommended by the National Academy of Sciences—National Research Council (underscored value in column 3 of table 2) should be retained.

The author wishes to acknowledge that Footnote 7 contained in this paper was submitted by Dr. Forest K. Harris. His contribution is gratefully appreciated.

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[6] The NAS–NRC committee actually accepted only the vacuum values of Craig, Hoffman, et al. [30], i.e., results obtained with silver melted in *vacuo*. The mean of these, however, agreed with the total mean of these authors but the vacuum values showed less spread, thus the lower uncertainty given in equation 9. The NAS–NRC committee also defined the Faraday in terms of a mole of electrons or singly charged ions.

[7] A new ampere determination, using a Pellat dynamometer, has just been completed at NBS by Driscoll and Olsen, but has not yet been published. Prior to this determination, a number of modifications were made on the dynamometer to improve its performance, and the resulting value is in better agreement with the value published in 1958 by Driscoll and Cutkosky, using the NBS Current Balance. Accepting the value of gravity used for the ampere determinations reported in 1958, and taking the mean of the 1958 NBS current balance determination and the 1968 Pellat dynamometer determination, one may say that

$$1 \text{ NBS ampere} = 1.000009 \pm 0.000005 \text{ absolute amperes.}$$

If one uses Tate's value of gravity [36, 37] rather than the Dryden reduction (17 ppm below Potsdam), one would say that

$$1 \text{ NBS ampere} = 1.000010 \pm 0.000005 \text{ absolute amperes.}$$

It seems likely that this latter value must be considered together with that reported by Vigoureux in 1965 [38], before the Advisory Committee for Electricity of the International Committee of Weights and Measures makes a final recommendation on the value to be adopted.

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