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Chemistry and History

Millikan's Oil-Drop Experiments

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Millikan established the quantization of charge and measured the fundamental unit more accurately and precisely.

Millikan's oil-drop experiments are justly regarded as a major contribution to twentieth-century physics [1, 2]. They established the quantization of electric charge, the existence of a fundamental unit of charge, and also measured that unit of charge precisely. As Gullstrand remarked in his Nobel Prize presentation speech, "Millikan's aim was to prove that electricity really has the atomic structure, which, on the base of theoretical evidence, it was supposed to have.... By a brilliant method of investigation and by extraordinarily exact experimental technique Millikan reached his goal.... Even leaving out of consideration the fact that Millikan has proved by these researches that electricity consists of equal units, his exact evaluation of the unit has done physics an inestimable service, as it enables us to calculate with a higher degree of exactitude a large number of the most important physical constants" [3].[1]

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[1] The use of the value of the charge on the electron in the determination of these constants will be discussed below.

Historical Background

The background to Millikan's work began in 1897 with the discovery of the electron by J. J. Thomson [4]. Thomson had shown, by deflecting cathode rays in both electric and magnetic fields, that the rays were negatively charged particles. He then measured m/e, the mass-to-charge ratio of those particles. The value he found, 1.29×10^{-7}, was far smaller, by a factor of 1000, than the smallest value previously obtained, 10^{-4}, that of the hydrogen ion in electrolysis. Thomson remarked that this might be due to the smallness of m or to the largeness of e. He argued that m was small, citing Lenard's work on the range of cathode rays in air. The range, which is related to the mean free path for collisions, and which depends on the size of the object, was 0.5 cm. The mean free path for molecules in air was approximately 10^{-5} cm. If the cathode ray traveled so much farther than a molecule before colliding with an air molecule, then it must be much smaller than a molecule. The fact that the value obtained for m/e was independent of both the gas contained in the cathode ray tube and of the cathode material led Thomson to conclude that these particles were constituents of all atoms.

The next step was to measure e, and thereby to determine m. The early determinations of the charge of the electron did not establish whether or not there was a fundamental unit of electricity.[2] This was because the experiments, which used a cloud of charged water droplets and observed the motion of the cloud under the influence of both gravity and an electric field and under gravity alone, measured the total charge of the cloud and did not demonstrate that the value obtained wasn't a statistical average.[3]

Millikan's Method

One source of uncertainty in these measurements was due to evaporation of the droplets. Millikan believed that he could reduce that uncertainty by suspending the cloud with an electric field. It was in this attempt that Millikan found that he could isolate a single droplet and perform all the measurements on that droplet.

> My original plan for eliminating the evaporation error was to obtain, if possible, an electric field strong enough to exactly balance the force of gravity on the cloud and by means of a sliding contact to vary the strength of this field so as

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[2] For a discussion of some of these early experiments see Millikan [5].

[3] The same was true for Thomson's measurement of e/m for a beam of cathode rays.

to hold the cloud balanced throughout its entire life. In this way it was thought that the whole evaporation-history of the cloud might be recorded, and suitable allowance then made in the observations on the rate of fall to eliminate entirely the error due to evaporation. It was not found possible to balance the cloud as had been originally planned, but it was found possible to do something very much better; namely to hold individual drops suspended by the field for periods varying from 30 to 60 seconds [6].

Although Millikan had lessened the problem of evaporation he had not eliminated it completely. He then substituted oil drops for water drops, which considerably reduced the evaporation. He also found that he could increase the precision of the measurement by letting a single drop fall under the influence of gravity, then allowing it to rise under the influence of both an electric field and of gravity, and repeating this procedure several times. In fact, Millikan found that he could observe single drops for periods of an hour or more. This was the method Millikan used in his 1911 and 1913 papers. Millikan's first order of business was to establish the existence of the fundamental charge unit. In the introduction to his 1911 paper Millikan remarked that he had found it possible

1. To catch upon a minute droplet of oil and to hold under observation for an indefinite length of time one single atmospheric ion or any desired number of such ions between 1 and 150.

2. To present direct and tangible demonstration, through the study of the behavior in electrical and gravitational fields of this oil drop, carrying its captured ions, of the correctness of the view advanced many years ago and supported by evidence from many sources that all electrical charges, however produced, are exact multiples of one definite, elementary, electrical charge, or in other words, that an electrical charge instead of being spread uniformly over the charged surface has a definite granular structure, consisting, in fact, of an exact number of specks, or atoms of electricity, all precisely alike, peppered over the surface of the charged body [1].

He further remarked that he had been able "To make an exact determination of the value of the elementary electrical charge which is free from all questionable theoretical assumptions and is limited in accuracy only by that attainable in the measurement of the coefficient of viscosity of air [1]."
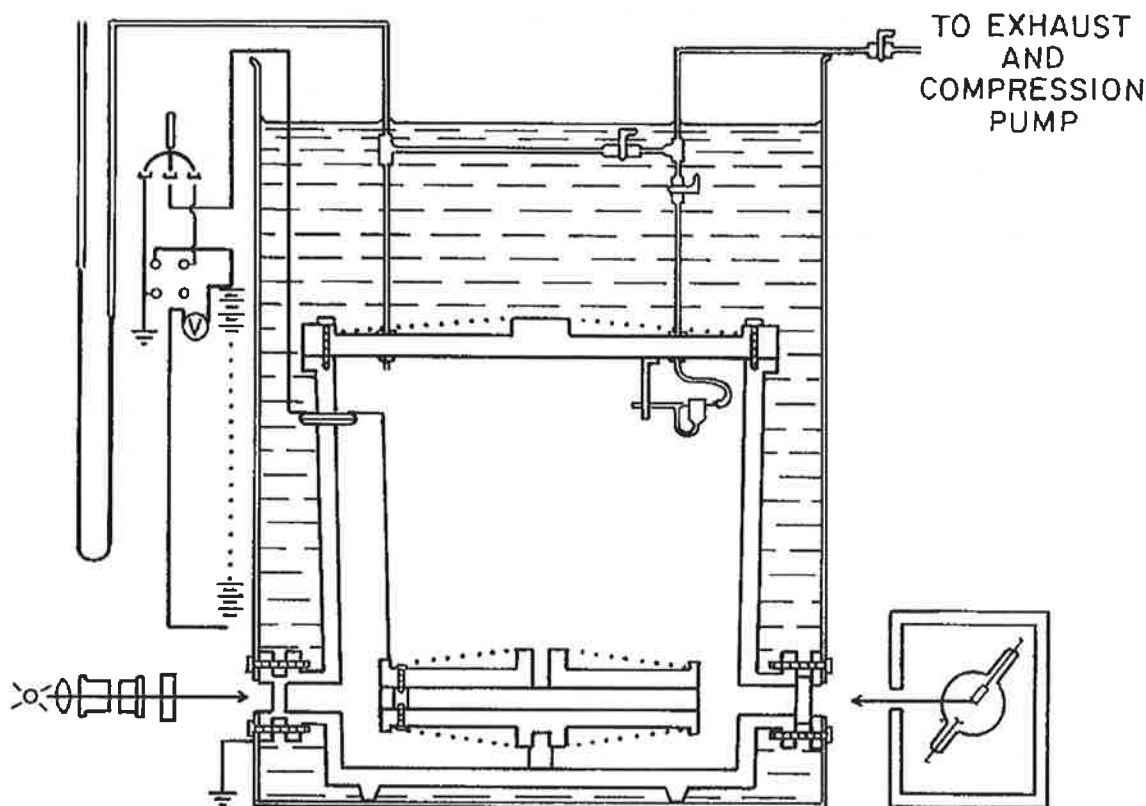
FIGURE 1. MILLIKAN'S OIL-DROP APPARATUS. THE PLATES TO WHICH THE VOLTAGE WAS APPLIED ARE SHOWN IN THE LOWER CENTER. THE OPTICAL SYSTEM AT THE LOWER LEFT AND AN X-RAY SOURCE TO INDUCE CHARGES IN THE CHARGE ON THE DROPS IS SEEN AT THE LOWER RIGHT [2].

Let us examine how Millikan demonstrated the existence of a fundamental unit of electrical charge and measured its value, so that we can understand the credibility of his results. The experimental apparatus is shown in Figure 1. Millikan allowed a single oil drop to fall a known distance in air. Millikan did not measure the time of fall from rest, but allowed the drop to fall freely for a short distance before it passed a crosshair, which was the start of the time measurement. Because of air resistance the drop was then traveling at a constant, terminal velocity. After the drop passed a second crosshair, which determined the time of fall at constant speed for the known distance between the crosshairs , an electric field was turned on. The charged oil drop then traveled upward at a different constant speed and the time to ascend the same distance was measured. These two time measurements allowed the determination of both the mass of the drop and its total charge.

The equation of motion of an oil drop falling under an upwards electric field F is

$$m\ddot{x} = mg + K\dot{x} - e_n F$$

where e_n is the drop's charge and m its mass compensated for the buoyant force of air. According to Stokes' law, which holds for a continuous retarding medium, $K = 6\pi a\mu$, where a is the drop's radius and μ the air's viscosity; to take into account the particulate character of air Millikan replaced K by $K/(1 + b/pa)$, where p is the air pressure and b a parameter determined from all of the experimental data. Because all measurements were made at terminal velocities $\ddot{x} = 0$, whence

$$e_n = \frac{mg}{F}\frac{v_t + v_g}{v_g}$$

where the subscripts indicate terminal velocities without v_g and with v_f the field, respectively. Now m can be replaced by a using $m = 4/3\pi a^3(\sigma - \rho)$, σ and ρ being the densities of oil and air, respectively; a can be done away with in favor of μ using Stokes' law; and the ratios of distance d to times of fall and rise, t_g and t_f, can be substituted for the velocities. Altogether

$$e_n = ne = \frac{9\pi d\sqrt{2/g}}{F}\left[\frac{\mu^3}{\sigma - \rho}\left(1 + \frac{b}{pa}\right)^3\right]^{1/2}\left[\sqrt{v_g}\left(\frac{1}{t_g} + \frac{1}{t_f}\right)\right]$$

where e_n, the total charge on the drop, is assumed to be an integral multiple of a unit e, d is the distance traveled, either up or down, and g is the acceleration of gravity.

Not only did the charge on the oil drop sometimes change spontaneously due to absorption of charge from the air or by ionization, but Millikan induced such changes with either a radioactive source or an x-ray source. When the charge changes one can calculate a similar quantity using successive times of ascent with the field on.

$$\Delta e_n = (\Delta n)e = \frac{9\pi d\sqrt{2/g}}{F}\left[\frac{\mu^3}{\sigma - \rho}\left(1 + \frac{b}{pa}\right)^3\right]^{1/2}\left[\sqrt{v_g}\left(\frac{1}{t'_f} - \frac{1}{t_f}\right)\right]$$

where t'_f and t_f are successive times of ascent. If both the total charge on the drop and

the change in charge are both multiples of some fundamental unit of charge then $1/n(1/t_g + 1/t_f)$ should equal $(1/\Delta n)(1/t'_f - 1/t_f)$. Millikan could easily estimate $(1/t'_f - 1/t_f)$ because Δn was usually a very small number, often equal to one, for the smallest change in the charge of the drop. "Since n' [our Δn] is always a small number and in some of the changes always had the value 1 or 2 its determination for any change is obviously never a matter of the slightest uncertainty. On the other hand n is often a large number, but with the aid of the known values of n' it can always be found with absolute certainty as long as it does not exceed say 100 or 150 [2]."

Sample data sheets from Millikan's experiments are shown in Figures 2 and 3. (These sheets are from Millikan's notebooks of 1911 and 1912. The results of that experiment were published in 1913). The columns labeled G and F are the measurements of t_g and t_f, respectively. The average value of t_g and its inverse are given at the bottom of column G. To the right of column F are calculations of $1/t_f$ and of $[1/\Delta n(1/t'_f - 1/t_f)]$. Further to the right is the calculation of $[1/n(1/t_f + 1/t_g)]$. The top of the page gives the date, the number and time of the observation, the temperature t, the pressure p, and the voltage readings, which include the actual reading plus a correction, and the time at which the voltage was read. The data combined with the physical dimensions of the apparatus, the density of clock oil and of air, the viscosity of air, and the value of g are all that is required to calculate e.

Millikan's Results

Millikan could determine e from both the total charge of the drop and from the changes in the charge. Not only did these values agree, but the average values obtained from different drops was also the same. Millikan remarked, "The total number of changes which we have observed would be between one and two thousand, and *in not one single instance has there been any change which did not represent the advent upon the drop of one definite invariable quantity of electricity or a very small multiple of that quantity* [1]." For Millikan, and for most of the physics community, these results established the quantization of charge. The value that Millikan found in 1911 for the fundamental unit of charge, the charge on the electron, was 4.891×10^{-10} esu. (Millikan did not cite a numerical uncertainty, but estimated the uncertainty as approximately 0.2 percent).
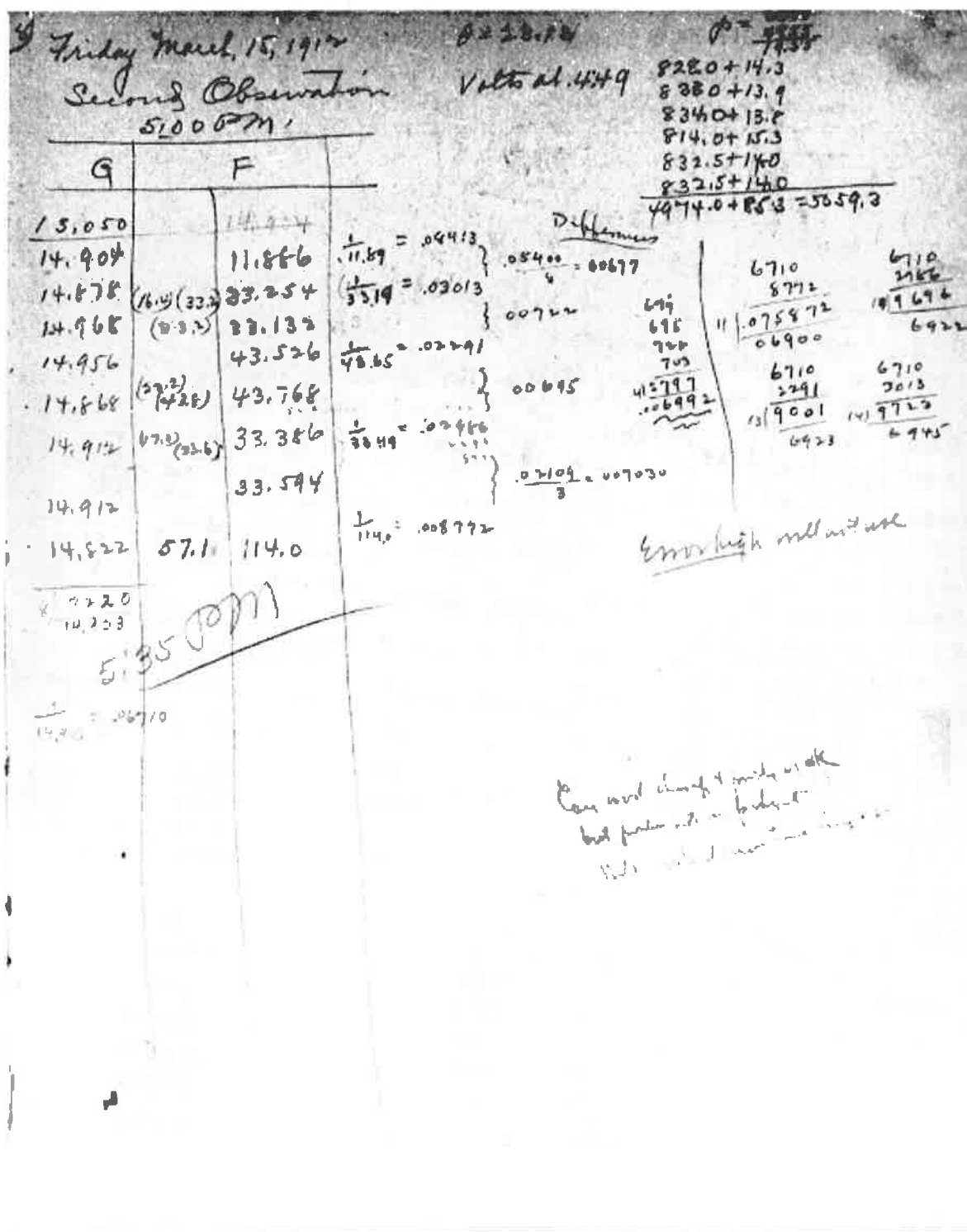
FIGURE 2. ,MILLIKAN'S DATA SHEET FOR MARCH 15, 1912 (SECOND OBSERVATION). COURTESY OF THE ARCHIVES, CALIFORNIA INSTUTUTE OF TECHNOLOGY.
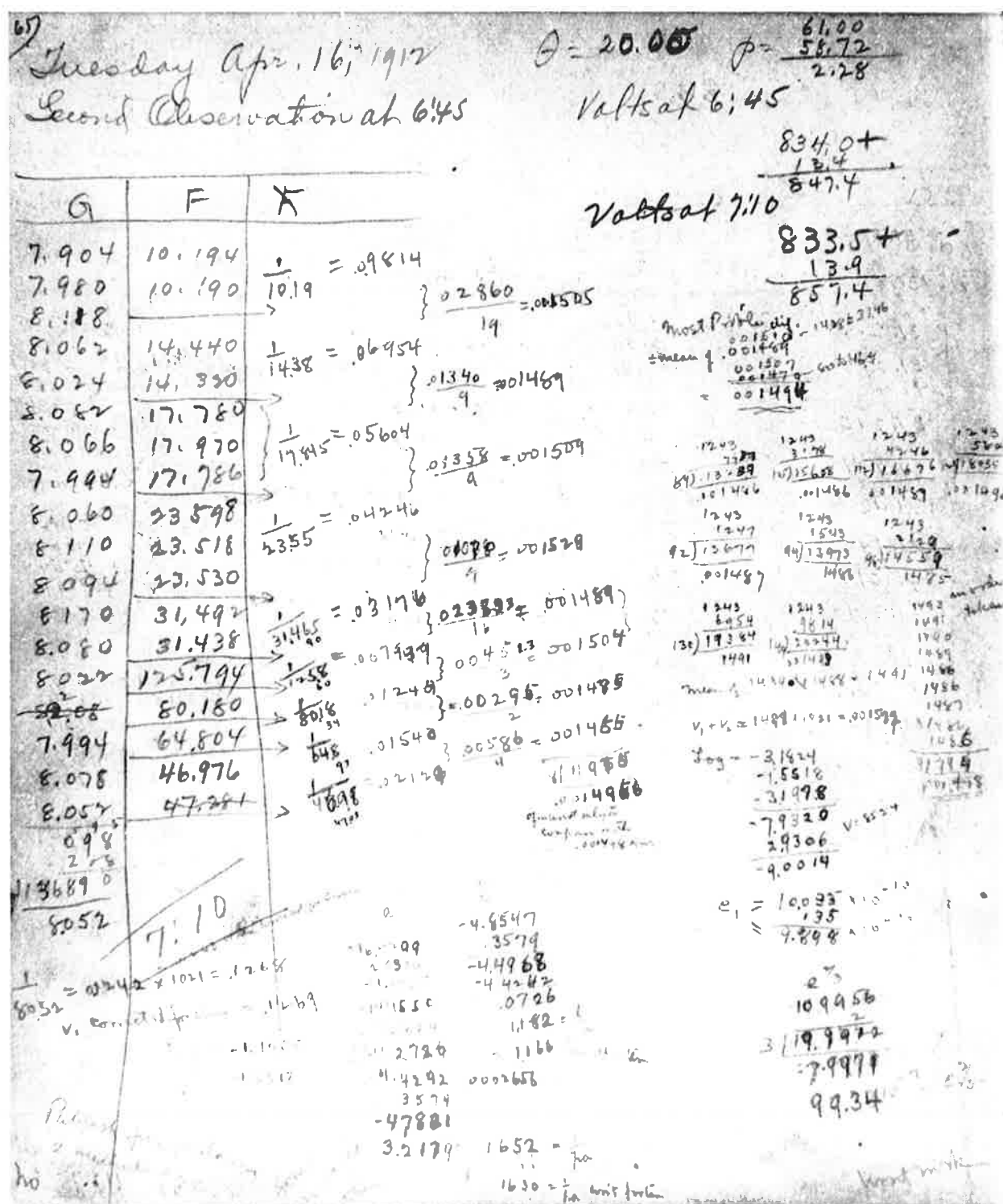
FIGURE 3. MILLIKAN'S DATA SHEET FOR APRIL 16, 1912 (SECOND OBSERVATION). NOTICE "WON'T WORK" IN THE LOWER RIGHT-HAND CORNER. COURTESY OF THE ARCHIVES, CALIFORNIA INSTITUTE OF TECHNOLOGY.

Following the completion of his 1911 paper, Millikan continued his oil drop measurements. His intent was to improve both the accuracy and the precision of the measurement of e. He made improvements in his optical system and determined a better value for the viscosity of air. In addition, he took far more data in this second experiment. Millikan's new measurement gave a value of $e = (4.774 \pm 0.009) \times 10^{-10}$ esu.[4] This value differs considerably from his 1911 value of 4.891×10^{-10} esu. Millikan stated that," The difference between these numbers and those originally found by the oil-drop method, $e = 4.891$, was due to the fact that this much more elaborate and prolonged study had the effect of changing everyone of the three factors η [the viscosity of air], A [related to the correction parameter b in Stokes' Law], and d [the distance between the crosshairs], in such a way as to lower e and to raise N [Avogadro's number]. The chief change, however, has been the elimination of faults of the original optical system [7]."

Oddly enough, although Millikan in his 1913 paper used his value of e to recompute the values of six other physical constants, he did not use it to determine the mass of the electron from the measurements of e/m.[5] This appeared first in *The Electron* [5]. Using his measured value of e, Millikan reported that the mass of the electron was 1/1845 that of the hydrogen atom.

Some Historical Details

The history presented thus far is a rather sanitized one, concentrating solely on Millikan's published measurements. Not surprisingly, the actual history was more complex. In 1910, for example, Millikan obtained a result from one water drop that gave a value for e that was 30 percent low. That was attributed to the rapid evaporation of that water drop. During the period 1911–1916 and even beyond, Millikan was also involved in a controversy with Felix Ehrenhaft and his collaborators over the

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[4] Millikan's value for e differs from the modern value $e = (4.8032068 \pm 0.0000015) \times 10^{-10}$ esu. This difference is due, in part, to a difference between the modern value for the viscosity of air and the one that Millikan used.

[5] The constants were: (1) N_o, Avogadro's number, and the number of molecules in 1 cm^3 of an ideal gas at 0 °C, (2) the mean kinetic energy of a molecule at 0 °C, (3) The constant ε of molecular energy defined by E (the kinetic energy) $= \varepsilon T$, (4) Boltzmann's constant, (5) Planck's constant, and (6) the constant c_2 in the Wien–Planck radiation law.

quantization of charge.[6] Ehrenhaft and his collaborators had failed to observe the quantized charges that Millikan had found, but had obtained continuous values for the charge on the electron. Although Millikan, along with most of the physics community, regarded the question of charge quantization as settled by Millikan's 1911 paper, Ehrenhaft disagreed. During 1912–13 there was a lull in the controversy. This was the period during which Millikan continued his measurements and others reported experimental results that supported his result. For example, Karl Przibram, a younger colleague of Ehrenhaft's, wrote to Millikan in 1912 acknowledging his earlier mistakes and stating his agreement with Millikan's work. Despite Przibram's concession, Ehrenhaft and two of his pupils returned to the attack in 1914 and 1915. Millikan answered the new criticism in a 1916 paper [7], which included his 1913 results and which pointed out errors in Ehrenhaft's experimental method. (For details of this controversy see [8].

Millikan also engaged in selectivity in both the data he used and in his analysis procedure. In presenting his results in 1913 Millikan stated that the 58 drops under discussion had provided his entire set of data. *"It is to be remarked, too, that this is not a selected group of drops but represents all of the drops experimented upon during 60 consecutive days,* during which time the apparatus was taken down several times and set up anew [2]."* This is not correct. Millikan took data from October 28, 1911 to April 16, 1912. My own count of the number of drops experimented on during this period is 175.[7] Even if one were willing to count only those observations made after February 13, 1912, the date of the first observation Millikan published, there are 49 excluded drops. We might suspect that Millikan selectively analyzed his data to support his preconceptions.[8]

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[6] This controversy continued even after Millikan had won the Nobel Prize for his work.

[7] My work here is based on Millikan's notebooks at the California Institute of Technology. All notebook references are to Folders 3.3 and 3.4. For information about the collection see Gunns, A. F. and Goodstein, J. R. *Guide to the Robert Andrews Millikan Collection*; New York, 1975; and Goodstein, J.R. ed. *The Robert Andrews Millikan Collection, guide to a microfilm edition*; Pasadena, 1977. For details of my recalculation of Millikan's data see Franklin [9].

[8] Daniel Siegel raises the same question. "Millikan was in this sense choosing data according to his presuppositions, and then using those data to support his presuppositions [10]. As discussed in [9], and below, I don't agree with Siegel's statement.

Millikan's selectivity included the exclusion of all of the data of single drops, exclusion of some of the data within the data set for a single drop, and a choice in the methods of calculating e. In discussing this selectivity we should, however, remember that Millikan had far more data than he needed to improve the measured value of e by more than a factor of ten over anyone else's measurement. He used only the 23 published drops, out of a total of 58, which had a Stokes' Law correction of less than six percent. This was to guard against any effect of an error in that correction.

In his experimental work before February 13, 1912, Millikan was concerned with getting his apparatus to work properly. He worried about convection currents inside his apparatus that could change the path of the oil drop. He made several tests on slow drops, for which the convection effects would be most apparent. Millikan's comments on these tests are quite illuminating. On December 19, 1911 he remarked, "This work on a very slow drop was done to see whether there were appreciable convection currents. The results indicate that there were. Must look more carefully henceforth to tem[perature] of room."[9] On December 20: "Conditions today were particularly good and results should be more than usually reliable. We kept tem very constant with fan, a precaution not heretofore taken in room 12 but found yesterday to be *quite* essential." On February 9,1912 he disregarded his first drop because of uncertainty caused by convection; after the third drop he wrote, "This is good for so little a one but on these very small ones I must avoid convection still better." No further convection tests are recorded. On February 13, 1912 Millikan used the data from his first drop in his published results. This indicates that he thought his apparatus was working properly. Prior to that time he excluded the data from 68 drops because he was not convinced that his experimental apparatus was working properly. After this date, we must assume that the apparatus was working properly unless we are explicitly told otherwise. There are 107 drops in question, of which 58 were published. Millikan made no calculation of e on 22 of the 49 excluded drops. The most plausible explanation why Millikan did not calculate them is that when he performed his final calculations in August 1912 he did not need them for the determination of e.

The 27 events that Millikan excluded and for which he calculated a value of e are more worrisome. Millikan knew the results he was excluding. Twelve of these were

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[9] The quotations are from Millikan's notebooks.

excluded because they seemed to require a second-order correction to Stokes' law, and also were not needed to improve the determination of e. Of the remaining 15 calculated events Millikan excluded two because the apparatus was not working properly, five because they had insufficient data to make a reliable determination of e, two for no apparent reason. We are left with six drops. One is quite anomalous and will be discussed below. In the other five cases Millikan not only calculated a value of e but compared it with an expected value. The four earliest events had values of pa that would place them in the group Millikan used to determine e. His only evident reason for rejecting these five events is that their values did not agree with his expectations. The effect of this rejection was quite small, as shown below.

Millikan's cosmetic surgery touched 30 of the 58 published events, from which he excluded one or more (usually less than three) observations. My recalculation of these events, using all of the data, gives results little different from Millikan's. Millikan did not selectively exclude these observations on the basis of any discrepancy in his calculations, because, in general, he did not perform any calculations using them.

As discussed earlier, there are two ways to calculate e from the oil-drop data. The first uses the total charge on the drop, whereas the second uses the changes in charge. Millikan claimed that he had used the first method exclusively because the large number of measurements of t_g provided a more accurate determination of e. In at least 19 of the 58 published events, however, he used either the average value of the two methods, some combination of the two that is not a strict average, or the second method alone. In general, the effects are small and the result of his tinkering is to reduce the statistical error rather than to change the mean value of e.

The effect of Millikan's selectivity was quite small and is shown in Table 1. This includes Millikan's results along with my own recalculation of Millikan's data.

As we can see the effects of Millikan's selectivity are quite small.

I will end with a discussion of the second drop of April 16, 1912 (The data sheet for this drop is shown in Figure 3). This event is quite anomalous, and is quite worrisome because it is among Millikan's most consistent measurements. Not only are the two methods of calculating e internally consistent, but they agree with each other very well. Millikan liked it: "Publish. Fine for showing two methods of getting v." My own

TABLE 1. Comparison of Millikan's and Franklin's values of e.

Published drops	values of $e \times 10^{10}$ esu			
	e(RM)	e(AF)	σ(RM)[a]	σ(AF)
First 23[b]	4.778[c]	4.773	±0.002	±0.004
All 58	4.780	4.777	±0.002	±0.003
Almost all drops[d]	4.781	4.780	±0.003	±0.003

[a] Statistical error in the mean
[b] These are the events that Millikan used to determine e.
[c] Although Millikan used a value $\mu = 0.001825$ for the viscosity of air in almost all of his calculations, in his final calculation of e he used $\mu = 0.001824$. In order to make the most accurate comparison I used $\mu = 0.001825$ in all of my calculations. This accounts for the change from 4.774 to 4.778 in Millikan's final value.
[d] This includes the 58 published drops, 25 unpublished drops measured after February 13, 1912, and some small corrections. For details see Franklin [9].

calculation of e for this event gives a value $e = 2.810 \times 10^{-10}$ esu, or approximately 0.6e.

Millikan knew this. Note the comment, "Won't work" in the lower right-hand corner. Both the charge on the drop as well as the changes in charge, must be fractional, a highly unlikely occurrence. There were no obvious experimental difficulties that could explain the anomaly. Millikan remarked, "Something wrong w[ith] therm[ometer]," but there is no temperature effect that could by any stretch of the imagination explain a discrepancy of this magnitude. Millikan may have excluded this event to avoid giving Ehrenhaft ammunition in the controversy over the quantization of charge. In retrospect Millikan was correct in excluding this drop. In later work William Fairbank Jr. and I [11] found that Millikan's apparatus gave unreliable charge measurements when the charge on the drop exceeded a value of about 30e. This drop had a charge of greater than 50, and the data point was quite unreliable.

Conclusion

What can we conclude from this episode? Millikan established the quantization of charge and measured the fundamental unit more accurately and precisely. There is no

reason to disagree with his assessment that in 1913 there was "no determination of e... by any other method which does not involve an uncertainty at least 16 times as great as that represented in these measurements." His massaging of the data, a possible worry, had, as we have seen, a negligible effect on his final result.[10]

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[10] I would not, however, recommend this method of analyzing data to students.