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Our Knowledge of the Fundamental Constants of Physics and Chemistry in 1965

E. RICHARD COHEN
North American Aviation Science Center, Thousand Oaks, California
JESSE W. M. DUMOND
California Institute of Technology, Pasadena, California

Experimental data bearing on the precision determination of the numerical values of the fundamental physical constants are reviewed, with particular emphasis being placed on the identification and isolation of discrepancies and inconsistencies. The purpose of the analysis is to present a consistent set of values of the fundamental constants and to present a careful and complete description of the steps taken to reach this end. The Introduction discusses the significance of such an analysis and indicates the general method of approach. The indispensability of local unit systems and conversion factors connecting them, in order to avoid a sacrifice of precision peculiar to different metrological techniques, is emphasized. The point is stressed that conversion constants introduce the danger of ignoring error-statistical correlations between physically measured quantities, and the effects of such correlations on the assignment of errors is discussed. All available sources of experimental information relative to the necessary input data are presented, and changes in definitions of units since our last review are discussed. After the available stochastic input data have been reviewed and the less reliable items eliminated, the third section examines the remainder for mutual compatibility by means of an analysis of variance in which special criteria for recognizing the incompatibility of a datum are developed, using the analogy of the energy of internal strain introduced in overdetermined mechanical structures. Tables of least-squares adjusted values of fundamental constants and conversion factors of physics and chemistry based on the 1963 adjustment are given. Research pertinent to the constants which has been completed or published subsequent to the 1963 "recommended" adjustment is discussed, and the effect of these on our knowledge of the numerical values of the fundamental constants is presented.

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1. INTRODUCTION

In 1960 the authors of this review were requested to prepare a complete new least-squares adjustment of the fundamental constants of physics and chemistry. The request came from the joint committee of the Divisions of Chemistry and Physics of the U. S. National Research Council, and was to a large extent prompted at that particular time by the fact that a new scale of atomic weights, the "Unified Scale" on which the nuclide, ^{12}C, is defined as having exactly weight 12, had been adopted by IUPAP and IUPAC at the general assembly of these two Unions at Ottawa, Canada, in 1960. Although the demand was triggered, as it were, by the adoption of the unified scale, this was far from being the only or the most urgently important reason for making a complete new review of the constants. A revision of our old values (our last previous review of the constants was made in 1955[1]) merely in the light of the change of the scale of atomic weights, could have been accomplished in a few moments on a desk calculator. Since 1955 however a wealth of new and improved experimental data bearing on the constants had become available, errors in some of the old data used as input information in our 1955 adjustment had been discovered by both the theoreticians and the experimentalists, and other arbitrary changes or adoptions in defined quantities and units have occurred. It would have been most misleading therefore to have corrected and republished the 1955 constants after merely modifying them to agree with the new unified scale of atomic weights.

1.1. When Should Re-evaluations of the Constants Be Made?

A wise choice of the correct time to make a fresh evaluation of the fundamental constants is indeed difficult and can only be made by those who have followed the subject with detailed attention over a considerable period of years. At every epoch there is almost always a number of unsatisfactory situations, unresolved discrepancies between various measurements, theoretical uncertainties regarding questionable corrections, and ill-defined conventions which render the comparability of measurements made by different workers open to question. One is always tempted to wait a little longer until the questions hanging fire are cleared up. The trouble with exaggeration in this temptation is that the very process of improvement in accuracy and reliability (which the specialists in reviewing the constants themselves stimulate by calling attention to the discrepancies and troubles) whets the appetite for increasing precision, so that the discrepancies, which would have been of negligible magnitude a few years before, become of increasing importance. Thus, too long a delay, too much exercise of caution, can lead to our never having any consistent set of values of the constants with which to work! All one can do is pick a time just after the resolution of some major discrepancies, or the invention of some important new metrological technique, when one feels that the situation is likely to be stabilized for a few years to come on the newly established improved level of precision.

It is difficult sometimes to make one's colleagues, who may be impatiently clamoring for a new set of adjusted values of the fundamental constants, understand that the time is not yet quite ripe, that one is waiting for this, that, or the other question to be more satisfactorily settled. Failure to understand in these situations comes from the fact that few physicists or chemists fully realize in what a complicated, intricate way the fundamental constants, together with the measurements from which they are derived, are interconnected and interrelated. Everything depends upon everything else (as will be clear from the present article), and one flaw in the picture propagates its defect, to a greater or lesser extent, throughout all the numerical values of the fundamental constants and conversion factors we seek.

1.2. Discrepancies in X-Ray Data

The above remarks were particularly true in the process of preparing a new least-squares adjustment requested in 1960, but which we were only able to submit to our satisfaction to the NRC Committee on 28 February 1963. We had indeed completed a tentative adjustment in late 1961, but we did not feel too well satisfied (nor did some of our fellow committee members) with some of the discrepancies which that least-squares adjustment had revealed, particularly in the domain of x-ray measurements which were relevant to the Avogadro number, N, and the conversion constant, Λ, between the nominal (Siegbahn) scale of x-ray wavelengths (expressed in so-called x-units) and the scale of absolute wavelengths (in centimeters or Angstrom units). These discrepancies actually became more glaring when further precision x-ray measurements were later included in the adjustment, and we finally felt obliged, since increasing pressure was being brought by our colleagues of the committee (and others) for a

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[1] E. R. Cohen, J. W. M. DuMond, T. W. Layton, and J. S. Rollett, Rev. Mod. Phys. **27**, 363 (1955). A more complete account of this adjustment will also be found in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXXV, pp. 1–87.

new set of values without further delay, to exclude completely from our adjustment all data from the x-ray measurements. Only by so doing was it possible for us to produce the above-mentioned adjustment which we submitted in February 1963, and which we shall, throughout this review, refer to as the "1963 Adjustment."

Although the trouble with the x-ray data is of long standing, dating back as it does to the early days of M. Siegbahn and other famous workers in this field, it is only becoming evident and troublesome at the present time because the general level of precision in other fields of physics has overtaken the precision of the early x-ray workers and brought to light weakness of definition and convention as well as metrological errors.

1.3. Importance of Overdetermination

Unfortunately, since on the quantum energy scale the field of x-ray emission-line spectroscopy is sandwiched in-between that of optics (in which our cgs units are defined and maintained) and that of nuclear gamma-ray spectroscopy, in which there is now an ever-increasing demand for better absolute precision expressed in terms of quantum energies (electron volts), the defects and weakness of definition and convention in the field of x-ray spectroscopy are now imperatively demanding rectification. There are a few alternative ways of bridging the x-ray gap and relating the measurements in nuclear spectroscopy to our absolute unit system without calling upon x-ray measurements, but it is an axiom in this field that we must never be satisfied with only one or two methods of linking together the various fields of measurement. No stone must be left unturned, no method promising better precision or a different route for arriving at a conversion constant left untried, in efforts to eliminate systematic error. Only by such diligent thoroughness can we locate the sources of trouble and eliminate them. For in the last analysis the only test we have of the correctness of our theories and our measurements is the test of consistency of the system as a whole, and the test of consistency becomes the more searching the greater the overdetermination of the measurements.

No one knows that the quantities we call "constants" are indeed absolutely changeless with time. At present we merely have no clear experimental evidence to the contrary, although variations in the values of the constants on a cosmological time scale have certain appealing theoretical features. But even if we knew the constants were immutable in value, there is every reason to expect *our knowledge* of them to be subject to change.

All we can hope to do at any given epoch can be the following. First we examine the entire body of experimental measurements which bear on the constants and which are available at that time. These usually consist of measurements of rather complicated functions of conceptually simple "fundamental" quantities whose values we wish to obtain, such as the electronic charge, e, the electronic rest-mass, m, Planck's action quantum, h, etc. In the light of *accepted theory* as of that date we then form a system of equations equating the functions of the "unknowns" (fundamental constants) to the measured experimental values. We then examine this overdetermined set for compatibility.

If one particular subset, consisting of a large majority of the original data, turns out to be both highly overdetermined and markedly more consistent (compatible) than the other subsets, one may be encouraged to hope that this is "the good set" and that the data which were rejected in order to form it were "systematically erroneous" for some reason. But all this is merely a *clue*; it is not *proof*. Also, more likely, it will turn out that no single, highly preferable, subset will be clearly distinguishable.

As experimental physicists it is our duty in any case, to examine all of the input data very critically, in an effort to find possible sources of systematic error. This may frequently involve corresponding at considerable length with the authors of the data and in many cases visiting their laboratories, recomputing their original data of observation, discussing their methods of error estimation and trying to re-express all error estimates on as comparable a footing as possible. This latter task, probably the most difficult and trying of all, deserves and will receive more careful discussion in its proper place in this article.

Now it should be clear from the above rough description of the process, that those who are making a critical review of the constants, are obliged to use judgment and to make decisions which unavoidably must involve, to some degree, the subjective element. It is, of course, our duty to try to eliminate the subjective element by every means at our command, but since choices and decisions must be made (no one wants two alternative sets of constants!) it becomes sometimes necessary to base a choice, between two or more nearly equally likely alternatives, on statistical odds of weak significance. When one has exhausted every other recourse in an effort to be objective, there may be nothing better to be done. There is one way of avoiding such situations of which we strongly disapprove. This is to take *all of the available data* at a given epoch, cast it uncritically into the least-squares melting pot, and closing ones eyes to the incompatibilities of the various equations in the adjustment, simply expand all of the output errors, relative to their values by the criterion of internal consistency, applying a factor dictated by the chi-squared (measure of incompatibility) of the adjustment. It should be perfectly clear to any reasonable physicist that the input data, to which *must* be given assigned *a priori* weights, cannot be safely weighted in inverse ratio to the squares of the input error estimates if these data are mutually incompatible by three, four, or perhaps even more times the standard deviations of the discrepancies between the different items. Under such circumstances the suspicion becomes close to a certainty that the disagreement is not a statistical fluctuation but a systematic error in one or more of the data. In such a case the appropriate weighting is probably quite unrelated to the supposed standard deviations. We are thus obliged to make a choice of some data for rejection.

No one can guarantee that an evaluation of the fundamental constants at a given epoch yields the "true" values. Absolute truth, if these words have meaning, is beyond the realm of physics. All we can do at each time of re-evaluation is to try to determine a set of values which, in the sense of least squares, and in the light of accepted theory at that time, does least violence to a chosen budget of observational data then believed to be the "best" and most accurate. From this statement it should be clear that minor disagreements between the results of different evaluations at any given time are sure to arise and that changes and revisions from time to time are unavoidable.

Thus the greatest merit in a re-evaluation of the constants resides not in the numerical output values, useful as these may be, but in the fact that the re-evaluation constitutes a new test of the validity of all our theoretical preconceptions and their experimental verification over the widest possible domain. The only test of such validity we have is the consistency of the data, and this indeed is all we ask for.

For this reason, it should be clear that the prime object of these re-evaluations of the constants must always be to *look for discrepancies* and to resolve them by finding the errors in either theory or experiment which account for them.

1.4. Error Estimation, Weighting of Data, and Related Problems

This extremely important task of weeding out systematic errors and discrepancies from the input data of a least-squares adjustment of the constants requires a somewhat different and more careful treatment of the error estimates to be assigned to the measured data than is current practice among most experimentalists. H. A. Kramers once said, "The statistical theory of errors is like love; one cross word can spoil it all!" Yet we *must* face this morass of semantic disagreement and misunderstanding-as-to-purpose. We must try to express all the error assignments for a large mass of precise observational data, coming from many different people, on a comparable basis.

Perhaps the most difficult obstacle one faces in doing this stems from the fact that there seem to be two completely incompatible ways in which experimentalists regard the problem. Some regard the number following the sign of ambiguity as expressing "limits of error" with the unstated implication that the true value lies anywhere within the gap and that there is something rather virtuous in overestimating the magnitude of this gap "for safety" or "to take care of possible but unknown sources of systematic error." Clearly such an error estimate is of little value to one who must compare and weigh data from different sources because it is not a quantitative estimate, but a statement of inequality: the error is less than or equal to so-and-so much.

The other and far more useful way is of course to regard the number following the plus-or-minus sign as an estimate of the width parameter of some statistical distribution of observed values which would be obtained if the measurement were replicated a number of times. The final error estimate of a complicated physical measurement usually is compounded out of many different sources of error, some of which are of such a nature that replication is not a feasible or practical way of estimating the uncertainty of every contributing source. Nevertheless, we deem it preferable, even in such cases, to make the estimate as impartially as can be without biasing it either in the direction of the too large or the too small.

The Gaussian error distribution is frequently assumed to be the type-form applicable to all physical measurements. This is of course not at all true. The nature of the measuring process largely determines the error distribution, without doubt. For example, measurements of the diameters of cylindrical shafts with "go–no-go" gauges may be expected to result in a more-or-less flat-topped distribution of shaft diameters. Fortunately the theories of error statistics and least squares, as developed by the mathematicians Gauss, Laplace, and Markoff, though frequently presented to students, for simplicity, as though they were restricted to the Gaussian error distribution alone, are actually far more general in their applicability, In fact they are applicable to any error distribution curve with the sole restriction that the minimum second moment of the curve must exist (i.e., must have a finite value).[2] However, in order that this much broader interpretation may be given to the theory, it is necessary to modify the nature of our goal slightly. We must no longer ask for "the most probable value" of a stochastic variable. Instead we must ask for that value to which the maximum weight can be assigned. Clearly it would be physically meaningless to ask for the most probable value of a variable having a flat-topped or a bimodal distribution.

Because of this more general applicability of the theory to a very wide variety of distribution, we prefer, in accord with modern error-statistical practice, to express all of our error measures in terms of "standard

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[2] This restriction requires us to exclude such distribution curves as the "witch," "Cauchy distribution," "Lorentzian," or "Breit–Wigner curve," as it is variously called, the curve $y=A/(1+x^2)$. For this curve, even the first moment diverges logarithmically.

deviations," that is to say, root-mean-square deviations from the mean, rather than in terms of "probable errors." It is a grave mistake, in the light of this more general applicability, to regard the error expressed in standard deviations as simply differing by a multiplying factor (1.48) from the probable error. The probable error is defined as that measure of dispersion such that the odds are even that the observation may lie either inside or outside the given limits. Only for the Gaussian distribution are the standard deviation and the probable error related to each other by the numerical factor just cited. They are two entirely different *kinds* of dispersion measures, and the standard deviation is far more general in its applicability under the theory of least squares. Throughout this article, unless otherwise stated, all of our error measures are given in standard deviations. In reducing the data of other experimentalists who quote their errors as "probable errors" we have usually assumed the above numerical factor for the Gaussian to convert the quoted error to a standard deviation, but wherever a critically important error measure was involved we have corresponded with the worker and requested him to clarify to the best of his ability his meaning or intention. We fully realize that error estimates are difficult and uncertain things but they are nevertheless worthy of one's best effort.

The idea that an overestimate of error "for safety" is somehow more laudable or virtuous than an effort to be as accurate as one can with as little bias as possible in either magnifying or minimizing the standard deviation estimate, is somehow deplorably prevalent. We ask, for whom is such an overestimate "safe"? Certainly not for the general scientific community who wish to use the result. For them it is a concealment of the true facts regarding the results of the measurements. For the author of the result it may appear to be "safe" in the sense that at some later date his measurement might be less likely to be contradicted by later work; but even for him this unworthy timidity may be an illusory safety for, because of the unwarranted exaggeration of his error estimate, a crucial discrepancy, which might otherwise reveal some basically important new fundamental fact, may have been buried and lost forever as far as his reputation is concerned. For courageous men of science there is only one "safe" refuge, the plain, unvarnished truth as to their methods and results.

1.5. Local Unit Systems and Conversion Factors

The tendency of the physical sciences to split up into smaller and smaller domains of specialization and the demand for ever increasing precision in many of these domains has forced upon us the adoption of local unit systems, each chosen for use in a given domain, so as to afford the highest degree of relative precision which metrological techniques permit for comparing magnitudes in that domain. But since the physical sciences constitute an indissoluble unit, over-all consistency including all domains is also a mandatory requirement (in fact, it is the only way of verifying the success of our efforts both in theory and in experiment) so that we are obliged, with whatever precision can be attained, to link the entire system to a set of fundamental units which we usually refer to as "absolute units" and we do this by determining numerical "conversion factors."

Nobody likes this situation because of its complexity and one continually encounters proposals to simplify it from specialists who, seeing only a part of the picture, propose solutions which if adopted would only make confusion worse. We have to live with almost all the presently existing local units and conversion factors because (1) their abolition would lead to concealment of the metrological–operational truth as to how measured values were obtained, and (2) their abolition would frequently entail a sacrifice of real observational precision of great value in the localized domains. Note that these are in both cases requirements imposed by practical reasons related to metrological techniques having little or nothing to do with physical theory or conceptual simplicity.[3] Thus, the requirements are capable of changing with time as new techniques of precision measurement are developed and old ones improved. When such advances permit elimination of a conversion factor and a simplification or unification of two or more unit systems, the distaste for unnecessary complexity will almost surely and immediately result in a reform. At any given time, therefore, the existence of a conversion factor is almost a sure guarantee of its indispensability.

It is worthwhile to call attention to a few specific cases of presently indepensable local units and conversion factors so as to illustrate this necessity.

(1) Conversion Factor from Linear to Volumetric Measure

Length measurements of the order of 1 m in magnitude can be maintained, reproduced, and intercompared with relative precision of order perhaps 10^{-7} or better. Volumes can be intercompared by weighing with a relative precision of the same order or better. Here then we have two metrological domains each admitting of high precision *for comparisons of magnitudes within* the same domain. The determination of a conversion factor linking the two domains so as to permit volume measure to be expressed in cubic length units is a much more difficult metrological problem. The liter is defined as the volume of a kilogram of water at standard atmospheric pressure and at its temperature of maximum density, approximately 4°C. (On a level of sufficient precision this is an ambiguous definition

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[3] It is for this reason that theoreticians are particularly unaware of the need for local units and conversion factors. For them the difference between lengths and volumes is merely the writing of a superscript 3!

since it does not specify the isotopic constitution of the water, but let us ignore this for the present discussion.) The meter is the fundamental cgs unit of length. The linkage between length measure (in cm) and volume measure (in cm^3) was established by very long, difficult, and painstaking determinations of "the maximum density of water" (or the volume of a liter of water as the latter is defined above) chiefly by measuring to very high precision the linear dimensions of solid bodies and then hydrostatic weighing of these. de Lepinay, Buisson, and Benoit[4] in 1910 at the Bureau Internationale des Poids et Mesures (hereinafter abbreviated as BIPM) at Sevres obtained a result which was later corrected upward by Guillaume, also at the BIPM, by 1 part per million:

$$1\ \text{liter} = 1000.028 \pm 0.004\ \text{cm}^3 \tag{1}$$

which is still generally accepted.

Note that here, after the greatest precautions, the conversion factor between the domains of length measure and volume measure could only be determined to an uncertainty of 4 parts per million (parts per million will be hereinafter abbreviated as ppm), a precision perhaps 50 to 100 times poorer than that with which either *lengths* can be intercompared with lengths or *volumes* intercompared with volumes! There is thus no escape from the situation that if we wish to retain the higher precision technically possible within each of the two domains and still be in a position to express measurements made in each of them in the same fundamental units (length), we are obliged to resort to the use of the above conversion factor. This means that precision in terms of the local unit (liters), must be degraded in precision to a level of ±4 ppm if they are to be expressed in cubic centimeters or cubic decimeters. There is no help for this; it is the best we can do and stick to the metrological truth.

The following are a few other very commonplace (though frequently ignored) examples of the same sort of situation requiring introduction of a conversion constant less accurately determined or determinable than are the local unit magnitudes it connects.

(2) *Relative and Absolute Nuclidic Mass Scales*

The scale of "atomic weights" (more precisely the scale of relative nuclidic masses) is an outstanding case. Thanks to the high precision of mass-spectroscopic and nuclear-reaction data, we can compare on this relative scale the mass ratios of nuclides (now expressed in terms of the base unit, $^{12}\text{C} = 12$, if the newly adopted "unified scale" is used) with relative accuracies in some cases better than two parts in 10^8, but the "absolute" mass in terms of our primary standard, the prototype kilogram at the BIPM is much less well known. In this case, the reciprocal of the Avogadro number is the conversion factor between the two scales. It is known only to about 16 ppm. We would make an enormous sacrifice of relative precision if we were to express the masses of all the nuclides in grams.

(3) *The X-Unit-to-Milliangstrom Conversion Factor*, Λ

The wavelengths of x-ray emission lines, which are chiefly measured (intercompared) using the atomic lattices of crystals as diffraction gratings, could probably be related to each other, on a properly defined nominal scale, to a precision of one part in 10^6. To express these same wavelengths in absolute units, that is to say, in centimeters or Angstrom units, is a far more difficult matter, and at the present time our knowledge of a conversion factor for doing this is perhaps no more accurate than ±20 ppm. One trouble here will be discussed in much more detail later in this article. The accepted definitions and conventions in precision x-ray spectroscopy are at the present moment themselves not sufficiently well defined to avoid a deplorable degree of semantic confusion.

(4) *The Acceleration of Terrestrial Gravity*

A similar example of the sort of difficulty we are discussing comes from the important metrological problem of measuring at any given point on the globe the quantity g, the acceleration of terrestrial gravity in absolute cgs units. The value of g is not a constant. It varies from point to point on the earth's surface because of (a) the oblateness of the earth's figure, (b) variations in centrifugal force with latitude, (c) variations in altitude, (d) local fluctuations in the density of the earth's crust, and (e) other causes such as the gravitational effects of extraterrestrial bodies and the like. Save for the latter effects which are quite small and predictable, g at a given location is very constant in time. But it is much easier to measure the *small differences* in g from point to point on the globe, even to a microgal ($1\ \text{gal} = 1\ \text{cm/sec}^2$), than it is to measure its absolute value at any one point. The absolute value is known scarcely better than several milligal. Measuring the differences merely requires carrying a pendulum from one point to another and comparing its natural period of oscillation at the different stations. By such methods, geophysicists have determined the "gravity net" for many points on the earth's surface and these measurements form a highly overdetermined system. The work has been performed by many different observers using different types of apparatus and the results yield a high and rather satisfactory degree of consistancy as regards the differences from point to point. The normalization of the entire system in terms of absolute gals is a far more difficult problem and it turns out from recent measurements that the world has been using a value of g which was everywhere about 14 ppm too high, based on

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[4] J. M. de Lepinay, H. Buisson, and J. R. Benoit, Trav. Mem. BIPM **14** (1910).

measurements made at Potsdam by Kühnen and Fürtwangler[5] in 1906.

The absolute value of g at a given point on the earth's surface where measurements of force or energy are to be standardized with high accuracy in terms of our fundamental cgs units is crucial. It is not feasible at present to maintain a separate standard of force which can be "put on the shelf" and reproduced when required with accuracy comparable to that with which our primary units of length, mass, and time are capable of reproduction. Those three magnitudes still remain our fundamental ones because they are still the most accurately (as well as conveniently) definable, maintainable, and reproducible choices. As soon as this ceases to be the case, but not before, an alternative set should undoubtedly be adopted, for it is this practical consideration which must dominate. But there is still no immediate prospect of such a revision. If then we are to relate force and energy to mass, length, and time, the process must involve the measurement of an acceleration. The reason for the choice of terrestrial gravity as the acceleration to measure is again a practical one: first, it is sufficiently constant in time at any given place so that, once the difficult and time-consuming task of an absolute determination to ±1 ppm (preferably better if possible) has been accomplished, one is not likely to have to repeat it soon again, and second, it is convenient because it lends itself so readily to the standardization of forces in absolute units by *weighing*, one of the most accurate metrological operations. Thus we are to think of the local absolute value of g at any given locality as the conversion factor there between mass-by-weighting and force. Here then we are again confronted with the same situation which we have been discussing above in which two different physical magnitudes can each be measured on its own local scale (i.e., local to its own domain of measurements) more accurately than the two can be related to each other through a conversion factor.

(5) "As Maintained" and Unqualified Absolute Electrical Units

Many more instances like the four preceding could be cited, but we shall only mention one other because of its great importance and also because it involves the one we have just described. For many years two sets of electrical units, the "International" and the "Absolute" units, were in use. Here, as in most other cases, the reason was related to practical metrological considerations. The units of voltage and resistance were the two best choices to define, reproduce, and maintain experimentally with high accuracy (by means of frequent intercomparisons using banks of standard cells and standard resistors). On the other hand, the metrological problem of relating these units with comparable accuracy to our fundamental units of length, mass, and time was, and still is, a very difficult one. If we are to have a consistent physical system it is indispensable to have such a relationship established so that mechanical energy and force shall be comparable to their electrical counterparts. The method of establishing this relationship which has now been under study and in use for about thirty years is to determine the absolute ampere by weighing the magnetic force which two helical current-carrying solenoids of wire exert upon each other. The geometry of the two solenoids must be determined with extremely high accuracy. A knowledge of the absolute value of g at the site of the experiment is also clearly required. The absolute ohm, on the other hand, is determined by means of a similar current-carrying solenoid whose inductance is accurately calculable from its measured geometry. If an alternating current of accurately known frequency is used, the reactance of this solenoid in ohms can be compared by bridge methods with the resistance of a standard resistor. These two descriptions are greatly oversimplified statements of the procedures for normalizing the absolute electrical units *in principle*, with no claim to accuracy in detail.

Much more recently a third procedure, that of the Lampard condenser, has been under study. This consists of a way of building capacitors from whose accurately measured geometrical dimensions their electrical capacities in absolute cgs electrostatic units can be calculated. Since only two electrical quantities need be standardized in absolute units to normalize the entire system, the addition of this third approach will, it is hoped, introduce the much-to-be-desired overdetermination which will furnish a check on previous results. The velocity of light will of course be involved in such a check.

In 1946 it was decided to abolish the international electrical units and to quote the calibrations of all electrical standards (cells and resistors) in absolute amperes and ohms starting 1 January 1948. The stated reason for this step[6] was that the techniques of establishing the absolute units had advanced to a point where they compared favorably in precision with the reproducibility and constancy of the International Units (based on intercomparisons of standard cells and resistors, thanks chiefly to work at the US-NBS and at the British NPL).

Unfortunately this step has tended to conceal some of the operational facts about the metrology of standardization and maintenance of the "absolute" electrical units. *The actual process consists of two distinct operational procedures*: (1) the difficult, painstaking pro-

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[5] F. Kühnen and P. Fürtwangler, Veröffentl. Preuss. Geodat. Inst. N.F. No. 27 (1906).

[6] The history of this development and the eventual establishment of the electrical units on the absolute cgs system is well described in a circular of the National Bureau of Standards (U.S.); F. B. Silsbee, "Establishment and Maintenance of the Electrical Units," Natl. Bur. Std. (U.S.) Circ. **475,** 1–30 (1949).

cedure (with precision solenoids) of establishing the absolute ampere and ohm, which can scarcely be done to much better precision than about 3 or 4 ppm, and which has been repeated in the U. S. approximately once in a decade, and (2) the *maintenance* of these units (in terms of the mean values of banks of frequently intercompared standard cells and resistors). Cells or resistors which exhibit sudden or marked changes in value from the average of a large bank are rejected and replaced. In this way only a very slow slippage in the mean value of a bank can be expected to occur. However, if the results of two absolute standardizations effected ten years apart (even using the same solenoids) are compared in this manner, it is quite impossible to say how much of the observed discrepancy should be assigned to random and systematic errors in the standardization procedure itself and how much to slippage in the maintenance procedure during the ten-year interval. Little or nothing can be done about this save to try to improve and make more frequent the absolute standardizations. But what we aim to point out here is that there are really two distinct steps in the process of arriving at certification in absolute electrical units of a cell or resistor: (1) absolute standardization once per decade, (2) maintenance of the standard over a period of years.

All national standardizing laboratories pay homage to this fact in the language used in their electrical certifications. The voltage of a standard cell is certified by the US-NBS as so-and-so many absolute volts "as *maintained* at the U. S. National Bureau of Standards." But it is important to realize that a similar certification in absolute volts "as maintained at the British NPL" or "as maintained at the Mendeleef Institute of Metrology" are not necessarily exactly the same. Each of the national standardizing laboratories makes its own separate independent periodic absolute standardizations and maintains its own standardized units over the intervening periods of time. Every three years the "as maintained" absolute units of the different laboratories are intercompared at the BIPM in Sevres under the auspices of the "Consultative Committee on Electricity," and, as one would expect, there are found to be minor disagreements. For standard cells these were as large as 5 or 6 ppm in 1963.

(6) *The Absolute Gravity Net and Absolute Electrical Units*

It must be recalled that these dissonances are probably somewhat enhanced by the fact that each national laboratory uses its own absolute determination of the local value of g in reducing its current-balance data in its periodic restandardizations of the absolute ampere. To our knowledge no effort has yet been made to combine all such data on the world gravity net by means of a least-squares adjustment which would seek to eliminate systematic errors, and try to establish a "best" mean value for the normalization of the net in absolute units. Clearly the intercomparisons of the electrical units would perhaps furnish valuable contributory information to such a normalization. We think that such least-squares studies should be made in an effort to pull the physical standards of the world together into better agreement and we have suggested to the director of the BIPM that it be proposed.

At the time of this writing there is no international officially agreed-upon current "best" value of a conversion factor between the absolute electrical units "as maintained at the International Bureau of Weights and Measures" and the absolute units without qualification, i.e., as nearly as the latter can be ascertained by adjustment of *all* the national standardizations at the present time. Without such world-wide agreement, comparison of research results from different parts of the world is greatly hampered.

At this stage it is worth pointing out that while *agreement* is desirable, the really important and interesting things are the *disagreements* the causes of which we would like to find in order to eliminate them. Mere verbal and conventional agreement is not a solution. A danger threatens all organized institutional work that such an exaggerated value may become attached to mere stability and agreement as to offer a temptation to substitute agreement for accuracy.

In summary then, it becomes necessary to recognize that at any national standardizing laboratory there are still in actual fact two systems of so-called "absolute" electrical units: the "as maintained" absolute units and the absolute units without qualifying adjective. These last, ideally defined as they must be relative to our fundamental units of length, mass, and time, are operationally only approximately accessible at present, and comparative agreement about them in different world laboratories still exhibits discrepancies of several ppm. For this reason a conversion factor between "as maintained absolute units" and unqualified absolute units (as nearly as they are known) is, for purposes of highest precision, a factor which must be quoted by each laboratory at a given epoch. For example, the US-NBS has supplied us with the information that, to the best of their knowledge in 1962,

1 US-NBS ampere ("as maintained" at US-NBS) =
1.000012±0.000004 absolute ampere.

We have been at some length to illustrate the reasons for the inevitability of units of measurement local to limited domains of the physical sciences and the consequent necessity for conversion constants linking such local units to our fundamental units of length, mass, and time. In every case the reason and the inevitability reside in facts about the current state of available precision in different metrological techniques.

Unless we retain the local units and the associated conversion coefficients, we would be obliged to sacrifice the very valuable level of higher precision available in comparing magnitudes within each local domain.

It is strange how often we encounter proposals on the part of physicists and chemists to solve such situations by framing verbal conventions or by defining the numerical values of conversion coefficients by decree! A difficult problem of experimental precision metrology cannot be solved by verbal definition or decree any more than a state legislature was able to decree the legal value of the ratio of the circumference of a circle to its diameter![7] The structure of physics, as far as we know it, admits of only a small number of arbitrarily defined units, and once these are fixed the system becomes overdetermined and loses its consistency if others are arbitrarily injected without the introduction of conversion factors, factors which must be *experimentally determined.*

Since we must live with conversion coefficients (distasteful though this may be, especially to theoreticians) if the experimental verifiability of the physical sciences is to be retained, it is important to be alert to the danger of overlooking hidden error-statistical correlations which may be present between two or more items of experimental data because one and the same conversion coefficient has been used in reducing them. (Needless to say, it is of course even more important to avoid outright inconsistencies which may be introduced into a general least-squares adjustment because different values for the same conversion coefficient have been used by different experimenters in calculating the values of different items of input data. This mistake, less likely to be made by a reviewer because more obvious than the hidden correlation, comes from the fact that experimenters scarcely ever measure what they say they measured and frequently forget to report the values of the conversion factors they have used.)

1.6. Correlated Errors

The error-statistical correlation between the error distributions of experimentally measured data and the effect of such correlation in calculating the propagation of such errors into further data dependent upon them is often forgotten. In setting up the equations of observation of a least-squares adjustment to obtain recommendable "best" output values of the constants, careful attention must be paid to possible correlations which may exist between the numerical data of observation appearing in two or more of the equations because a common stochastic conversion factor may have been used whose error contributed substantially to the errors of the two or more equations. If this has been permitted to happen, the numerics of the two or more equations will have correlated error distributions. As a result, simple numerical weights to be assigned to each observational equation, are no longer appropriate to the situation. Instead a weight *matrix* is required which must take into account not only the variances associated with the numerics of each equation but also the covariances between pairs of equations. Such a complication is however usually easily avoided by recasting the observational equations to contain explicitly an adjustable unknown, the conversion coefficient in question, which in this way is no longer "buried" in the numerical data. No overdetermination need be sacrificed by this device because an additional observational equation is also to be added which expresses the source of information from which the value of the conversion constant had previously been secured.

One other very important caveat related to error correlation is needed at this point. *The output values of a least-squares adjustment are in general correlated.* As a result, if these output values are to be used in combination in formulas to compute further physical magnitudes, the generalized formula of error propagation, taking into account not only the variances of the stochastics in the formula but also the covariances between all possible pairs of them, must be used. If this is not done, the error assigned to the result may be either too small or too large depending on the algebraic signs of the contributions from the covariances. There is no help at all for this difficulty.[8] It is the price we pay for using least-squares adjusted best values. It reflects the actual complexity of the relationship of the output values to the input data from which they were derived. There is no other way known to us of obtaining *a completely consistent set of values* based on our experimental knowledge at a given epoch and consistent with the accepted theoretical relationships of that epoch.

Let the n error-statistically correlated data be the stochastic variables, $x_1, x_2, \cdots, x_n$. We wish to calculate the σ_y, of a quantity, y, which is given by a function of the x's.

$$y=f(x_1, x_2, \cdots, x_n). \tag{2}$$

Then the variance, σ_y^2, of y is given by

$$\sigma_y^2=\sum_{i,j=1}^{n}\frac{\partial f}{\partial x_i}V_{ij}\frac{\partial f}{\partial x_j}, \tag{3}$$

where V_{ij} is the variance matrix. Formula (3) may also

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[7] Action on House Bill 246, Indiana State Legislature (1897), was postponed indefinitely on 11 Feb. 1897, after preliminary acceptance by a unanimous vote of 67–0 nine days earlier. This bill would have defined π exactly, and granted to the citizens of the state the royalty-free use of this value.

[8] It would be possible to eliminate the correlations between the error distributions of the adjusted output values of the unknowns of a least-squares adjustment by a transformation to a new set of unknowns chosen so as to diagonalize the output variance matrix. However this, in general, leads to a set of output quantities which have no clearly defined physical interpretation. It must be recognized that the structure of the output variance matrix is a more-or-less accidental result of the state of precision of our knowledge of the different input data in any given adjustment.

be written in terms of the correlation coefficients, r_{ij},

$$\sigma_y^2=\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\sigma_i\right)^2+2\sum_{i<j}r_{ij}\frac{\partial f}{\partial x_i}\sigma_i\frac{\partial f}{\partial x_j}\sigma_j. \tag{4}$$

In Eq. (4) the first summation gives the ordinary propagated error when the variables x_i are error-statistically independent (all $r_{ij}=0$). The second summation may be either positive or negative and represents the modification in the ordinary formula for statistically independent errors because of the presence of correlation.[9]

1.7. The Single-Route Method

Since the generalized formula of error propagation described in the last paragraph is the price which must be paid for using values of the constants resulting from a least-squares adjustment of overdetermined experimental data, one hears occasionally the suggestion that this complication be circumvented by resort to the single-route method. This method implies that we select from the entirety of available data at the given epoch a preferred set just sufficient to determine the constants and that we ignore all other data of that epoch. One would naturally presume that the preferred set should be carefully chosen so as to be that set which yields the most reliable and accurate value of each desired constant, and that it be sufficient to determine all the "unknowns" required for calculating all the desired fundamental constants and conversion factors.

In the first place, the question immediately arises whether these two requirements are necessarily compatible. The selection of a set of measured input data just sufficient to yield without overdetermination the most accurate value of one unknown may not necessarily lead to the same set as one would select to get the most accurate value of another unknown. Thus, although there may be (in fact, is) a best set of data for determining any *one* physical constant, there may not be a unique best set from which to determine *all* of the fundamental physical constants.

It was pointed out in an earlier article[10] that the available data in 1954 (7 equations of observation in 4 unknowns) afforded as many as 14 distinct single routes for arriving at a value of the Avogadro number, N, for example. Each route gave a slightly different value of N with a different standard deviation. No one of these 14 results is, *a priori*, to be considered better than another. These different results are, however, clearly not error-statistically independent. One cannot get 14 independent results, given only 7 independent equations. In this overdetermined situation the only logical solution is one by least-squares adjustment. A statistically correct weighted averaging of the 14 statistical correlated results on N is a much more laborious method of solution than the straightforward method of least squares, applied directly to the 7 independent observational equations in 4 unknowns. One of us, in a survey of the sources of information available in 1959 on the x-unit-to-milliangstrom-unit conversion factor, Λ,[11] has listed 10 different just-determinate single routes for calculating that constant, routes which can be formed out of appropriate combinations of the 7 equations of observation in 4 unknowns representing the 7 independently observed items of experimental data. Here, again, precisely the same remarks apply as we have made for the earlier 14 routes for getting N. The same sort of embarrassment of choice would exist for almost any constant one might care to select as his objective. The arbitrariness and inconsistency inherent in the single-route method is too heavy a price to pay for avoidance of the slight additional trouble involved in the generalized formula of error propagation entailed by the use of a least-squares solution.

2. REVIEW OF THE EXPERIMENTAL DATA

2.1. Selection of the "Unknowns" to be Adjusted

With passage of time and accumulation of experimental and theoretical data, the words "fundamental constants" have come to include an ever wider domain until now the scope covers nearly all of classical physics and that much of atomic and nuclear physics as is concerned with the interaction between matter and radiation through the agency of electrons. Unfortunately, nuclear forces, and constants relative thereto, must still be excluded from our least-squares adjustments since our knowledge of them is at a so much lower level of precision and the theory is still inadequate and uncertain. Gravitational forces also remain disconnected theoretically from the domain we deal with, and experimentally the general Newtonian constant of gravitation which has been measured only to four significant figures, stands in lonely isolation from all the rest of physics.

The constants space required for the description of the analysis in 1960 is defined by: α, the fine-structure constant of Sommerfeld; e, the fundamental electronic unit of charge; N, the Avogadro number; and Λ, the conversion factor from x-ray wavelengths expressed on the Seigbahn (nominal) scale in x-units and the same wavelengths expressed in milliangstrom units. The selection of these *particular* unknowns is largely based on mathematical and computational convenience in the structure of the observational equations of the adjustment, and any other set of physical constants

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[9] A more detailed discussion of error correlation in general and of the values of a least-squares adjustment is given by E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, in *Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957), Chap. 7.

[10] J. W. M. DuMond and E. R. Cohen, Phys. Rev. **94**, 1790 (1954).

[11] Jesse W. M. DuMond, Proc. Natl. Acad. Sci. **45**, 1052 (1959).

developed from these which spans the space may be used equally well.

In the course of our studies of the input data, and after making a reasonably complete "analysis of variance" thereof[12] it became evident to us that we could no longer safely include any of the x-ray data in the 1963 adjustment; it was not that the x-ray data were notably more imprecise than in the past, but that the data from other sources had reached a level of precision such that we preferred not to run the risk of vitiating them with possible systematic errors which the inconsistencies in the x-ray data indicated the latter must contain. The probable sources of these inconsistencies will be discussed below at the proper place [Sec. 2.5(2) *et seq.*].

2.2. Classification of Experimental Input Data

Ever since the first studies[13] of R. T. Birge in 1929, it has been found convenient to classify the experimentally obtained input data of such least-squares adjustments into two groups: (a) "auxiliary constants" (the more precisely known numbers), and (b) the less accurate remainder of the data, considered nevertheless sufficiently precise for inclusion as input data. The "auxiliary constants," a term we owe to R. T. Birge, are those measured quantities whose precision is so much superior to the rest that they can, in comparison to the remainder of the data, be treated as though they were known without error. Since errors combine quadratically, a quantity known with a precision an order of magnitude better than the rest of the input data does not contribute appreciably to the output uncertainties. It can be treated as a fixed star, an exactly known quantity. The so-called imprecise or stochastic input data, on the other hand, are those data whose estimated error measures are large enough to affect the weighting of the observational equations. As already pointed out, there should be one, and only one, such stochastic quantity associated with each observational equation to avoid error-statistical correlations between them.

2.3. Changes in Definitions of Units Since 1955

(*1*) *The Unified Scale of Atomic Weights*

After several years of consideration by the IUPAP and IUPAC, the new unified scale of atomic weights was adopted by them in a joint action taken at Ottawa, Canada in 1960. This scale is based on the arbitrary assignment of the mass of exactly 12 units to the isotope ^{12}C. As such, this definition was selected to replace both the so-called physical scale of atomic weights based on the assignment of mass 16 to the isotope ^{16}O and the so-called chemical scale of atomic weights which assigns the mass 16 to the "natural" isotopic mixture of oxygen isotopes. The qualification "unified" was given this new scale because it was chosen to replace the two slightly different earlier ones. The urgent need for a revision, however, came not from the confusion resulting from the existence of two scales, but rather from the fact that the greatly improved level of precision reached by using physical methods of comparing nuclidic masses had so far outstripped the precision of atomic mass determinations (by the older stoichiometric methods) that the old definition of the chemical scale in terms of "a natural mixture of the oxygen isotopes" had become unsatisfactorily ambiguous. The transition to this new scale has been greatly facilitated by the excellent and exhaustive computations of Everling, Koenig, Mattauch, and Wapstra, first reported at the First International Conference on Nuclidic Masses held at McMaster University in 1960.[14] Revisions and additional data have been added to their work since then.[15,16] The work consists of a comprehensive least-squares adjustment of an enormous budget of highly overdetermined experimental data on the masses of all nuclides both as obtained by mass spectroscopy and as obtained by nuclear reaction measurements. The standard deviations of the masses are in all cases less than a few parts per million.

In the unified scale of nuclidic masses the mass of ^{16}O is given [15] as $15.99491494 \pm 0.00000028$, so that we have the following conversion factor from the unified scale to the old physical scale, $^{16}\mathrm{O}=16$:

$$\frac{\text{Mass on physical scale } (^{16}\mathrm{O}=16)}{\text{Mass on unified scale } (^{12}\mathrm{C}=12)} = 1.000317917 \pm 0.000000017.$$

The definition of the old chemical scale (O = 16) is confused by the uncertainty of the definition in terms of "natural isotopic abundances" for oxygen in the face of known variations in these abundances,[17] depending on the origin of the oxygen sample. These differences are possibly the result of biological processes since the $^{18}\mathrm{O}/^{16}\mathrm{O}$ ratio for oxygen from inorganic sources (FeO or water) is as much as 4% less than that from air or limestone. The nominal conversion factor often used for converting masses on the old chemical scale to masses on the old physical scale,

$$r = 1.000275 \pm 0.000005,$$

whose assigned uncertainty reflects the above variability in abundance of the oxygen isotopes, has been used in the past by the IUPAC as an *exact* value. At one time it was proposed to define the chemical

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[12] Over 150 least-squares adjustments of subsets of the data were examined for consistency. This "analysis of variance" is described in its proper place.

[13] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[14] F. Everling, L. A. König, J. H. E. Mattauch, and A. H. Wapstra, Nucl. Phys. **15**, 342 (1960); **18**, 529 (1960).

[15] L. A. König, J. H. E. Mattauch, and A. Wapstra, Nucl. Phys. **31**, 1 (1962); **31**, 18 (1962).

[16] J. E. H. Mattauch, W. Thiele, and A. H. Wapstra, Nucl. Phys. (to be published, 1965).

[17] A. O. Nier, Phys. Rev. **77**, 792 (1950).

scale in terms of the old physical scale by *adopting* the above conversion factor as an exact value.

One argument advanced in favor of the present "unified" ($^{12}C=12$) scale was that it coincides numerically with the old chemical scale to within 43 ppm, a difference which the chemists regard as negligible for many purposes. For somewhat more precise purposes we have the conversion factor

$$\frac{\text{Masses on the old chemical scale (O}=16)}{\text{Masses on the unified scale (}^{12}\text{C}=12)}=1.000043\pm0.000005,$$

in which the large uncertainty of 5 ppm is due to the indefiniteness of meaning of the definition of the old chemical scale in terms of "natural" oxygen.

A valuable study by Cameron and Wichers[18] has been made in which the results of the above-mentioned nuclidic mass tables[14] combined with the best selected nuclidic abundance ratios are used to compute mean atomic weights for comparison with the chemically determined atomic weights.

(*2*) *The Redefinition of the Thermodynamic Temperature Scale*

The thermodynamic temperature scale in the past, as exemplified by the centigrade scale, was based on the arbitrary assignment of 0° and 100° to the melting point and boiling point, respectively, of water under a pressure of one atmosphere. This definition leads experimentally to a thermodynamic temperature scale in which the absolute-zero temperature point is -273.16 ± 0.01°C. This scale has now been abandoned officially by action of the Tenth General Conference on Weights and Measures in October 1954, at which it was decided[19] "to define the thermodynamic scale of temperature by means of a triple-point of water as fixed fundamental point, by assigning to it the temperature 273.16° Kelvin exactly." Thus the two defining fixed points are officially now the triple-point of water and the absolute zero.[20] The melting point of water under one atmosphere pressure is then an experimental quantity determined by measurement to be 273.1500 ± 0.0001°K. On this thermodynamic scale the ice-point of water is 0.0000 ± 0.0001°C and the steam point is 99.9964 ± 0.0036°C. Thus we can no longer say that we have a centigrade scale in the sense that there exists a 100° temperature difference between two fixed points, and the name "centigrade" should be abandoned, although the designation °C is to be retained, with the new scale referred to as the "Celsius" scale. The Kelvin scale of temperature is defined by adding 273.15 to the Celsius scale as here defined.

2.4. Revisions of Auxiliary Constants

(*1*) *The Acceleration of Terrestrial Gravity*

Although the value of gravity in absolute cgs units is admittedly not a fundamental natural constant (nor, for that matter, strictly a constant at all) its importance as a "transfer constant" in precision metrology is enormous, since operationally it serves as a link of high precision between our fundamental, arbitrarily defined, but highly reproducible standard of mass (the prototype kilogram at Sevres) and all of our force and energy units. Gravity *differences* between two stations on the world gravity net [see Sec. 1.5(4)] can be determined in many cases to better than 0.1 ppm.[21] Wherever high-precision determinations or standardizations of forces or quantities related to force in absolute units are to be made, by far the most accurate way of doing this is by "weighing the force" with a precision balance. The mass whose gravitational pull equilibrates the force to be determined must then be multiplied by the absolute local value of g where the weighing is done to ascertain the force in dynes.

Since the differences in g between stations on the gravity net are known to better than a part in 10^7 of g itself, it would suffice, at least in principle, to normalize the entire net on an absolute basis by a single absolute determination at one point. So great at the present time, however, is the interest in ascertaining better absolute values of g that some eleven of the world's largest national standardizing laboratories have been working recently (or are preparing for work very soon) with great diligence and care on this problem.[22]

The experimental difficulties of defining the absolute base for gravity measurements to a precision of ±1 ppm are considerable. For many years the absolute determination made with the Kater reversible pendulum method in 1906 by Kühnen and Fürtwangler[5] at Potsdam (981.274 cm $\sec^{-2}$) was regarded as the international standard and was used to normalize the entire world gravity net. The system of absolute

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[18] A. E. Cameron and E. Wichers, Report of the International Commission on Atomic Weights, 1961 (unpublished); J. Am. Chem. Soc. **84**, 4175 (1962); Analyt. Chem. **35**, 23A (1963).

[19] E. C. Crittenden, "Report on the Tenth General Conference on Weights and Measures," Science **120**, 1007 (1954).

[20] In the official recommendation, natural water is specified for the triple-point determination, recognizing that the isotopic composition of the water will in principle affect the precise value of this equilibrium point although in describing the procedure no representative isotopic abundances for "natural" water are defined or discussed. However the present error limits for such measurements are such that the natural isotopic variation in water (that has not been purposely fractionated) is of little importance. When experimental techniques make a more precise definition necessary a selected isotopic composition will have to be specified.

[21] C. Morelli, "Absolute and First Order World Gravity Net," Special Study Group No. 5, Report to the International Union of Geodesy and Geophysics (IUGG), Aug. 1959 (unpublished).

[22] A. H. Cook, "Report on Absolute Measurements of Gravity," read at a meeting of the Standards Division, International Gravity Bureau, Paris, Sept. 1962 (unpublished). See also, A. H. Cook "Recent Developments in the Absolute Measurement of Gravity," Bull. Geodesique No. 44, 34–59 (1957).

gravity values derived in this way for all net points went by the name of the "Potsdam Gravity System." Since then, however, evidence has been accumulating that this Potsdam value is too high by something in the neighborhood of 15 ppm. The U. S. National Bureau of Standards has for twenty years or more used a gravity standard for g_0 at Washington of 980.082 cm $\sec^{-2}$, which is 17 ppm lower than the value on the Potsdam normalized network. The first suspicion of this systematic error was due to the work of P. R. Heyl at the US-NBS. The original data of the Potsdam determinations were then carefully re-examined by Hugh L. Dryden and the probable cause of the trouble was located chiefly in certain unjustified corrections made in the Potsdam determination. The downward correction of 17 ppm just mentioned is called "the Dryden reduction."[23]

The pendulum method of measuring g was employed to circumvent the difficulties which with earlier more primitive techniques accompanied the measurements of small time intervals to high accuracy. With recent improvements in time standards and the ability to measure nanosecond intervals, increasing attention has been given to gravity measurements utilizing the straightforward timing of bodies either in free fall or by what may be called the "upsy-daisy" method (the body catapulted straight upward in vacuum, then returning in free fall to its starting point). In the latter method the time differences for the transit of the body past two points differing in height by a precisely measured distance constitute the observed quantities. A surprising difficulty with the method of the free body (either falling or upsy-daisy) in vacuum has been reported by A. H. Cook in his work at the British NPL. As the body is disconnected electrically from ground (as it must be to fall freely) it appears difficult to avoid its becoming charged electrically. By permitting the freely falling body to pass without contact through a metal ring or tube in the vacuum (the ring being connected to an oscilloscope), Cook reports having observed signals indicating potentials on freely falling glass balls as large as 5000 volts. Electrically conducting coatings on the ball, Cook reports, apparently eliminate the trouble. One cannot help wondering whether this effect of electrical charging in vacuum may not also have vitiated the work done with the uncoated quartz reversible pendulums frequently used[24] which could only be electrically connected to ground through their supporting knife edges and on which accidental electrical charges would only leak away very slowly because of the very low electrical conductivity of quartz. Clearly the problem of determining the absolute acceleration of terrestrial gravity to the level of precision consistent with many present day physical measurements is a difficult one, not even yet solved as satisfactorily as could be wished.

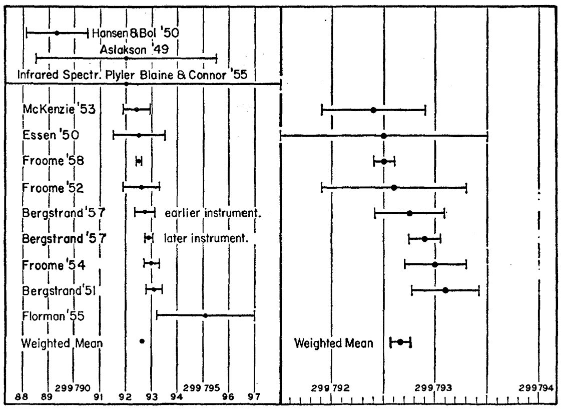

Fig. 1. Values of the velocity of light obtained between 1949 and 1958.

For the 1963 adjustment we have assumed, what now seems reasonably well established, that the traditional "Potsdam value" of gravity should be corrected downward by 13.0±0.4 milligals. This correction is important for the adjustment because of its effect on the absolute determination of the ampere. The change of 4 ppm from the Dryden reduction implies a change of 2 ppm in the value of the ampere as maintained by the U. S. National Bureau of Standards during the past decade.

(2) The Velocity of Light

In the past 15 years there have been some 11 notable measurements of the velocity of light, probably the most important of all constants. These are listed with the references in Table I. The four, Aslakson; Hansen and Bol; Plyler, Blaine, and Conner; and Florman, claim so much lower precision than the rest as to carry little weight in any judgment as to the consistency or inconsistency of the entire group. The remaining seven show quite good consistency. Weighting them as the inverse squares of their error assignments one obtains $c=299792.66\pm0.09$ km/sec. Figure 1 exhibits this situation graphically. All of the data are shown on the left. The more precise data, with omission of the four above-mentioned measurements of lower precision, appear on the right. We shall not, however, adopt precisely the foregoing weighted average value. We have evaluated it for purposes of illustration of certain fairly important points applicable in many instances to our efforts to arrive at recommendable values of oft-measured fundamental constants.

The striking difference of about 17 km $\sec^{-1}$ between the present general region of values obtained for c and the older result, $c=299776$, adopted in 1941 by R. T. Birge[25] as a "best" weighted average, based

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[23] P. R. Heyl and G. S. Cook, J. Res. Natl. Bur. Std. **17**, 805 (1936); H. Jeffreys, Monthly Notices Roy. Astron. Soc. (Geophys. Suppl.) **5**, 219 (1948); **5**, 398 (1949).

[24] For example by P. N. Agaletski and K. N. Egorov, Izmeritel. Tekhn. **1956**, No. 6, 29.

[25] R. T. Birge, Rept. Progr. Phys. **8**, 90 (1941).

Table I. Some measurements of the velocity of electromagnetic waves and of light published between 1949 and 1958.

Author	Date	Method	c in km sec^{-1}	Remarks
Aslakson[a]	1949	Shoran	299 792±3.5	
Hansen and Bol[b]	1950	FLCR	299 789.3±1.2	FLCR = fixed-length cavity resonance
Essen[c]	1950	VLCR	299 792.5±1.0	VLCR = variable-length cavity resonance
Bergstrand[d]	1951	Geodimeter[k]	299 793.1±0.32	
Froome[e]	1952	FSMWI	299 792.6±0.7	FSMWI = free-space microwave interferometer
Mackenzie[f]	1953	Geodimeter[k]	299 792.4±0.5	
Froome[e]	1954	FSMWI	299 793.0±0.3	
Plyler *et al.*[g]	1955	Inf. Spectr.	299 792±6.0	Infra-red spectrometer
Florman[h]	1955	FSMWI	299 795.1±1.9	
Bergstrand[i]	1957	Geodimeter[k]	299 792.75±0.34	Earlier instrument
			299 792.85±0.16	Later instrument
Froome[j]	1958	FSMWI	299 792.50±0.10	

[a] C. I. Aslakson, Nature **164**, 711 (1949).
[b] K. Bol, Phys. Rev. **80**, 298 (1950).
[c] L. Essen, Proc. Roy. Soc. (London) **A204**, 260 (1950); Nature **167**, 758 (1951)
[d] E. Bergstrand, Arkiv Fysik **2**, 119 (1950); **3**, 479 (1951).
[e] K. D. Froome, Proc. Roy. Soc. (London) **A213**, 123 (1952); **A223**, 195 (1954).
[f] I. C. C. Mackenzie, *Ordnance Survey Professional Paper, No. 19* (Her Majesty's Stationery Office, London, 1954).
[g] E. K. Plyler, L. R. Blaine, and W. S. Connor, J. Opt. Soc. Am. **45**, 102 (1955).
[h] E. F. Florman, U. S. Natl. Bur. Std. Tech. Bull. **39**, 1 (1955).
[i] E. Bergstrand, Ann. Franc. Chronom. **II**, 97 (1957).
[j] K. D. Froome, Proc. Roy. Soc. (London) **A247**, 109 (1958).
[k] Bergstrand's Geodimeter is a Kerr-cell modulated device for measuring the group velocity of visible light over paths of the order of 10 km.

chiefly on work of A. A. Michelson and co-workers,[26,27] using the rotating polygonal mirror, and of W. C. Anderson,[28] using Kerr-cell modulation, has caused wide-spread surprise and discussion and has gone a long way to discourage the practice of trying to arrive at "best" weighted average values of the constants. In particular, R. Dupeyrat[29] in an interesting review of recent work on c, in which the several results are carefully classified according to the nature of the velocity measured and the method employed, arrives at the conclusion that "there is no point in taking a weighted mean" of the different results. A similar conclusion has been reached by A. G. McNish, Chief Metrologist of the US-NBS. The present authors are also convinced that blind weighted averaging of a mass of data without critical examination of how the items were determined is to be deplored. In fact, by far the most arduous part of the work of the reviewer who prepares a critical study such as the present one is precisely this careful examination of the sources of data. As R. T. Birge[25] has very aptly pointed out, "one must go far behind the scenes," correspond with the experimenters, if possible in crucial cases visit their laboratories, to form an opinion of the reliability of the work. The case of the 17 km sec^{-1} discrepancy between the old Birge-recommended value of c and the newer values obtained by more modern methods of measurement has been described by Birge as one of the most astonishing systematic errors in the history of physics. In point of actual fact the chief source of error in the older estimate came from a systematic error in the experimental result of Michelson, Pease, and Pearson, performed in a mile-long evacuated tube laid on unstable soil near Santa Ana, California. Although some 2885 replicated observations of the time of flight were made, there were only a few (2 or 3) determinations of the distance. All the time measurements were made at night and the distances in the daylight. The site was near the ocean and variations in the results which seems correlated with the tides were observed. No one knows now what caused the systematic error in this work, but it is valuable to look at a frequency curve of the replicated time-of-flight data, reproduced here in Fig. 2. This frequency plot gives the number of observations of time of flight which yielded a value of c in each velocity interval of 5 km sec^{-1}. Above the peak of this curve we have plotted the mean value and probable error adopted by R. T. Birge in 1941 as indicative of the results of the Michelson, Pease, and Pearson experiment. The heavy vertical line on the right represents, by its position and roughly by its thickness, the value

$$c = 299792.5 \pm 0.4 \text{ km sec}^{-1}.$$

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[26] A. A. Michelson, Astrophys. J. **65**, 1 (1927). Although this work on a light path between Mt. Baldy and Mt. Wilson, California, came much closer to the presently accepted value, Birge gave it lower weight, chiefly because of the great replication of the 1935 measurements.

[27] A. A. Michelson, F. G. Pease, and F. Pearson, Astrophys. J. **82**, 26 (1935).

[28] W. C. Anderson, Rev. Sci. Instr. **8**, 239 (1937); J. Opt. Soc. Am. **31**, 187 (1941).

[29] R. Dupeyrat, J. Phys. Radium **19**, 557 (1958).

This last is the value adopted by the International Scientific Radio Union at their Twelfth General Assembly in 1957 and also accepted by the International Union of Geodesy and Geophysics. It is in close agreement with Froome's most recent and most accurate measurement of microwave velocity made in 1958 with his free-space microwave interferometer. Froome, however, claims an even smaller error, ±0.1 km sec^{-1}. Note also that this officially adopted value is not in significant disagreement with our above mentioned mean of the seven most accurate determinations of Table I. The adopted value quoted above is that which we have adopted for c in our 1963 adjustment.

It is perhaps significant to note (see Fig. 2) that the *standard deviation* of Michelson, Pease, and Pearson's time-of-flight observations is 13.3 km sec^{-1}, more than three times the probable error assigned by Birge to the mean value. Thus the systematic error of 17 km sec^{-1} is in fact only 1.3 standard deviations and, looked at in this light, is not particularly shocking. Birge explains in his 1941 review, referring to the frequency curve (here shown in Fig. 4) "—the distribution of the residuals deviates appreciably from a normal error curve. But I find that a very good fit can be obtained if one takes the sum of two such curves, one with a standard deviation of 5 km sec^{-1} (for a single observation) and the other of 15 km sec^{-1}." If there could be said to be any error of judgment on Birge's part, then, it is perhaps that he was a little too optimistic in assuming that the narrower of the two component normal error curves into which he was able to decompose the observed frequency distribution, was representative of the "good" observations. It is all too easy in the light of hind-sight, however, to be unduly critical of this subjective choice. As a reviewer he was obliged to make *some* choice or to abdicate his extremely useful function.

What is the lesson to be learned from Fig. 2 and from this history of a rather drastic revision which was found to be required in a constant thought to be well established up to 1949, but later, with improved methods of measurement, found to have been erroneous by more than four times the probable error assigned to the earlier value? We believe the following four points are worth mentioning.

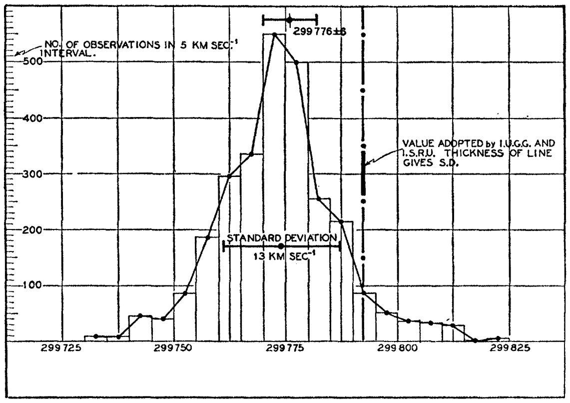

Fig. 2. Histogram of the distribution of Michelson, Pease, and Pearson's 2885 observations of the time of flight of light in a mile-long evacuated tube.

(a) It would be quite unjust to stigmatize adoption and recommendation of the value 299776±4 km sec^{-1} in 1941, because later and more accurate methods of measurement proved that value to be 17 km sec^{-1} too low. Birge's choice in 1941 was made after a very careful study and consideration of all the data available to him at that time. Two things contributed strongly to mislead him and would have mislead anyone else in the same circumstances. These were the great prestige of Michelson's name as an expert in this field,[30] and the fact that W. C. Anderson's two measurements using Kerr-cell modulation in 1937 and 1941, agreed quite well with the Michelson–Pease–Pearson result.

Birge[31] makes the following important (and for any reviewer, disturbing) remark, whose origin he credits to E. O. Lawrence. "In any highly precise experimental arrangement there are initially many instrumental difficulties that lead to numerical results far from the accepted value of the quantity being measured... Accordingly, the investigator searches for the source or sources of such errors, and continues searching until he gets a result close to the accepted value. Then he stops!... In this way one can account for the close agreement of several different results and also for the possibility that all of them are in error by an unexpectedly large amount." This dangerous tendency for numerical results done at about the same time to agree somewhat better than should be expected, has been remarked by others. P. A. Franken has described it as "intellectual phase locking." Our first point then is that, having done one's best with the available data, we must all learn not to be too surprised or disappointed if more highly developed methods subsequently reveal the presence of systematic errors unsuspected at the earlier date and of considerably larger magnitude than the earlier estimate of random error.

(b) It would also be a grave mistake to condemn all efforts to arrive at "best" values because of the discovery of occasional surprising systematic errors such as the present example. That science, in spite of its blunders and mistakes, does make progress in the long run is indisputable. It does so precisely because we keep trying to do a better job in spite of such reverses. If we as reviewers refuse to take the risk of being found wrong at a later date, we are not being very helpful toward the goal of achieving at least a temporary consensus for those of our colleagues who have not the time to devote to such detailed review studies.

(c) It would be an equally grave mistake to rec-

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[30] Michelson's influence during the performance of this experiment was unfortunately almost nil on account of his poor health. He died before the experiment was completed.

[31] R. T. Birge, Nuovo Cimento, Suppl. 6, 39 (1957).

ommend that the reviewer enlarge his error estimates "to take care of possible but unknown systematic errors." Systematic errors in physical measurements do not obey any known statistics. There are, of course, limitations to the applicability of the experimental method. We simply have to learn the hard fact that, having arrived at a determination of a physical quantity and its estimated uncertainty in the light of all the best information available at a given epoch, this may prove at a later epoch, when we have more and better information, to have been wrong.

(d) It is not only unwise to average blindly and indiscriminately a mass of data without careful study of how each item was obtained, it is unwise, even after careful study of the items, to average together data whose estimated error measures differ too widely. The reason for this is that, in practice, experimental physicists rarely worry about eliminating or correcting causes of systematic error likely to perturb their results by amounts of much smaller order of magnitude than the random errors to which their chosen measuring technique is subject. Scarcely any experimenter will worry about a possible source of systematic error likely to cause a shift of one tenth of a standard deviation of the random error of his measurements and many will be far less meticulous than this. Thus if we mix into our weighted average a large proportion of items of low accuracy, in spite of the fact that these will receive low weight, we may be doing more harm than good to our mean value because of the systematic errors these imprecise data may bring with them.

Two further review articles concerned with the velocity of light are worth mention here, one by K. D. Froome,[32] the other by E. Bergstrand.[33]

In the 1955 Adjustment, the velocity of light was treated as a variable; now, however, we are considering it as an auxiliary constant. There are two reasons for this. Firstly, even if we take the value with its larger error conventionally adopted in 1957 by ISRU and IUGG, that relative error corresponds to only slightly more than 1 ppm, and this is about one-quarter the relative error estimated for the most accurate of the unknowns which we treat as subject to adjustment. Froome's estimated error in c, for the same numerical value, is only one-quarter of this. Secondly, because of this, the velocity of light, if treated as an adjustable variable, enters into the structure of the equations of observation in such a manner as to have its output value insensitive to the rest of the input data. Thus, there is little information to be gained by making c an adjustable unknown.

(3) The Electron Magnetic Moment Anomaly

The anomalous magnetic moment of the electron was first calculated to second order in α by Karplus and Kroll.[34] The calculation has been shown to be in error by the more recent work of Sommerfield,[35] Peterman,[36] Kroll (who repeated the earlier calculation and verified the correct formula), and Smrz and Ulehla,[37] all of whom are in agreement with regard to the value of the coefficient of the second-order term. The corrected result is

$$\mu_e/\mu_0 = 1 + \alpha/2\pi - 0.328(\alpha/\pi)^2 + \cdots. \tag{5}$$

Using a value of $\alpha^{-1} = 137.039$, the above formula gives

$$\mu_e/\mu_0 = 1.00115961. \tag{5a}$$

Since a relative change in α in Eq. (5) results in a relative change in μ_e/μ_0 only 1.16×10^{-3} times as large, and since this value $\alpha^{-1} = 137.039$ is consistent with both our input and output values for our 1963 adjustment, we feel that the numerical value of μ_e/μ_0 is certainly trustworthy to a few parts in 10^8, provided the unknown terms of order higher than the second in α/π do not exceed 1×10^{-8}. Such would be the case if their numerical coefficients were of order unity or less, and since the first two such coefficients are 0.5 and -0.328 such an assumption is not implausible. No calculation of the higher order coefficients has been made. The calculation is long and arduous but there is no reason to expect that the magnitude of the third-order term would be found to be an order of magnitude larger than unity. At the time of completing our 1963 adjustment, we *assumed* that the above value of μ_e/μ_0, Eq. (5a), was reliable to at least 1 ppm and adopted it therefore, as one of our auxiliary constants. Fortunately, the direct experimental evidence obtained by Crane and Wilkinson[38] supports our adopted value of μ_e/μ_0. Their experimentally measured value of μ_e/μ_0, 1.00115962, differs from our adopted value by only one part in 10^8 with an uncertainty of 3 parts in 10^8. This close agreement may be fortuitous. Further critical discussion of this work appears in a later section [2.5(10)].

(4) Magnetic Moment of the Proton in Bohr Magnetons

Eight sources of information obtained between 1949 and 1959 on this important datum are listed in Table II. The accuracy with which this constant is known permits us to treat it as an auxiliary constant. It is possible to measure the proton moment directly in Bohr magnetons by measuring the ratio of the cyclotron frequency of the free electron to the proton resonance frequency in the same magnetic field. Items 1 to 4 of Table II are examples of this method. Items 5 to 8 in that table represent experiments where the ratio of the

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[32] K. D. Froome, J. British Inst. Radio Engrs. **16**, 497 (1956).

[33] Eric Bergstrand, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXIV, p. 1.

[34] R. Karplus and N. M. Kroll, Phys. Rev. **81**, 73 (1951).

[35] C. M. Sommerfield, Phys. Rev. **107**, 328 (1957).

[36] A. Peterman, Nucl. Phys. **5**, 677 (1958).

[37] P. Smrz and I. Ulehla, Czech. J. Phys. **10**, 966 (1960).

[38] D. T. Wilkinson and H. R. Crane, Phys. Rev. **130**, 852 (1963).

TABLE II. Proton moment in Bohr magnetons (corrected to the bare proton). Diamagnetic corrections: -29.7 ppm, mineral oil, spherical sample; -26.0, H_2O spherical sample.

	ω_e/ω_p	μ_0/μ_p	
1. Gardner, Purcell	657.475 ± 0.008 (oil, H_2O)	657.4565	Phys. Rev. **76**, 1262 (1949) Phys. Rev. **83**, 996 (1951)
2. Liebes, Franken	657.462 ± 0.004 (oil)	657.442	Phys. Rev. **104**, 1197 (1956) Phys. Rev. **116**, 633 (1959)
3. Hardy, Purcell	657.4676 ± 0.0005 (gas)	657.4501	Bull. Am. Phys. Soc. **114**, 37 (1959)
4. Sanders, Tittel, Ward	657.4620 ± 0.0024 (oil)	657.4436	Proc. Roy. Soc. (London) **A272**, 103 (1963)
	g_j/g_p'	g_s/g_p	
5. König, Prodell, Kusch	658.2171 ± 0.0004 (oil)	658.2096	Phys. Rev. **88**, 191 (1952)
6. Beringer, Heald	658.2181 ± 0.0003 (oil)	658.2106	Phys. Rev. **95**, 1474 (1954)
7. Geiger, Hughes, Radford	658.2169 ± 0.0004 (oil)	658.2094	Phys. Rev. **105**, 183 (1957)
8. Lambe, Dicke	658.21591 ± 0.00002 (H_2O)	658.2105	Thesis, Princeton University, 1959 (unpublished)

$$g_j/g_s - 1 = \tfrac{1}{3}\alpha^2 = 17.75 \text{ ppm}$$

$$\mu_0/\mu_p = (g_s/g_p)_{\text{Lambe}}/(\mu_e/\mu_0) = 657.4481$$

$$\mu_p/\mu_0 = 0.0015210325$$

g factors for the electron and proton were measured and the results then corrected by the ratio, μ_e/μ_0.

The earlier measurement of μ_0/μ_p by Gardner and Purcell[39] was repeated with increased accuracy by Hardy and Purcell.[40] This measurement, which claims an accuracy (standard deviation) of 0.0005, disagrees with the measurement by Liebes and Franken[41] by 0.0071 ± 0.0030. On the other hand, the measurement by Sanders, Tittel, and Ward[42] is in excellent agreement with the Liebes and Franken result. The most accurate determination of μ_0/μ_p, however, comes from the measurement of the electron and proton g factors. The measurement by E. B. D. Lambe[43] gives $g_j/g_p' = 658.21591 \pm 0.00002$ with the proton g factor uncorrected for diamagnetism of the spherical H_2O proton sample. This measurement represents an accuracy of one part in 30 million. The bound-electron correction (see Table II) is $+17.75$ ppm and the proton diamagnetic correction is -26.0 ppm. Although this latter correction may be inaccurate by several parts in 10^7, if we use it as an adopted correction factor, Lambe's measurement yields $g_s/g_p = 658.2105$. Using the theoretical value for μ_e/μ_0, we then calculate

$$\mu_0/\mu_p = 657.4481.$$

This value is smaller than the Hardy and Purcell measurement by 0.0030 and larger than the Sanders, Tittel, and Ward measurement by 0.0045. We shall therefore adopt it as our best estimate of the auxiliary constant μ_0/μ_p.

(5) *Rydberg Constant for Infinite Mass, R_∞*

This constant, known to a precision of 1 part in 10^7, clearly belongs among our auxiliary constants. It has been recalculated[44] from the original observational data taking into account the "Lamb shift" discovered by W. Lamb, Jr. and R. C. Retherford[45] in 1947 and other relevant developments connected with the fine-structure splitting in the spectra of hydrogen[46] and ionized helium.[47–53] In the recalculation[44] of R_∞ the work of W. V. Houston, of Drinkwater, Richardson, and Williams, and of D. Y. Chu were reviewed. Houston's and Chu's data were spectroscopic measurements in both cases, based on the value 5015.675 Å for a reference line in the He spectrum measured by P. W. Merrill[54] at Mt. Wilson Observatory. To normalize the Houston and Chu results to the higher accuracy for

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[39] J. H. Gardner and E. M. Purcell, Phys. Rev. **76**, 1262 (1949); **83**, 996 (1951).

[40] W. A. Hardy and E. M. Purcell, Bull. Am. Phys. Soc. **114**, 37 (1959).

[41] S. Liebes and P. Franken, Phys. Rev. **104**, 1197 (1956); **116**, 633 (1959).

[42] J. H. Sanders, K. F. Tittel, and J. F. Ward, Proc. Roy. Soc. (London) **A272**, 103 (1963).

[43] E. B. D. Lambe, thesis, Princeton University, 1959 (unpublished).

[44] E. R. Cohen, Phys. Rev. **88**, 353 (1952).

[45] W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **72**, 241 (1947); **75**, 1325 (1949); **79**, 549 (1950); **86**, 1014 (1952).

[46] H. Kuhn and G. W. Series, Nature **162**, 373 (1948); Proc. Roy. Soc. (London) **202**, 127 (1950).

[47] W. E. Lamb, Jr., and M. Skinner, Phys. Rev. **78**, 539 (1950).

[48] J. E. Mack and N. Austern, Phys. Rev. **72**, 972 (1947); **73**, 1233 (1948); **74**, 1262 (1948).

[49] G. R. Fowles, Phys. Rev. **73**, 639 (1948); **74**, 219 (1948).

[50] H. Kopfermann and W. Paul, Nature **162**, 33 (1948).

[51] K. Murakawa, S. Suwa, and T. Kamei, Phys. Rev. **76**, 1721 (1949).

[52] H. Kopfermann, H. Krüger, and H. Ohlmann, Z. Physik **126**, 760 (1949).

[53] J. G. Hirshberger and J. E. Mack, Phys. Rev. **77**, 745 (1950).

[54] P. W. Merrill, Astrophys. J. **46**, 357 (1917).

appropriate comparison with the work of Drinkwater *et al.*, careful measurements were made by W. C. Martin[55] at the U. S. National Bureau of Standards, who reports the value 5015.6782±0.0003 Å, by G. W. Series and J. C. Field[56] at the National Physical Laboratory, Teddington, who report 5015.6775±0.0004 Å, and by J. Terrien[57] at the BIPM, Sevres, who gives 5015.6778±0.0001 Å, all subsequent to the 1952 study. With these improvements, the consistency of the three sources of data turned out to be satisfactory and the result

$$R_\infty = 109737.31\ \text{cm}^{-1}$$

has been adopted.

(6) *Mass Ratios, Hydrogen-to-Proton, H/M_p, and Deuterium-to-Deuteron, D/M_d*

These ratios are readily calculated with extremely high precision using the atomic mass of the electron, of H and of D on the unified scale. We adopt

$$\text{H} = 1.00782522 \qquad (^{12}\text{C} = 12)$$

$$\text{H}/M_p = 1.000544607$$

$$\text{D} = 2.01410219 \qquad (^{12}\text{C} = 12)$$

$$\text{D}/M_d = 1.000272448.$$

(7) *Conversion Factor: 1 NBS "As Maintained" Coulomb to Absolute emu*

The conversion factor between NBS electrical units and absolute cgs units is discussed in Sec. 1.5. The difficulties associated with the determination of this factor were there described and the best value, as determined by the U. S. National Bureau of Standards as of 1962, was given as

1 NBS coulomb $= 0.1000012 \pm 0.0000004$ cgs emu.

We list in Table III the auxiliary constants discussed in this section and adopted for use in the 1963 adjustment.

2.5. Input Data Subject to Least-Squares Adjustment

We are presented with seven different types of experimentally determined physical magnitudes which can be functionally related, either directly or through the use of the accurately known auxiliary constants of Table III, to the unknowns, α, e, N, and Λ, the quantities which we have selected as our objectives for least-squares solution. For brevity we shall call each of these experimentally measured input data a stochastic. It is a datum the estimated imprecision of which is sufficient to warrant its inclusion as an item subject to adjustment through the least-squares process.

In many cases one of the seven types of physical magnitudes may have been determined by several different teams of research workers, sometimes in different ways, and whenever the different determinations seemed to have comparable or nearly comparable claims to precision we have retained them as separate items in our equations of observation. We have done this in some cases when two or more determinations of the same physical magnitude exhibited suspiciously large discrepancies in value, relative to their estimated errors, expressly for the purpose of seeing, from their residues (and other tests) in a trial least-squares adjustment, which ones fitted into the entire adjustment better. Each observational equation involves one and only one stochastic, the experimental input datum the imprecision of which determines the error and weight associated with that equation.

The different equations of the overdetermined set are connected in such a way that no single experiment (stochastic) can be said, in general, to define any one of the fundamental constants, α, e, N, and Λ, uniquely. It is for this reason that statistical analyses, such as the method of least-squares, must be used not only to extract the maximum information from the entire set of experimental data, but also to give an indication of those experiments which, because of their inconsistency with the consensus of the remaining experiments, are likely to be afflicted with various systematic errors. We shall first list and describe the experiments and their numerical results and then discuss more fully the relationships which exist among them and the formation of the adjustment.

The stochastic data about to be discussed, as far

TABLE III. Fixed auxiliary constants used in the 1963 adjustment.

1. Velocity of light, c	299 792.5 km sec^{-1}
2. Electron moment in Bohr magnetons, μ_e/μ_0	1.001159615
3. Proton moment in Bohr magnetons, μ_p/μ_0	0.0015210325
4. Rydberg constant for infinite mass, R_∞	109 737.31 cm^{-1}
5. Atomic masses and ratios (unified scale, ^{12}C=12)	
H	1.00782522
H/M_p	1.000544607
D	2.01410219
D/M_d	1.000272448
6. 1 US-NBS Coulomb=0.1000012 abs. emu[a]	

[a] The standard deviation of 4 ppm assigned to this conversion factor by the US-NBS metrologists is by far the largest uncertainty attributable to any of our auxiliary constants.

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[55] William C. Martin, Phys. Rev. **116**, 654 (1959).

[56] G. W. Series and J. C. Field, *Proceedings of the Symposium on Interferometry, 1959* (National Physical Laboratory, Teddington, 1960), Suppl. No. 11, p. 93.

[57] J. Terrien, *Proceedings of the Symposium on Interferometry,* 1959 (National Physical Laboratory, Teddington, 1960), Suppl. No. 11, p. 103.

as we know, comprised all of the available precision measurements bearing on the fundamental constants of sufficient accuracy to qualify for inclusion in our 1963 adjustment. As we shall see, after a trial adjustment and an "analysis of variance" of the input data, the data from the field of x rays exhibited internal inconsistencies of sufficient magnitude that we decided to reject all of it from our input data for the final 1963 least-squares adjustment.

(*1*) *X-Ray Data Bearing on the Avogadro Number*

Crystals may be idealized as three-dimensional periodic lattice structures built up of unit cells the geometry of which can be precisely determined by the methods of x-ray crystallography, so that the *volume* of the unit cell can be known very accurately *on the relative* scale of x-ray wavelengths, i.e., in cubic x-units, though unfortunately much less accurately in terms of our macroscopic cgs units (e.g., Angstroms or centimeters), because of the imprecision in our knowledge of the conversion factor, Λ, between the two scales. The x-unit (a quantity proposed by M. Siegbahn *circa* 1928) was originally intended to be 1 milliangstrom or 10^{-11} cm; however, through ruled-grating diffraction measurements it has been shown to be larger than the milliangstrom by about 0.2%.[58] Unfortunately, not only is the conversion factor not sufficiently accurately determined at present; worse still the *definition* of the x-unit is such that a deplorable degree of ambiguity has existed with respect to the whole table of x-ray emission-line wavelengths, and hence the very *meaning* of the conversion constant Λ is (on the presently desired level of precision for our least-squares adjustment) too ill-defined. We shall discuss the reasons and remedies for this below.

Each unit cell of a crystal, depending on the crystal symmetry system, consists of a whole number, or simple rational fraction, of molecules of its chemical formula. In any case this number, which we shall call f, is exactly known (f may equal for example $\frac{1}{2}$, or 8). Thus the product of f and the molecular mass, M, gives the molecular mass of the unit cell. The product of the density, ρ, of the crystal by the absolute volume, v, of its unit cell should ideally give the absolute mass of the unit cell, and the quotient of Mf by ρv should thus give the Avogadro number N. However, since we do not in fact measure the absolute volume of the unit cell in cm^3, but do measure the density in g cm^{-3}, it is necessary to recognize that XRCD (x-ray crystal density) data alone do not, in fact, yield a value of N but rather a value of the product $N\Lambda^3$. The following equation is a statement of this for the case of an ideally perfect crystal lattice

$$N\Lambda^3 = (MF/\rho d_x^3 \phi)\cdot 10^{33} \qquad (6)$$

wherein d_x is the grating spacing of some set of the crystal's atomic planes, *measured in x-units by x-ray diffraction methods*, and ϕ is a dimensionless numerical shape factor depending on the shape of the unit cell in cubic x-units. Since ϕ can be determined by x-ray measurements of grating spacing *ratios* or by measurements of *angles* between atomic planes, it is independent of the wavelength *scale* employed in making the measurements. In Eq. (6), Λ is the conversion factor (roughly 1.0020) to convert wavelengths measured in x-units to wavelengths measured in milliangstrom units. Clearly, though Λ is ill-defined and uncertain, *the product* $N\Lambda^3$ is not, since all the factors in numerator and denominator of the fraction in Eq. (6) are measurable to high accuracy, if sufficient pains are taken.

Numerous direct determinations of Λ have been made[59–64] which depend on difficult precision measurements of x-ray emission lines reflected in grazing incidence on artificial ruled diffraction gratings. Several review papers summarizing such work on Λ have also been published.[65–67] Its true value by such means is doubtful to several tens of parts per million. Different precise determinations have fluctuated over a range much in excess of 100 ppm. Part of this spread is undoubtedly caused by the indefiniteness of definition of the x-unit itself.

The question immediately arises as to why we treat the XRCD determination of the conceptually awkward composite quantity, $N\Lambda^3$ of Eq. (6), and the determination of the conversion constant Λ as two separate data rather than combining them so as to determine the conceptually far more interesting Avogadro number directly. The reasons are twofold: (1) because, as we shall see, the present XRCD data yield a mean value of $N\Lambda^3$ with an uncertainty of order substantially less than ± 20 ppm (though various sources of such data using different x-ray emission-line wavelengths disagree with each other, as we shall see, by much more than this) whereas the value of Λ by direct determinations of x-ray wavelengths with ruled gratings is only established with considerably poorer accuracy and consistency than this, and (2) because the present state of our knowledge is such that, in any general least-squares adjustment of fundamental constants involving x-ray data, Λ must enter, explicitly or implicitly, as one of the unknowns subject to adjustment, and will do so in more than one of the fundamental obser-

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[58] This error is primarily due to the use by Siegbahn of an incorrect (but at that time accepted) value of the electron charge (4.774×10^{-10} esu).

[59] J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

[60] J. A. Bearden, Phys. Rev. **48**, 385 (1935).

[61] M. Söderman, Nature **135**, 67 (1935); dissertation, Uppsala, 1934 (unpublished).

[62] E. Bäcklin, Z. Physik **93**, 450 (1935).

[63] F. Tyren, Z. Physik **109**, 722 (1938); dissertation, Uppsala, 1940 (unpublished); Nova Acta Reg. Soc. Sci., Uppsala **12**, No. 1 (1940).

[64] B. Edlen and L. A. Svensson, Arkiv Fysik **28**, 36 (1965).

[65] R. T. Birge, Am. J. Phys. **13**, 69 (1945).

[66] J. A. Bearden, J. Appl. Phys. **12**, 395 (1941).

[67] J. W. M. DuMond, Proc. Natl. Acad. Sci. **45**, 1052 (1959).

vational equations, thus resulting in objectionable correlations between equations.

There were at least 17 high-precision XRCD measurements bearing on $N\Lambda^3$ which we deemed worthy of consideration in connection with the 1963 adjustment. Since some of these measurements were made as much as 30 years ago, often with a purpose other than our primary one of the high-precision determination of the atomic constants, it has been necessary in all cases to go back to the original observational data in order to extract the maximum amount of information in a consistent manner from all of the measurements. In all cases the molecular weights of the crystals used were recomputed on the basis of current best values of nuclidic masses and measured isotopic abundances. Except for crystals of anisotopic composition, such as Al, the limiting factor in the molecular weight determination is the abundance of the isotopes rather than the nuclidic masses. In all cases those physical molecular weights so computed are more precise than the adopted chemically determined weights, but generally not inconsistent with the latter. The only exception to this statement is in the case of germanium, for which the physically computed atomic weight is 72.630±0.006, whereas the chemical atomic weight, as determined by gravimetric methods is 72.60.[68] It has also been necessary in many cases to recompute lattice spacings from the measured x-ray diffraction angles, including, where appropriate, a correction for the crystal index of refraction.

A vital source of uncertainty in these data is the wavelength of the characteristic x-ray line used to measure the crystal lattice spacing. X-ray measurements can determine only diffraction angles. Thus the measurement gives dimensions in *x*-units and does so only relative to an adopted wavelength (in *x*-units) for the line used. For many years the original conventional definition arising from the early work of M. Siegbahn has been in use. This definition is implicit in the assumption that the "effective"[69] grating space of the calcite cleavage planes at 18°C for first-order Bragg reflection and for a crystal of *purest calcite* is given by

$$d_1(18°)=3029.040\ x\text{-units}.$$

The trouble with this definition, on the level of precision of interest for us, is that it gives us no prescription how to know when we have in hand a sample of "purest calcite," nor is it certain that all samples of calcite, which show no detectable impurities will necessarily have exactly the same grating constants. The wide variation from sample to sample of natural crystals is well known and calcite is no exception. Different samples have been shown by Ievins and Straumanis[70] to exhibit wide fluctuations over a range exceeding 100 ppm. J. A. Bearden[71] has also observed similar variations and using gamma-ray emission lines (spectrally much narrower in width than x-ray lines) has lately reported clearly observable fluctuations from point to point in a single calcite sample.[72] In short, the adoption of the grating constant of *a species of crystal*, as a definition for a unit in terms of which to measure wavelengths is no longer sufficiently unambiguous in view of the level of precision required today for many purposes.

It is important to realize that, since the x-ray emission line wavelengths (perhaps some 3000 in all) were measured by many different people using different calcite crystals from sample to sample, there is no guarantee, to the precision desirable at present, that our tables of x-ray wavelengths in so-called *x*-units are really all expressed in terms of one and the same length standard.

A test of the chemical purity of one's calcite crystal is today no guarantee that one is using the same *x*-unit as that used by even so famous an authority as M. Siegbahn. One of us has been informed by M. Straumanis that in an answer to his (Straumanis') written inquiry whether a famous well-known sample of calcite, much used by M. Siegbahn in his precision wavelength determinations had ever been tested for impurity content, Siegbahn replied by letter that it had not been analyzed, adding "but how could so clear and beautiful a sample contain impurities!" This is not cited to ridicule great pioneers such as Siegbahn, who worked in ignorance of many facts now better known, but to illustrate the danger in assuming that the old wavelength determinations can be accepted as being expressed in terms of a common well-defined unit, the very existence of whose *name* creates the illusion that it stands for something reproducible and better defined than in fact it really is.

Another grave source of uncertainty concerning the presently accepted tabular x-ray wavelength values stems from the fact that there has never been any universally established and accepted convention as to

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[68] *Both* of these numbers are on the unified ($^{12}C=12$) scale; by "physical" and "chemical" we here imply only the basis of the methods of determination, i.e., isotopic abundances and nuclidic masses in the one case and gravimetric determination of chemical equivalent weights in the other.

[69] W. Stenström [dissertation, Lund University, 1919 (unpublished)] demonstrated the existence of a deviation from Bragg's law ($n\lambda=2d\sin\theta$) for the case of Bragg reflection from crystalline atomic planes parallel to the x-ray beam's entry–exit boundary surface. This he correctly attributed to the fact that x-rays have an index of refraction in the crystal slightly lower than unity. To satisfy Bragg's law connecting λ and θ, "effective" values of the grating constant, depending on the order number, n, of the reflection must replace the true d. For higher orders, d-effective approaches the true d. In the case of Bragg reflection in the nth order from the calcite cleavage planes, the following empirical formula for the effective grating constant d_n has been often used:

$$d_n=(1-135\cdot10^{-6}/n^2)d,$$

where d is the true grating constant for those planes. This correction only applies in the case of Bragg reflection when the planes are parallel to the entry–exit boundary surface of the crystal; for *internal* reflection in a slab of crystal from planes *normal* to the two parallel exit and entry surfaces, the correction vanishes.

[70] A. Ievins and M. Straumanis, Z. Physik **116**, 194 (1940).

[71] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).

[72] J. A. Bearden, Bull. Am. Phys. Soc. **9**, 387 (1964).

just what feature of the natural spectral profile of an x-ray emission line is referred to when *the* wavelength is quoted. Possible features which the tabular values *could* refer to are (1) the peak or point of maximum intensity (more operationally defined below), (2) the centroid (a term which also requires more discussion), (3) the center of the area of the natural profile, and (4) the wavelength which bisects the horizontal chord taken at half-maximum height. (Many others could no doubt be imagined.) Since many x-ray emission lines have markedly asymmetric natural profiles (Cu $K\alpha$, for example) and since $\Delta\lambda/\lambda$, the relative half-width at half-maximum height of most x-ray lines, is quite broad (of the order of 3×10^{-4} for K lines and 5×10^{-4} for L lines), different features of the line profiles can differ in wavelength *by many tens of ppm.* Of course no one ever really observes the true natural spectral profile of a line, but one can come close to doing so with perfect crystals and instrumentation such as the two-crystal spectrometer. Further corrections are also possible, to "unfold" the instrumental effects from the line profile which perhaps renders its shape even a little closer to the natural shape. No such precautions have been taken, however, until fairly recently in the case of a very few lines. Many tabulated wavelengths have been estimated by setting a cross-hair on the "center" of the streak of blackened silver grains in a photographic spectrogram (e.g., the "tube spectrometer" method of Siegbahn). There is no telling which of the above listed four line features this might refer to depending on how underexposed or overexposed the photographic image might happen to be.

We strongly favor choice of feature (1) above, the peak-of-profile, as that feature probably capable of highest wavelength reproducibility with use of the following method (often attributed to Rayleigh) for determining it. One draws chords across the profile (parallel to any background upon which the line profile may be superposed) locates their midpoints, and extrapolates the locus of these to the peak of the curve. For substantially symmetric lines such as Mo $K\alpha$, or W $K\alpha$, the locus will be sensibly a vertical straight line and the root-mean-square deviations of the various chordal midpoints from such a vertical can be made as small as 0.001 of the half-width with sufficient care and good statistics.

We believe that the centroid is, from the point of view of definiteness and reproducibility, an undesirable choice for defining to high precision a fiducial wavelength. This is because x-ray line profiles tend to the Lorentzian line shape which falls off in the wings only as the inverse square of the distance from the line center. If this line shape is strictly obeyed in the wings, the centroid does not exist except as the principal value of a divergent integral. The position of the actual centroid point therefore becomes very sensitive to deviations, either of random or characteristic nature, in the remote wings of the profile.

Those who use the data of x-ray spectroscopy today are chiefly interested in crystal structure determination. For such work a relative precision much better than 10^{-3} is rarely needed. This no doubt explains the unfortunate state of affairs in this field when precision several orders of magnitude better becomes imperative. There is a certain insularity about present users of x-ray spectroscopic data and techniques. They see only the immediate needs of their field and overlook the fact that the spectroscopic domain of x-ray wavelengths is sandwiched in between that of nuclear gamma rays on one side and that of ultraviolet and optical wavelengths on the other. All of our primary reference units of length, mass, and time are defined, maintained, and reproduced by means of standards and techniques on the optical side of this gamut. This is not by arbitrary choice, but for excellent practical operational reasons. To link our primary standards and definitions with measurements in the domain of nuclear spectroscopy and nuclear physics so as to express everything on a common basis with all possible precision, important reforms of semantics and conventional definitions, together with a considerable program of high precision x-ray metrological work is needed.

In the absence of such conventions, definitions, and terminology, in order to make our work as unambiguous as possible, we have used the values 707.831 x-units for the peak of the Mo $K\alpha_1$ line and 1537.396 x-units for the peak of the Cu $K\alpha_1$ line. Let it be understood, however, that each of these adopted values we take as an *independent definition* of the term "one x-unit." These two definitions may or may not, upon trial, turn out to be consistent with each other. These numerical values are those listed in oft-consulted wavelength tables such as those of Cauchois and Hulubei,[73] or the more recent tabulation of Sandström.[74] J. A. Bearden has, on the other hand, recently measured the Mo $K\alpha_1$ line relative to Cu $K\alpha_1$, with a resulting ratio different by 17 ppm from the ratio of the tabular values. Because of this, Dr. Walter Bond and A. S. Cooper[75] of the Bell Telephone Laboratories have, at our request, kindly measured this wavelength ratio independently and have verified the Bearden result. In this work, the single-crystal spectrometer method of Walter Bond was used with artificially grown single crystals of germanium. The purpose was, not only to check the new Mo-to-Cu wavelength ratio of Bearden *et al.*, but also to check if possible the Bragg angle measurements of A. Smakula *et al.*, in his determination of $N\Lambda^3$ for germanium. Reflections were obtained by Cooper up to high orders to verify the correction for refractive index from the data itself. In the Bond instrument a Hilger and Watts goniometer measured the angle through which the crystal was turned from

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[73] Y. Cauchois and H. Hulubei, *Longuers d'onde des emissions x et des discontinuities d'absorption x* (Hermann et Cie., Paris, 1947).

[74] A. E. Sandström, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX, p. 164.

[75] A. S. Cooper (to be published).

Table IV. Comparison of wavelength ratios of λ(Mo $K\alpha_1$) and λ(Cu $K\alpha_1$).

	From tables (x-units)	Bearden, Johns Hopkins (Two-crystal spectr.)	Cooper, Bell Labs. (Single-crystal spectr.)
Mo $K\alpha_1$	707.831	707.845	707.840
Cu $K\alpha_1$	1537.396	1537.400	1537.395
Ratio Mo/Cu	0.460409	0.460417	0.460415
Ratio of ratios	0.460417/0.460409 = 1.000017; 0.460415/0.460409 = 1.000013		

its position for the nth-order reflection on one side to that for nth-order reflection on the other side of the incident beam (rather than, as in Smakula's case, the angle through which a detecting slit for the reflected beam, relative to the direct beam, was turned).

The measurements of Mo $K\alpha_1$ and Cu $K\alpha_1$ wavelength are compared in Table IV. The wavelength values of both columns 2 and 3 are peak-of-profile values.

On the basis of the ratio from Bearden's laboratory if we retain our quoted value for the Mo $K\alpha_1$ wavelength (as defining the term "x-unit"), we would infer the value 1537.370 for Cu $K\alpha_1$. Because of this disagreement in calibration it has seemed to us best to maintain a separation between data measured on the one hand with Mo radiation, and on the other with Cu radiation. Table V thus lists 16 independent determinations of $N\Lambda^3$ by the XRCD method grouped into two sets of 8 measurements each, one made using Mo $K\alpha_1$, the other using Cu $K\alpha_1$. Henins[76] has recently reported a value of $N\Lambda^3$, using silicon crystal samples with Cu $K\alpha_1$ radiation. If renormalized to a Cu $K\alpha_1$ wavelength of 1537.400 x-units, this gives $N\Lambda^3 = (6059.76 \pm 0.24) \times 10^{20}$, which is in excellent agreement with the Mo data of Table V, but possibly in disagreement with the Cu data. Later work by Henins and Bearden[77] in which 17 silicon crystal samples were studied gives, when normalized to 1537.400 x-units for Cu $K\alpha_1$, $N\Lambda^3 = (6059.77 \pm 0.15) \times 10^{20}$.

The major uncertainty in this determination is the calculation of the atomic weight of silicon. Silicon has three stable isotopes with mass numbers 28, 29, 30 and approximate abundances, respectively, of 0.922, 0.047, 0.031. Seven different measurements of the isotopic abundances[78] show a mean variation of atomic weight of ±0.001 but the quoted accuracy of the abundances is insufficient to indicate whether this variation is due to errors in measurement or to a real variability in isotopic composition. A real variation in composition has been found by Allenby[79] in mass-spectroscopic analyses of Si.

Henins and Bearden have recomputed $N\Lambda^3$ (Mo), i.e., that part of the XRCD data from which we derived a mean value of $N\Lambda^3$ based on measurements of crystal grating constants using the Mo $K\alpha_1$ line (corresponding to the first eight items in Table V). Henins and Bearden, however, reject Brogen's measurements on quartz and calcite because Brogen's densities were not from measurements on the identical samples whose grating constants he had measured. They also reject Tu's density measurements of diamond and replace these by earlier measurements of diamond density by Bearden. They further reject the measurements of Tu on NaCl and KCl, to which we also gave low weight, because of their low accuracy. With these revisions, and using 707.831 x-units for λ(Mo $K\alpha_1$) in order to provide a direct comparison with Table V, they obtain $N\Lambda^3 = 6059.64 \pm 0.55$. With this much larger standard deviation assigned to the Mo data, Henins and Bearden are able to say that the Cu and Mo data "appear quite consistent."

Nevertheless we feel that since the errors we assigned to the items in both our sets of data of Table V yielded a good ratio of external to internal consistency for

Table V. Data on $N\Lambda^3$ (1962).

Crystal	Value of $N\Lambda^3$	Weight w_i	Author
(Mo $K\alpha_1$, 707.831 x-units)			
KCl	6058.23	4	Yuching Tu[a]
Calcite	6059.60	20	G. Brogen[b]
Diamond	6059.60	21	Yuching Tu[a]
Calcite	6059.60	20	J. A. Bearden[c]
Diamond	6059.81	23	Yuching Tu[a]
Calcite	6059.98	35	Yuching Tu[a]
Quartz	6060.06	3	G. Brogen[b]
Rocksalt	6060.11	5	Yuching Tu[a]
Weighted average value $N\Lambda^3 = 6059.72 \pm 0.10$			
(Cu $K\alpha_1$, 1537.396 x-units)			
Silicon	6059.90	23	Smakula *et al.*[d]
CaF_2	6060.05	10	Smakula *et al.*[d]
CsI	6060.08	2	Smakula *et al.*[d]
TlCl	6060.14	5	Smakula *et al.*[d]
Aluminum	6060.17	28	Smakula *et al.*[d]
TlBr	6060.28	5	Smakula *et al.*[d]
Germanium	6060.42	3	Smakula *et al.*[d]
LiF	6060.81	12	Straumanis *et al.*[e]
Weighted average value $N\Lambda^3 = 6060.18 \pm 0.11$			

[a] Y. Tu, Phys. Rev. **40**, 662 (1932).

[b] G. Brogen, Arkiv Fysik **7**, 47 (1953).

[c] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).

[d] A. Smakula and J. Kalnajs, Nuovo Cimento Suppl. **6**, 214 (1957); Phys. Rev. **99**, 1737 (1955); A. Smakula and V. Sils, *ibid.* **99**, 1744 (1955); A. Smakula, J. Kalnajs and V. Sils, *ibid.* **99**, 1747 (1955).

[e] M. Straumanis, A. Ievins, and K. Karlsons, Z. Phys. Chem. **B42**, 143 (1939).

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[76] I. Henins, Bull. Am. Phys. Soc. **7**, 339 (1962).

[77] I. Henins and J. A. Bearden, Bull. Am. Phys. Soc. **9**, 388 (1964); Phys. Rev. **135**, A890 (1964).

[78] G. H. Fuller, *Nuclear Data Tables*, edited by K. Way *et al.* (U.S. Atomic Energy Commission, Washington, D.C., 1959), p. 66.

[79] R. J. Allenby, Geochim. Cosmochim. Acta **5**, 40 (1954).

the weighted means in both cases and yet exhibited a discrepancy between means for Mo and for Cu of 126 ppm with a standard deviation for this discrepancy of 25 ppm, that it is dangerous to wash away this evidence of a systematic error somewhere, merely by assigning an enlarged uncertainty.

In a recent paper, Bearden *et al.*[80] have redetermined the wavelengths of Cr $K\alpha_2$, Cu $K\alpha_1$, Mo $K\alpha_1$, Ag $K\alpha_1$, and W $K\alpha_1$ chiefly using a two-crystal spectrometer in reflection. Assuming a definition of the x-unit such that the peak of the line profile of Mo $K\alpha_1$ is assigned the wavelength 707.831 x-unit, their resulting values for the other four wavelengths are given as:

$$\text{Cr } K\alpha_2,\quad 2288.854\pm0.003\ x\text{-unit};$$

$$\text{Cu } K\alpha_1,\quad 1537.370\pm0.002\ x\text{-unit};$$

$$\text{Ag } K\alpha_1,\quad 558.2486\pm0.0006\ x\text{-unit};$$

$$\text{W } K\alpha_1,\quad 208.5770\pm0.0003\ x\text{-unit}.$$

More recently Bearden[81] has published an extensive survey and re-evaluation of all existing x-ray data, in which the wavelengths have all been corrected as far as possible to these five standard lines. This is the first table of x-ray wavelengths, all of which purport explicitly to be related to a single standard reference x-ray emission line the peak-intensity value of which is taken as the reference for defining the meaning of the arbitrary unit (the "x-unit") in terms of which the relative scale of wavelengths is established. This is a much-needed reform which has been urged by one of us ever since 1957. These tables thus abandon for the first time the older ill-defined definition of the x-unit in terms of the grating spacing of the cleavage planes of "purest calcite."

For these tables Bearden and his group have used the $K\ \alpha_1$ line of tungsten as the fundamental standard. Their "x-unit" is *defined* as such that the wavelength of the W $K\alpha_1$ line at the peak intensity value of its profile is 208.5770 "x-units." Bearden also defines another unit which is neither the traditional x-unit nor an angstrom, but which contains aspects of both these standard quantities. This new unit, which is denoted by A*, is *defined* by the relationship

$$\text{wavelength of peak of W } K\alpha_1 \equiv 0.2090100\ \text{A}^*.$$

The unit A* is thus numerically close to 1 angstrom, but it is operationally an x-ray, not an optical, unit. Its relation to the x-unit is a precisely defined numerical factor,

$$\text{A}^* = 997.92833\ x\text{-units} = \frac{1000\ x\text{-units}}{1.00207597}.$$

The problem of expressing the unit A* in centimeters however is no different than the problem of relating x-units to centimeters, although the numerical factor is close to 10^{-8}, and the distinction between A* and 10^{-8} cm may be neglected if one is interested only in accuracies which are poorer than 50 ppm. The difficulty with the use of this unit however is that one is prone to forget the distinction even when one does require accuracies where the difference is important.

(2) *Conversion Factor,* Λ, *from Siegbahn x-Units to Milliangstroms*

The wavelengths of x-ray spectral lines measured relative to each other by the high precision methods of crystal diffraction are known with a precision which often exceeds one part in 10^5. Unfortunately, as we have indicated in the previous paragraphs, the accuracy with which these wavelengths can be expressed in centimeters or Angstrom units is poorer by approximately a factor of 10. It is for this reason that for many years we have had two scales of x-ray wavelengths—on the one hand a relative scale of x-units on which (if only an operationally better method of *defining* it had been universally adopted and observed) x-ray emission-line wavelengths could be *compared* with all the accuracy permitted by the best crystal diffraction techniques, and on the other hand a less accurately known conversion factor Λ established for converting from x-units to centimeters or Angstroms.

In 1945 R. T. Birge[65] obtained a weighted average value[82] of 1.002030±0.000030, based on ruled grating determinations of Bearden, Bäcklin, Söderman, and Tyren. In 1946 the X-Ray Analysis Group of the (British) Institute of Physics, after consultation with the American Society for X-Ray and Electron Diffraction, recommended[83] for general adoption the somewhat smaller value[84] 1.002020±0.000045. The chief argument for this downward revision was based on measurements of F. Tyren.[63] In this work Tyren had used a concave grating vacuum spectrograph to compare the wavelengths of x-ray lines with the wavelengths of hydrogenic Lyman series spark lines from highly ionized atoms. The absolute wavelengths of these calibration lines were calculated from the Sommerfeld–Dirac theory. In 1947, however, the discovery of the Lamb shift[45] invalidated this entire scheme. The corrections to the Lyman series lines resulting from this are shown in Fig. 3. Tyren's computed calibration line wavelengths required corrections varying from 25 to 100

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[80] J. A. Bearden, A. Henins, J. G. Marzolf, C. Sauder, and J. S. Thomsen, Phys. Rev. **135**, A899 (1964).

[81] J. A. Bearden *et al.*, *X-Ray Wavelengths* (USAEC Div. of Technical Information Extension, Oak Ridge, Tennessee, 1964), NYO-10586. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

[82] Birge states this value as 1.002030±0.000020, but his quoted error is expressed as a probable error, computed from the standard deviation assuming a Gaussian distribution, as $\text{PE}=0.675\sigma$. For consistency with all of the other errors given in this paper we will quote the standard deviation or root-mean-square error.

[83] W. L. Bragg, Acta Cryst. **1**, 46 (1948); J. Sci. Instr. **24**, 27 (1947); E. A. Wood, Phys. Rev. **72**, 437 (1947). In view of the corrected results of Edlen and Svensson this Bragg edict must henceforth be ignored.

[84] Cf. footnote 82.

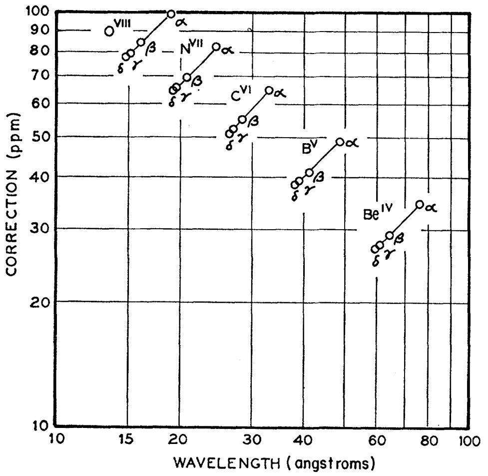

Fig. 3. Lamb-shift corrections to Lyman series lines for hydrogenic spark spectra.

ppm. Without the details of his data (not given in his thesis) it was impossible to make an after-the-fact correction of Tyren's result. The x-ray lines were recorded in several orders and his data did not permit one to tell whether the calibration for example of an 8-Å x-ray line was based on comparison in second order with the Lyman line of O^{VIII}, in third order with N^{VII}, in fourth order with C^{VI}, in fifth or sixth order with B^{V} or in eighth order with Be^{IV}. Tyren's work had therefore to be rejected for our 1963 adjustment.

After a careful study made by us in 1961 and 1962 of all available data on Λ, we decided to retain tentatively for consideration as possible input data to our adjustment the following items:

1. $\Lambda = 1.002020 \pm 0.000035$, J. A. Bearden 1931[59];
2. $\Lambda = 1.002110 \pm 0.000075$, J. A. Bearden 1935[60];
3. $\Lambda = 1.002011 \pm 0.000033$, E. Bäcklin 1935.[62]

Items 1 and 2 are determinations by measuring the diffraction angles on artificial ruled gratings of the Cu $K\alpha$ lines while item 3 is a similar ruled grating determination of the absolute wavelength of the Al $K\alpha_1\alpha_2$ lines.

However, some 18 months after completion of our 1963 Adjustment, a preview copy of a paper by B. Edlen and L. A. Svensson[64] has been received by us. At the time of our first realization[85] that Tyren's numerical results on Λ were invalidated by the discovery of the Lamb shift, we had apprised both F. Tyren and B. Edlen (who had been Tyren's supervisor on this subject) of this point by letter. Professor Edlen in subsequent correspondence with us promised to see what could be done to recover Tyren's original data and his spectrographic plates. The paper of Edlen and Svensson is the result of a very painstaking remeasurement of the Tyren spectrograms to redetermine the wavelengths of the aluminum K lines and a complete recalculation of the resulting data taking the Lamb shift corrections into account. Their result $\Lambda = 1.002060 \pm 0.000023$ shows a change upward of 70 ppm from that of Tyren in 1940 in part due to the Lamb shift corrections and in part to more recent work by Nordford[86] to establish the aluminum line wavelengths more accurately on the x-unit scale.

It becomes immediately important to consider to what precise definition of the x-unit this value of Λ refers, in order, if possible, to normalize the above numerical value, so as to make it comparable to the values involved in the foregoing discussion of $N\Lambda^3$. That is to say, we must seek to relate Nordfors' measurement of the aluminum K x-ray lines in "x-units" to the peak values of either, or preferably both, the Mo $K\alpha_1$ line and the Cu $K\alpha_1$ line. This is an instructive exercise since it reveals how many steps by different workers in different laboratories with different diffracting crystal lattices and different techniques are involved. It serves as a good illustration of the feeling of insecurity one receives regarding the establishment of a consistent scale of x-ray wavelengths in terms of a single unit of measurement to an accuracy comparable with the level of precision attainable from other sources of information on the fundamental constants. Until such a scale is established it is meaningless to quote a value of Λ to ±10 ppm.

Nordfors used the bent quartz crystal spectrometer (1010 planes) of Sandström to compare his Al $K\alpha_1\alpha_2$ wavelengths, reflected in first order, with Ag $L\alpha_1$ and β_1 wavelengths reflected in second order. Several other Al lines, the satellites Al $K\alpha_3$ and α_4 and the Al $K\beta$ line were also measured and wavelengths for both pure aluminum and oxidized targets were studied.

Thus, our next step is to relate Nordfors' reference wavelengths, the Ag $L\alpha_1$ and β_1 line wavelengths, to the Mo and Cu K wavelengths. Unfortunately, as so frequently happens to frustrate the reviewer, Nordfors does not say explicitly what wavelength values he assumed for his Ag reference lines nor how they were obtained or to what they were referred.

The literature apparently reveals only two authors of work on these Ag L lines, L. G. Parratt[87] and P. Haglund.[88,89] Parratt's work, however, used wavelength values taken from Haglund's work for precisely these same two lines to normalize all his other L-series wavelengths, so we must fall back on Haglund's determinations alone. These were accomplished[88] by means of photographic registration with a vacuum-tube spectrometer utilizing a flat calcite crystal. Haglund's paper shows the Ag $L\alpha_1$ line strongly overexposed so that it seems doubtful whether either the sub-

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[85] J. W. M. DuMond and E. R. Cohen, Phys. Rev. **103**, 1583 (1956).

[86] B. Nordfors, Arkiv Fysik **10**, 279 (1955).

[87] L. G. Parratt, Phys. Rev. **54**, 99 (1938).

[88] P. Haglund, Z. Physik **84**, 248 (1933).

[89] P. Haglund, Arkiv Mat., Astron., Fysik **28A**, No. 8 (1941).

TABLE VI. Wavelengths of Al $K\alpha$ lines in x-units and the conversion factor Λ. (The conversion factor Λ is computed using Edlén and Svensson's measurement, $\lambda K\alpha_{1,2}=8.33992\pm0.00020$ Å.)

	Haglund (Ref. 89)	Siegbahn (Ref. 89)	Shearer (Ref. 90)	Cauchois (Ref. 91)	Nordfors (Ref. 86)	Bearden (Ref. 81)
α_2	8324.62	8324.59	8322.35	8323.82	8324.30	8324.45
α_1	8322.18	8322.19	8319.88	8321.37	8321.96	8322.06
Δ	2.44	2.40	2.49	2.47	2.34	2.39
$\bar{\alpha}_{1,2}$	8322.99	8322.99	8320.71	8322.19	8322.74	8322.86
Λ	1.002034	1.002034	1.002308	1.002130	1.002064	1.002050

jectively judged center of the line or the peak of the microphotometer curve traced from the same photograph, gives the peak value of the true spectral profile with sufficient accuracy.

Nordfors cites four earlier results (by Haglund,[90] Siegbahn,[90] Shearer,[91] and Cauchois[92]) of measurements of the aluminum lines. In the most recent and probably the most critically careful of these four, that of Cauchois, a bent mica crystal spectrometer was used to compare the Al $K\alpha$ doublet lines with Cr $K\beta_1$ and Ni $K\alpha_1$ as reference lines. These latter were taken as 2080.597 x-units, and 1654.505 x-units, respectively, based on the two-crystal spectrometer work of Bearden and Shaw.[93] Relative to these lines, Cauchois reports for the two aluminum $K\alpha$ lines from a pure aluminum target: Al α_1 8321.37±0.20; Al α_2 8323.82±0.20. In this case again two steps are required to connect the Cauchois values of Al $K\alpha_1\alpha_2$ with the Cu $K\alpha_1\alpha_2$ lines by way of the Cr $K\beta_1$ and Ni $K\alpha_1$ lines. The mean results on the Cu $K\alpha_1\alpha_2$ line wavelengths of Bearden and Shaw quoted by them on the assumption of the nominal (Siegbahn) value for the calcite crystals they used, are 1537.400 x-units and 1541.219 x-units. Thus one may safely assume that the unit in terms of which these reference lines are quoted is essentially that which we have been using above in the $N\Lambda^3$ determinations with the Cu $K\alpha_1$ line and therefore that the Cr $K\beta_1$ and Ni $K\alpha_1$ wavelengths which Cauchois used as calibration lines to determine the Al $K\alpha_1\alpha_2$ lines are also expressed in these units. Cauchois' results on the Al $K\alpha_1$ lines are slightly lower than those of Nordfors, however, and if Cauchois' values for the α_1, α_2 lines had been used by Edlen and Svensson instead of Nordfors' values, they would have obtained $\Lambda=1.002126\pm0.000023$.

There is even wider variation in Λ if we use the Al $K\alpha$ wavelengths determined by other observers. This is indicated in Table VI. As a matter of consistency therefore, and because it represents a unified tabulation based on a clearly defined specification of the operational realization of the x-unit scale, we shall use the wavelengths in x-units as given in Bearden's tables of x-ray wavelengths.[81] Bearden gives for Al $K\alpha_{1,2}$, $\lambda=8322.86\pm0.14$ x-units where the error has been converted to a standard error. For this line Edlen and Svensson measure 8.33992±0.00020 Å, and hence $\Lambda=1.002050\pm0.000029$. For the $K\alpha_3$ line they measure $\lambda=8.28582\pm0.00030$ Å while Nordfors obtained $\lambda=8268.7\pm0.4$ x-units. We infer from Bearden's tables that this should be corrected to 8268.88 in order to express this wavelength relative to Bearden's W $K\alpha_1$ standard. Hence from the Al $K\alpha_3$ measurement we infer $\Lambda=1.002049\pm0.000050$.

Work such as that of Tyren and Edlen and Svensson, in which Lyman-series spark lines from highly ionized hydrogen-like atoms are used as reference lines, is afflicted with still another uncertainty coming from the fact that these calibration lines are themselves doublets which, to date, no concave ruled-grating technique has been able to resolve. The spectroscopic formulae give the wavelengths of the two members of these doublets and the ratio of their intensities is ordinarily *assumed* to be 2:1. The recorded calibration line position on the plate is assumed to correspond to the centroid of the two lines (i.e., the "center of gravity" with 2:1 weighting). Unfortunately there is no way at present of being certain that this intensity ratio is indeed the correct one or even that the actual intensity ratio is fixed and reproducible. Theory in this respect is of no avail since not sufficient information is known about conditions in the "hot spark" to predict how the levels in the highly ionized atoms may be expected to be populated. The intensity ratio in question may depend upon which technique is employed, the Millikan hot spark, the Vodar "sliding spark," or the Vodar "triggered spark," and upon the details of the voltage transient generated in the discharge, the vacuum pressure maintained, and on other factors.

(3) *Measurements of the Voltage–Wavelength Conversion Product*

The determination of the short-wavelength limit of the continuous x-ray spectrum, generated when electrons of an accurately measured kinetic energy (measured in volts) impinge on a material target, has been the subject of many studies ever since the effect was

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[90] P. Haglund, Z. Physik **94**, 369 (1935).

[91] J. Shearer, Phil. Mag. **21**, 501 (1936).

[92] Y. Cauchois, Compt. Rend. **221**, 25 (1945).

[93] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

first observed by D. L. Webster in William Duane's laboratory at Harvard circa 1915. The experiment amounts to a precision measurement of the wavelength, λ_m, at the short-wave limit of the continuous x-ray spectrum emitted by an x-ray target bombarded by electrons accelerated by a voltage V. This leads to a determination of the voltage–wavelength conversion product, $\lambda_m V = hc^2/e\Lambda$, and is frequently referred to simply as a measurement of h/e. Determinations made prior to 1956 have been discussed in many review papers and will not be listed here. Since then, publications bearing on this subject by Fujimoto,[94] Ulmer *et al.*,[95–98] Sandström,[99] Hagstrom *et al.*,[100] and Spijkerman[101] have appeared.

Hagstrom *et al.*[100] describe an interesting new way of determining the voltage–wavelength conversion product. Photoelectrons from the same atomic shell in a convertor material are photoelectrically ejected by the characteristic x-radiation ($K\alpha_1$) from two different elements. The electron lines are brought to a common focus in a high-precision iron-free magnetic beta-spectrometer by accelerating or retarding the photoelectrons. Equating Ve, the total applied voltage times the electronic charge, to the energy difference between the two x-ray lines, $h(\nu_1-\nu_2)$ or $hc(\lambda_1^{-1}-\lambda_2^{-1})$, gives $hc^2/e\Lambda$. These authors used the Cu $K\alpha_1$ and Mo $K\alpha_1$ lines to eject electrons from the K shell of a manganese convertor. The numerical wavelength values in x-units they used for λ_1 and λ_2 were the tabular values (Table IV) rather than the new values from Bearden's laboratory. Since the two wavelength ratios differ by 17 ppm in these two cases, a corresponding uncertainty enters as to precisely how to define the "x-units" in terms of which the result is given. Hagström *et al.* give as the voltage–wavelength product

$$(E\lambda_s) = 12372.7 \pm 1.5 \text{ kilovolt } x\text{-units}.$$

The stated error includes a provision for systematic error. The purely random (statistical) error of the voltage measurements is only ±0.50 kV x-units. If however we use Bearden's table[81] with Mo $K\alpha_1 = 707.831$ and Cu $K\alpha_1 = 1537.370$ we find, using Hagström's error estimate

$$(E\lambda_s) = 12373.1 \pm 1.5 \text{ kV } x\text{-units}.$$

There are other reasons also why we have felt wary of using this and similar work. The spectral width and asymmetry of the Cu $K\alpha_1$ line raises doubts regarding the interpretation of the electron line spectra, which appear superposed on a sloping background. Does the *apparent* peak of the electron line, photoelectrically ejected from a manganese convertor by the Cu $K\alpha_1$ radiation truly correspond to electrons ejected by the peak wavelength of that x-ray emission line? One would feel happier about this matter, for purposes of highest precision, if *both* x-ray lines were symmetric in profile, and if a more complete theory of photoemission were available.

The novel and ingenious method just described was undoubtedly conceived in an effort to circumvent an analogous difficulty of interpretation encountered in all of the efforts to measure h/e or the voltage–wavelength conversion product by means of the short-wavelength limit of the continuous x-ray spectrum. This is the difficulty of identifying precisely what feature of the "isochromat" or of the curve of continuous-spectrum intensity vs wavelength, should be taken as the fiducial limit point. Such curves in the case of solid targets exhibit a well-known structure in the vicinity of the limit, first detected by Ohlin[102] and later carefully studied by others,[95,103,104] which is intimately related to the band structure of the electron energy levels in the target material and to the discrete energy-losses sustained by the bombarding electrons as they enter the target. Furthermore, the extreme limit of the continuous spectrum is always more or less concealed by a transition or "fillet" connecting the foot of the last maximum of this Ohlin structure with the background as a result of the finite resolving power of the x-ray monochromator or spectrometer employed. The uncertainty concerns how best to choose a fiducial point in the region of this fillet corresponding to a coincidence of the peak intensity of the monochromator window curve with the short-wavelength limit of the continuous spectrum. We do not even know whether the true shape of the continuous spectrum exhibits a first- or a second-order discontinuity at the limit.

Because of this uncertainty there have been several suggestions by different authors to measure the *difference* in wave-number at the short-wave limit *for two different applied voltages* in the hope that, for each of these two cases, the spectral structure near the limit would be sufficiently similar so that the shift in *spectral* position could be measured by matching the shapes of the two identical structures without the need for specifying any fiducial point in them. Perhaps the most promising of such proposals has been that of Sandström,[99] to match the first peak of Ohlin in this way for two different voltages, rather than seeking the true short-wave limit, because it seems more promising to match line peaks than to match one-sided edges, limits or discontinuities. At the present time, however, no definitive results have been obtained by this method.

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[94] Hirofumi Fujimoto, Sci. Rept. Tohoku Univ. Ser. 1, **41**, 15 (1957).

[95] K. Ulmer and H. Vernickel, Z. Physik **153**, 149 (1958).

[96] K. Ulmer, Phys. Rev. Letters **3**, 514 (1959).

[97] J. Kessler and J. Ulmer, Z. Physik **159**, 443 (1960).

[98] K. Ulmer, Z. Physik **162**, 254 (1961).

[99] R. Sandström, Arkiv Fysik **18**, 305 (1960).

[100] S. Hagström, O. Hörnfeldt, C. Nordling, and K. Seigbahn, Arkiv Fysik **23**, 145 (1962).

[101] J. J. Spijkerman and J. A. Bearden, Phys. Rev. **134**, A871 (1964).

[102] P. Ohlin, Arkiv Mat. Astron., Fysik **29A**, No. 3 (1943).

[103] B. R. A. Nijboer, Physica **12**, 461 (1946).

[104] L. Albert, Z. Physik **143**, 513 (1956).

The work of Spijkerman and Bearden[101] is worthy of mention here. A mercury vapor jet rather than a solid served as a target material, the purpose being to avoid the difficulties of interpretation arising from the electronic energy band structure of a solid target. This difficult and beautiful piece of work yielded an isochromat in which there were no Ohlin fluctuations but only the expected monotonic transition to zero. To interpret the results, an assumed one-parameter profile (with assumption of a first-order discontinuity at the limit) for the true spectrum in the absence of instrumental blurring was folded into a profile taken to represent the spectral window of the monochromator, the latter a profile also with one adjustable parameter corresponding to the spectral position of the center of the window. The two parameters were varied until the folded curve was found which seemed best to fit the experimental data and indeed a quite convincing fit was obtained.

This experiment yielded the value of the voltage-wavelength conversion product, $V\lambda_s=12373.26\pm0.40$ V x-units. The value of $V\lambda_g=12398.10\pm0.13$ eV cm was obtained in our 1963 adjustment of the constants without any use of x-ray data; the mercury target determination therefore implies a value of $\Lambda=1.002008\pm34$ ppm, a value clearly much lower than inferred by Henins and Bearden's work[77] on $N\Lambda^3$ with silicon, namely $\Lambda=1.002079\pm7$ ppm, where both these values have been corrected from Cu $K\alpha_1=1537.400$ as used in their papers to Cu $K\alpha_1=1537.370$ of Bearden's more recent tables. No explanation has been found for this discrepancy by these authors.

(4) *Annihilation-Radiation Wavelength Measurements*

The annihilation-radiation wavelength, $\lambda_A=h/(mc)$, which results when positrons and electrons annihilate each other and two photons of equal energy and opposite momenta are formed, was first directly measured by means of the bent crystal spectrometer,[105,106] but probably with greatest accuracy by J. W. Knowles[107] with his two-crystal spectrometer, an instrument specifically designed for the spectroscopy of nuclear gamma rays. The relationship, $\lambda_A=h/(mc)$ may also be written in terms of α and R_∞ as

$$\lambda_A=\alpha^2/2R_\infty. \qquad (7)$$

For these equations to be exact, the annihilating pairs must have zero kinetic energy (zero velocity for their center of mass). This condition is nearly fulfilled when positrons annihilate in matter with structure electrons because the cross section for annihilation becomes appreciable only when the relative velocity of the members of the pair is small. J. W. Knowles, using the large positron flux from the NRU reactor measured θ_A, the Bragg angle for wavelength λ_A reflected in Laue (i.e., internal) reflection from the (211) planes of calcite at 18°C, and obtained $\theta_A=3996.205\pm0.15$ microradians.[108] The lattice spacing of a sample of the calcite crystal used by Knowles was measured in Bearden's laboratory[109] to be 3029.402 x-units relative to the tungsten $K\alpha_1$ standard. From the equation $\lambda_A=2d\sin\theta_A$ one computes then the result

$$\lambda_{Ax}=\alpha^2/(2R_\infty\Lambda)=24.21216\pm0.00075 \; x\text{-units}.$$

Using the accurately known value[44] of R_∞ and the value of α [see Sec. 2.5(7) below], probably good to about ±5 ppm, obtained from the measurement by W. Lamb, Jr. *et al.* of the fine-structure splitting in deuterium, this gives a value for the x-unit-to-milliangstrom-unit conversion constant Λ of

$$\Lambda=1.002063\pm0.000033 \text{ (Knowles, 1962).}$$

More recently with his two-crystal method, J. W. Knowles has been able to establish through a series of intermediate steps by crystal diffraction in different orders the wavelength ratio of the annihilation radiation, λ_A, to the W $K\alpha_1$ x-ray emission line[110] with the following result:

$$9\lambda_A/\lambda(WK\alpha_1)=1.044811\pm0.000014 \; (\pm13.5 \text{ ppm})$$
$$\text{(Knowles, 1963).}$$

This is the first time that it has been possible to establish the wavelength and quantum energy of a well-known x-ray emission line in cgs units without appeal to uncertain data from the field of x rays and with a precision (±14 ppm) of this high order. Our 1963 least-squares adjusted value is $\lambda_A=24.26216\pm0.00022$ milliangstroms; hence, combining this with Knowles' result given above yields

$$\lambda(\text{W } K\alpha_1)=0.2089942\pm0.0000035 \text{ Angstrom units}$$
$$(\pm17 \text{ ppm}).$$

We may now compare this value directly with the definition of the x-unit in terms of the W $K\alpha_1$ wavelength as defined by Bearden,[81] $\lambda(\text{W } K\alpha_1)=208.5770$ x-units. This gives the surprisingly low value:

$$\Lambda=1.002000\pm0.000017.$$

The importance of Knowles' two-crystal method of measuring the annihilation-radiation wavelength is very great indeed, especially for the purpose of normalizing his crystal grating spacings and, with these, all of his measured gamma-ray emission-line wavelengths and energies, independently of x-ray data, directly in

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[105] J. W. M. DuMond, D. A. Lind, and B. B. Watson, Phys. Rev. **75**, 1226 (1949).

[106] D. E. Muller, H. C. Hoyt, D. J. Klein, and J. W. M. DuMond, Phys. Rev. **88**, 790 (1952).

[107] J. W. Knowles, Can. J. Phys. **40**, 237 (1962); **40**, 257 (1962).

[108] This is the angle after a small correction to allow for the mean kinetic energy of motion of the positron-electron pair.

[109] J. S. Thomsen (private communication, 2 April 1965).

[110] J. W. Knowles, *Proceedings of the Second International Conference on Nuclidic Masses, 1963*, edited by W. Johnson (Springer-Verlag, Vienna, 1964), p. 113.

TABLE VII. Determinations of μ_p/μ_n, the ratio of proton magnetic moment to the nuclear magneton (with diamagnetic correction).

	Date	μ_p/μ_n
1. Sommer, Thomas, and Hipple	1951	2.792757±0.000025
2. Bloch, Jeffries, and Trigger	1950–1956	2.79275±0.00010
3. Boyne and Franken	1961	2.792906±0.000056
4. Sanders, Dellis, Turberfield, *et al.*	1962	2.79277±0.00007
5. Mamyrin and Frantsuzov	1964	2.79287±0.00002

milliangstrom units. More people with high-flux reactors at their disposal should be doing it. Here we have one of the few methods of bridging the gap in the spectrum between our primary standards of wavelength and energy and our measurements in nuclear spectroscopy, both by crystal diffraction and by magnetic spectroscopy, without introducing the present uncertainties of the x-ray data and of the conversion factor, Λ. For this reason we are happy to learn that Knowles plans to redetermine the grating constant of his crystals in absolute units by a still more accurate measurement of the diffraction angle for λ_A, this time using annihilation radiation from the decay of positronium in ice. In 1958 de Zafra and Joyner[111] were the first to observe that the annihilation radiation line from the decay of positronium in ice exhibits a spectral component of much narrower structure superposed upon the peak of the familiar Doppler-broadened annihilation line. Graham and Geiger[112] have confirmed this observation with their 1-meter optic circle radius magnetic spectrometer. It is conjectured to be the result of trapping of some of the positronium in "holes" in the ice structure so that much of the Doppler broadening is suppressed.

(5) *Ratio of the Proton Magnetic Moment to the Nuclear Magneton*

The value of the proton magnetic moment measured in nuclear magnetons has been independently determined with high precision by five different groups.[113–117] Table VII lists the results of these groups in chronological order.

The method consists in determining the proton-spin resonance frequency and the proton cyclotron frequency in the same magnetic field, H. The cyclotron frequency ω_c is given by

$$\omega_c = He/(m_p c). \tag{8}$$

The NMR frequency, ω_p, of the proton in the field H is given by

$$\omega_p = 2\mu_p H/\hbar. \tag{9}$$

Therefore,

$$\frac{\omega_p}{\omega_c} = \frac{\mu_p}{eh/(4\pi m_p c)} = \frac{\mu_p}{\mu_n}, \tag{10}$$

where $\mu_n = eh/(4\pi m_p c)$ is the nuclear magneton.

Since our 1963 adjustment had initially as unknowns the quantities, α, e, N, and Λ, it is of importance to clarify how these are to be related to the measured quantity under discussion, μ_n/μ_p. The following equation gives this relationship which constitutes one of our primitive observational equations for forming the adjustment:

$$\frac{\mu_p}{\mu_n} = \left(\frac{\mu_p}{\mu_0}\right)\frac{m_p}{m} = \left(\frac{\mu_p}{\mu_0}\right)\frac{M_p c^2}{4\pi R_\infty}\frac{\alpha^3}{Ne^2}. \tag{11}$$

The first equality follows from the relationship which defines the fundamental moment associated with a particle of mass m, $\mu = e\hbar/2mc$; the second equality results from the substitutions $m_p = M_p/N$ and the Rydberg formula $R_\infty = 2\pi^2 me^4/(h^3 c) = \alpha^3(mc^2/e^2)/4\pi$. Note that we have expressed the proton moment (in nuclear magnetons) in terms of mathematical constants (such as 4, π), auxiliary constants, whose numerical values are accurate enough so that for the present purposes at least, they may be considered as exact (M_p, c, R_∞, μ_p/μ_0) and the variables, α, e, N of the least-squares adjustment. The total error contributed by all of the auxiliary constants in Eq. (11) is completely negligible by comparison to the error of μ_n/μ_p, which is thus the single error-determining factor in this observational equation. It is our aim in every case to formulate each observational equation thus, with the experimentally measured quantity expressed as the product of two terms—one, an "exact numeric" which is made up of numerical constants or of physical quantities so accurately known that its total uncertainty makes a negligible contribution to the error of the equation as compared to the error-determining quantity and the other, a function of the variables to be adjusted by least squares. As already pointed out, all of the different observational equations must be error-statistically independent, so as to avoid correlations in the weighting of the equations.

Figure 4 gives a highly simplified representation of the three types of measuring apparatus employed for the proton cyclotron determinations. Sommer, Thomas, and Hipple[113] (at the US–NBS) used the Omegatron—an apparatus which is essentially a small cyclotron in

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[111] R. L. deZafra and W. T. Joyner, Phys. Rev. **112**, 19 (1958).

[112] R. L. Graham and J. S. Geiger, Nucl. Phys. **45**, 177 (1963).

[113] H. Sommer, H. A. Thomas, and J. A. Hipple, Phys. Rev. **82**, 697 (1951).

[114] F. Bloch and C. D. Jeffries, Phys. Rev. **80**, 305 (1950); C. D. Jeffries, *ibid.* **81**, 1040 (1951); K. R. Trigger, Bull. Am. Phys. Soc. **1**, 220 (1956).

[115] H. S. Boyne and P. A. Franken, Phys. Rev. **123**, 242 (1961).

[116] D. J. Collington, A. N. Dellis, J. H. Sanders, and K. C. Turberfield, Phys. Rev. **99**, 1622 (1955); J. H. Sanders, K. C. Turberfield, Proc. Roy. Soc. (London) **A272**, 79 (1962).

[117] B. A. Mamyrin and A. A. Frantsuzov, Dokl. Akad. Nauk SSSR **159**, 777 (1964) [English transl.: Soviet Phys.—Doklady **9**, 1082 (1965)].

which protons are accelerated to a maximum orbital radius of about one centimeter. The condition of cyclotron resonance was determined by detecting the ions when they spiraled out to sufficient radius to be caught by a probe. It was necessary to correct for space-charge forces and for the radial components of the weak dc trapping field (superimposed in order to prevent axial ion drift) since these forces acting on the protons in addition to the $\mathbf{v}\times\mathbf{H}$ force would modify the cyclotron frequency from that for an ideal cyclotron. However, by measuring the observed resonance frequency for ions of different masses, it was possible to extrapolate these perturbations to zero. The error estimate for the STH determination given in Table VII is not that assigned by the authors. Their original assignment was made following the school of thought under which a certain virtue was attached to *overestimating* an error. In order to put their error, as nearly as we could, on a basis comparable with the other items of Table VII, we have recomputed the error from the information given in their paper. The errors here assigned to items 2, 3, and 4 have also been similarly recomputed as required, from the authors' information in their papers.

The proton-spin resonance frequency measured in the same field H as that used for the cyclotron frequency, must be corrected for the fact that the field at the proton is slightly less than the field externally applied to the proton-containing sample (usually water or mineral oil). This diamagnetic correction consists of two parts, the larger due to the effect of the electrons in the Hydrogen molecule[118] and a smaller correction[119] for the bulk diamagnetism of the sample depending on its composition and shape. (See Table II.)

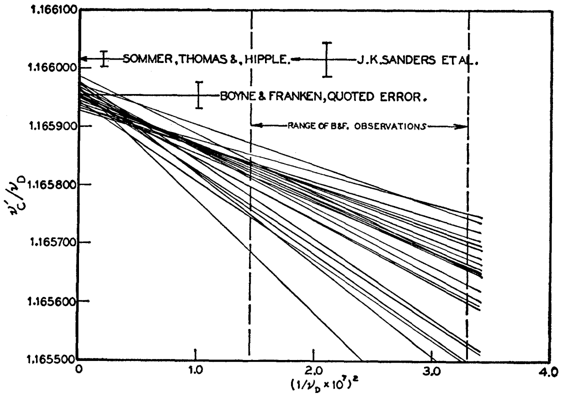

FIG. 5. Boyne and Franken's method of correcting their measurements of the cyclotron frequency of the proton for the effects of space charge by extrapolating ν_c'/ν_D to its value for infinite field. The numerical results of Sommer, Thomas, and Hipple and of Sanders and Turberfield are also shown for comparison.

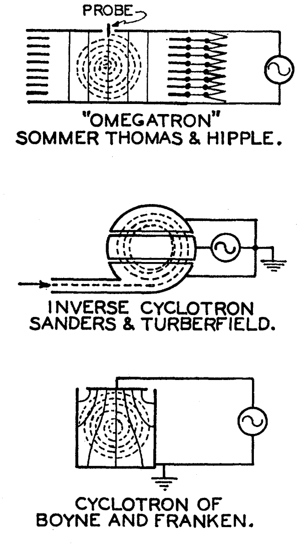

FIG. 4. Three methods of determining the proton magnetic moment. The applied dc magnetic field is normal to the plane of the figure.

In the work of Boyne and Franken,[115] the small cyclotron differed from that used by Sommer, Thomas, and Hipple. Less precautions were taken to insure a homogeneous radio-frequency electric field. No dc electric trapping field was applied to keep the spiraling protons from axial drift. Boyne and Franken used deuteron resonance to normalize their magnetic field intensity instead of proton resonance because it gave a frequency comparable to the cyclotron resonance frequency for H_2^+. The ratio ω_d/ω_p was separately measured by interchanging proton and deuterium resonance probes in the same magnetic field. The proton magnetic moment is then calculated from the relation

$$\frac{\mu_p}{\mu_n}=\frac{\omega_p}{\omega_c(H^+)}=\frac{\omega_d}{\omega_c(H_2^+)}\frac{\omega_p}{\omega_d}\frac{M_p}{2M_p+m}, \tag{12}$$

where M_p is the mass of the proton and m is the mass of the electron. The ratio ω_p/ω_d was found to be 6.514411 ± 0.000003, including the effect of the paramagnetic Cu^{++} ions in their deuterium sample. The condition of the cyclotron resonance was detected by the change of the impedance of the load on the oscillator supplying the high-frequency electric field, indicative of the increase in power supplied to accelerate the H_2 ions. A correction was required for the effect of radial forces due to space charge on the H_2^+ cyclotron frequency. The apparent cyclotron frequency, ν_c', was observed as a function of magnetic field H, and the ratio ν_c'/ν_D was plotted as a function of $1/\nu_D^2$ (i.e., essentially $1/H^2$), and extrapolated to infinite field, $1/\nu_D^2=0$. The effect of space charge in changing the cyclotron frequency can be shown to be

$$\omega=\omega_0\left[1-\frac{m_pc^2}{2eH^2}\left(4\pi\rho-\frac{\partial E_z}{\partial z}\right)\right], \tag{13}$$

where ρ is the space charge density, $\partial E_z/\partial z$ the electrical (space charge) field gradient parallel to the direction of $\mathbf{H}$, e/m_p the charge-to-mass ratio of the ions, ω_0 the ideal cyclotron frequency for zero perturbing force and ω observed frequency. Figure 5 copied from

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[118] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).
[119] C. F. Newell, Phys. Rev. **80**, 476 (1950).

their article shows the straight lines extrapolated to $1/\nu_D^2 \to 0$ for 24 of Boyne and Franken's runs. The range of field intensities over which the positions and slopes of these lines were determined is indicated with the dashed vertical lines. There is a fairly clear correlation between the slopes of the straight lines and their intercepts on the axis of $H^{-2}=0$ (corresponding to indefinitely small ionic orbital radii). There is also a suggestion that these lines, instead of tending to pass theough a common point on the axis (save for purely *random* fluctuations) tend rather to lie tangent to a common envelope or locus extending over the entire range of extrapolation.

Figure 5 shows for comparison with Boyne and Franken's result, the results of Sommer, Thomas, and Hipple, and of Sanders *et al.* The last two named items are in good mutual agreement but disagree with the Boyne and Franken result by 2.5 times the expected standard deviation of the difference. (We shall ignore the Bloch *et al.* result because of the low weight it must receive in view of its estimated error.) Thus the large disagreement of the Boyne and Franken result with the two others, coupled with the questionable nature of the space-charge correction lead us to regard it as open to suspicion of being systematically erroneous. We shall, nevertheless, retain all three items, 1, 3, and 4 of Table VII as separate items for examination in our analysis of variance to test their compatibility with the other input data of the adjustment.

In private correspondence, we have learned from P. A. Franken that he and Boyne are not too well satisfied with the results of their present measurements (for much the same reasons as we have presented here) and they plan to continue the work by the same method but employing more intense magnetic fields so as to permit observing points on the straight lines of Fig. 5 which come closer to the axis.

The method of Turberfield, Sanders, and Dellis[116] is a modification of the inverse cyclotron of Bloch and Jeffries, in which protons injected at high energy were decelerated by a high-frequency electric field in the gap between a pair of "dees" of the familiar cyclotron design. The modified design of TSD used three electrodes; a grounded dee on either side of a central section to which the high-frequency voltage was connected. Protons were injected tangentially near the outside of these electrodes as indicated in Fig. 4. The alternating potential applied to the center electrode was at a frequency close to an even harmonic of the cyclotron frequency. Those injected protons which crossed the central conductor in the appropriate phase received a net deceleration at each pair of gaps, but as they spiralled inward they approached a radius at which the time taken to cross the central conductor was just one cycle of the alternating voltage, which is the condition for no net change of energy. Thereafter the protons, having reached a stable orbital radius, described a large number of revolutions at constant radius under conditions approaching dynamic equilibrium. The attainment of many orbital revolutions is an obvious necessity if the measurements are to possess high accuracy.

The original experiments in 1955 have been augmented by an extensive set of measurements using H^+ and H_2^+ ions, and only the results based on these final measurements are given here.

The measurement by Mamyrin and Frantsuzov[117] has only recently been reported and the details of the work are not available to us. This is however a significant result because it lends strong support to the Boyne and Franken result in preference to the very consistent results of Sommer, Thomas, and Hipple, and of Sanders and Turberfield. In this experiment the cyclotron frequencies of He and Ne atoms were measured in a magnetic resonance mass spectrometer and the proton precession frequency in water was measured at the same time in the same magnetic field.

(6) *Gyromagnetic Ratio of the Proton*

In a magnetic field of intensity H, a proton has two quantum states separated in energy by $2\mu_pH$, where μ_p is the magnetic moment of the proton. Protons contained in a sample of hydrogenous liquid, such as water or mineral oil, are placed in a steady, homogeneous, magnetic field, and a coil about the sample supplies a small alternating magnetic field of radio frequency, ν, at right angles to the steady field. When ν is close or equal to the value $\nu_n=(2\mu_p/h)H$ it will cause transitions between the two energy states. The constant proportionality γ_p,

$$\gamma_p=\nu_n/H=(2\mu_p/h), \tag{14}$$

between the resonance frequency for protons and the field H at which that resonance occurs is called the gyromagnetic ratio of the proton. The phenomenon affords an extremely accurate and reproducible way of measuring (i.e., comparing) magnetic field intensities.

Several different techniques have been developed for measuring γ_p. These may be classified into strong-field and weak-field methods, the first for fields of several kilogauss developed in gaps between iron pole pieces, the second for fields of the order of 1 to 20 G developed by single-turn solenoids of great dimensional accuracy. The methods of measuring the proton resonance frequency ν_n for these two cases deserve brief explanation.

When the proton sample is in thermal equilibrium, the population of protons in the lower of the two energy states slightly exceeds that in the higher state, the population ratio of the two being given by the Boltzman factor $\exp[2\mu_pH/(kT)]$, where $2\mu_pH/(kT)$ is of order 10^{-4}. The observation of a net energy absorption at resonance as a means of detecting the resonant frequency relies on this small population difference. The resonance may also be detected by signals induced in a second coil at right angles to the exciting coil (so as to be decoupled from the latter).

In the "method of free precession," first used by Bender and Driscoll[120] for their case of weak magnetic fields, the proton sample is first strongly polarized in an intense magnetic field and then quickly transferred to the weak field to be measured. The larger Boltzman factor resulting from the strong field insures a sufficiently large population ratio so that the sample retains its polarization several seconds while the transfer to the weak field is being effected. This is done by shooting the sample pneumatically down a tube several meters long from one field region to the other. During transfer the polarized protons keep themselves aligned in a continuous way with whatever instantaneous field they experience from point to point. Once in the weak field to be measured, the field of the precision solenoid, the exciting radiofrequency signal is applied to the sample very briefly, after which the protons are left to precess freely about the applied weak field, gradually losing energy to the liquid. While doing so they induce a signal in the pick-up coil whose frequency, essentially the free-precession frequency for that field strength, can thus be measured.

We incorporate the measurement of γ_p into our least-squares adjustment in the following way. We express γ_p as a function of three of the unknowns of our adjustment, α, e, and N, and our accurately known auxiliary constants, c, R_∞, μ_e/μ_0, and μ_e/μ_p, by starting with the obvious identity

$$\gamma_p = \frac{2\mu_p}{h} = \frac{2\mu_0}{h}\frac{\mu_p}{\mu_e}\frac{\mu_e}{\mu_0}. \tag{15}$$

If we substitute the relationships

$$R_\infty = 2\pi^2 me^4/(h^3c) = \tfrac{1}{2}\alpha^2 mc^2/(hc),$$
$$\mu_0 = he/(4\pi mc),$$
$$\alpha = 2\pi e^2/(hc),$$

it is easy to verify that

$$\gamma_p = \frac{c}{8\pi R_\infty}\frac{\mu_p}{\mu_e}\frac{\mu_e}{\mu_0}\frac{\alpha^3}{e}. \tag{16}$$

The experimentally measured quantity, γ_p, is then expressed as a function of numerical constants, accurately known auxiliary constants, and the variables α and e of the least-squares adjustment.

The difficult metrological problem in determining $\gamma_p = \nu_n/H$ is not the measurement of ν_n but the establishment of the steady homogeneous field H, and the measurement of its intensity in absolute units (gauss). In strong magnetic fields the field intensity is measured by suspending a flat coil, usually of rectangular shape with one end of the rectangle in the strong field and the other end in a region within which the field has been nullified. An accurately measured current passes through the coil and the force with which it is pulled downward by the field is accurately determined by weighing with an analytical balance. The geometrical dimensions of the rectangular coil and its positioning in the field between the magnet pole pieces must be extremely accurately determined (this method is sometimes known as that of the Cotton Balance). The acceleration of gravity at the position where the $\mathbf{i}\times\mathbf{H}$ force on the coil is measured by weighing must of course be accurately determined.[121]

In the strong-field determinations the absolute value of gravity actually enters *in two ways* in the establishment of γ_p, once as $g^{\frac{1}{2}}$ because of its use in the determination of the absolute ampere (for standardizing the current in the coil of the Cotton Balance) and once as g^{-1} in weighing the $\mathbf{i}\times\mathbf{H}$ force. The net effect is therefore as $g^{-\frac{1}{2}}$. In the precision-solenoid method of establishing γ_p, however, g enters only once, as $g^{\frac{1}{2}}$ in the standardization of the ampere. It follows therefore, that in these two different methods an error in g affects the results in opposite senses.

Weak magnetic fields are set up by means of a single layer helical winding of current-carrying copper wire. The precise geometry, especially the *pitch* of the winding must be very accurately determined. The wire of circular cross section, drawn directly from a new die, is wound under tension into a helical V-groove, precision ground, and lapped on the cylindrical surface of a ceramic form. It is relatively easy to correct the uniformity of such a helical groove (screw-thread) by lapping it with a similar thread cut on the interior surface of a cylindrical lapping nut, since a true helix is the only curve exactly superposable upon itself in all positions. After winding and aging to reach dimensional stability, the dimensions of such a helical coil must be measured with micron accuracy at a carefully measured and stabilized temperature. Optical interference methods are used to determine the pitch (linear density of turns) of the coil. The technique of making such standardizing solenoids has been extensively developed for the purpose of standardizing the ampere and ohm in absolute units. From the measured current in absolute amperes passing through the helix, and its accurately measured geometrical parameters, the absolute value of the field in gauss in the region near its center can be calculated.

At the time of preparation of the 1963 adjustment there were six independent determinations of the gyromagnetic ratio of the proton.

The six measurements of Table VIII are not all of the same accuracy and at least one, the earliest, that of Thomas, Driscoll, and Hipple,[122] is afflicted with

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[120] P. L. Bender and R. L. Driscoll, IRE Trans. Instr. **I-7**, 176 (1958).

[121] R. D. Huntoon and A. G. McNish, Nuovo Cimento Suppl. **6**, 146 (1957).

[122] H. A. Thomas, R. L. Driscoll, and J. A. Hipple, J. Res. Natl. Bur. Std. (U.S.) **44**, 569 (1950); Phys. Rev. **78**, 787 (1950).

TABLE VIII. Gyromagnetic ratio of the proton, $\gamma_p = \omega_p/H = 2\mu_p/h = (\mu_p/\mu_e)(\mu_e/\mu_0)(e/mc)$.

Source	Field (G)	γ_p' ($\mathrm{sec}^{-1}\,\mathrm{G}^{-1}$)[a]	γ_p' (Corrected to BIPM units)[b]	γ_p After diamagnetic correction, cgs units (Cohen, DuMond, Vienna, 1963)[c]	(Yagola *et al.*, 1964)[d]
Thomas, Driscoll, Hipple	4800	26 752.7±0.6		26 753.4±0.6	26 753.4
Capptuller	2800	26 752.2±1.0	26 752.1	26 752.5±1.0	26 753.2
Yagola, Zingerman, Sepetyi	2400–4700	26 750.5±0.2	26 750.8	26 751.2±0.2	26 751.9[e]
Bender, Driscoll	12	26 751.51±0.08	26 751.5	26 751.92±0.08	26 751.92
Vigoureux	10–20	26 751.71±0.08	26 751.5	26 751.88±0.08	26 751.88
Yanovskii, Studentsov	0.6–1.2	26 750.6±0.3	26 750.4	26 750.8±0.3	26 750.8

[a] Values given here are not yet corrected for diamagnetism and are based on electrical standards "as maintained" by each national laboratory.

[b] Consultative Committee on Electricity, International Committee of Weights and Measures, Paris, May 1963.

[c] E. R. Cohen and J. W. M. DuMond, *Second International Conference on Nuclidic Masses* (Vienna, 1963), edited by W. H. Johnson (Springer-Verlag, Vienna, 1964), p. 152.

[d] Private communication, 24 March 1964.

[e] Includes the results of additional measurements.

considerable suspicion of the existence of systematic error. The results given in the last column of Table VIII have been corrected to the gyromagnetic ratio for the bare proton. The measurements represent work done in the United States, Germany, the Soviet Union, and England. There is, therefore, some uncertainty in these data with regard to the calibration of the standard ampere as maintained in the various national laboratories in terms of the absolute definition of the ampere. Vigoureux's measurement, performed at the National Physical Laboratory, Teddington, England,[123] was, however, based on electrical standards directly intercompared with the standard ampere maintained at the U.S. National Bureau of Standards. It is therefore reassuring that these two measurements are in such excellent agreement.

Thomas, Driscoll, and Hipple measured γ_p at a frequency of 20 Mc/sec in a field approximately 4800 G. The field was produced by an electromagnet with a 2-in. gap between 8-in.×12.5-in. pole faces. Although care was taken to insure that the faces were accurately parallel and vertical, no precautions were taken to insure that the two pole pieces were accurately coaxial. Thus the extent to which a vertical displacement of one of the pole faces relative to the other produced a tilting of the magnetic flux lines in the gap was not determined. Any departure of the flux lines in the gap from horizontal would introduce a cosine error in measuring the field by means of the vertical force exerted on the balance. It must be recalled, however, that this was the first attempt by precision metrologists to measure γ_p accurately. Much has been learned by experience since 1950.

The field intensity near the center of the gap was measured by weighing the force exerted on a rectangular current-carrying coil, wound on the edges of a rectangular coil form 10×70 cm in size which hung from one arm of an analytical balance. The glass coil form was 7 mm thick with 9 turns of copper wire lying in grooves cut in its edges. A small proton resonance probe explored the field distribution horizontally in the gap across the pole face to correct for small variations from uniformity and for the difference in mean magnetic field between the position of the coil and the position of the proton resonance sample. Such a probe exploration of the field was made in the midplane between the pole faces and also in planes 5 mm either side of gap center. Measurement showed that there existed local fluctuations from uniformity *in opposite directions* of the order of 0.5 G on opposite sides of the mid-plane indicating a *taper* in the field intensity in the horizontal direction, normal to the pole faces of about 1 G per cm; therefore a taper of field intensity of 200 ppm per cm. Clearly this implies that the centering of the measuring coil and the exact position of its turn on the edge of the 7-mm-thick glass plate would be a very critical consideration. Nickel shims were used to minimize the spatial variations in the field, but the abovementioned variations were those present *after* these precautions. In the light of the studies made later by the Soviet physicists at Kharkov it seems quite possible that these field inhomogeneities in this early work are sufficient to account for the 50 ppm discrepancy between its results and the later work done in iron-free solenoids at weak-field intensities. Also since the proton resonance frequency measures the total field intensity, while the weighing procedure measured only the horizontal component of this field, an obliquity of the magnetic field of 35 minutes of arc from the horizontal would be sufficient to account for the 50-ppm discrepancy. The magnet used has not been preserved, and because of these uncertainties we decided to reject this measurement in the final 1963 adjustment. However, it was retained along with items 4 and 5 to form

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[123] P. Vigoureux, Proc. Roy. Soc. (London) **A270**, 72 (1962).

three separate equations of observation for the purpose of the preliminary analysis of variance.

Because of its low estimated precision we eliminate the strong-field result of Capptuller,[124] done with a coil of variable width. It could only be given 1/300 as much weight as the work of Bender and Driscoll and the work of Vigoureux taken together.

The Soviet work, particularly the strong-field determinations made at Kharkov, deserve description. One of us (JWMD) has visited the Leningrad and Kharkov laboratories especially to discuss the work with the physicists who did it and to inspect the equipment.

The Leningrad work of Yanovskii and Studentsov,[125] done at the All Union Mendeleev Institute of Metrology (the national standards laboratory for the Soviet Union) was performed in weak fields of from 0.6 to 1.2 G. The reason for this, we are told, was that at the time the determination was made no precision solenoid suitable for setting up a field of intensity 10 or 20 G was available. Solenoids of this type existed in the Soviet Union but were in use for other purposes (presumably for absolute standardization of electrical units), and since the beautifully consistent work of Bender and Driscoll in the United States and of Vigoureux in Britain made a third check of immediate and pressing interest, the Mendeleev Institute used immediately available equipment capable only of giving the weaker fields. The actual measurements were made at a site quite remote from Leningrad on a promontory in a lake chosen especially to minimize stray local magnetic fields from ground currents and other sources. Nevertheless, since a whole order of magnitude precision could be obtained by working at the stronger fields with a more suitable precision solenoid, the Leningrad Laboratory plans to repeat the work under these improved conditions. The method of the Leningrad work resembles closely that of the weak field work at the U.S. National Bureau of Standards and at the British National Physical Laboratory.

The work of Yagola, Zingerman, and Sepetyi[126] at the Kharkov Institute of Measures and Measuring Instruments is of great interest because (1) it was done in strong fields with an iron pole piece magnet at intensities of the same order as the early U.S. work of Thomas, Driscoll, and Hipple, and (2) great care and elaborate precautions were taken to study the magnetic field distribution, the effects of the design and positioning in the magnet gap of the suspended field-measuring coil, and many other possible sources of systematic error in an effort to account for the discrepancy between the strong field results of Thomas *et al.* (item 1 in Table VIII), and the weak field results of Bender and Driscoll (item 4). Most interesting of all, however, is the fact that measurements obtained at Kharkov in 1963, subsequent to those in their published paper of 1962, indicate even better consistency with the weak-field results (items 4 and 5 in Table VIII) and also show fairly clearly the kind of precautions which must be taken in a strong-field experiment of this sort if highest accuracy is to be attained. This information was only available *after* completion of our 1963 adjustment, but it completely justifies our earlier decision to reject from that adjustment, the Thomas, Driscoll, and Hipple result.

In the Kharkov experiment greatest care was taken to insure (a) accurate plane parallel surfaces for the iron magnet poles, (b) strict coaxiality of these poles, which were cylindrical in shape, and (c) accurate verticality of the pole *faces*. By means of slides and screws the electromagnet could be adjusted in six degrees of freedom relative to the suspended Cotton Balance coil. In addition, the pole piece faces could be independently aligned for parallelism and coaxiality. The Kharkov physicists mapped the magnetic field in the gap in order to explore the effects of departures from parallelism and coaxility. As might be expected, a maximum field intensity was found at the center of each circular pole face when the poles were coaxial and their faces parallel, with approximately concentric circular contours of diminishing intensity as one approached the periphery of a face. With slight departures from parallelism or coaxiality, however, the positions of the two maxima and the shapes of the contours varied to a surprising degree. By careful exploration of the entire gap it was found possible to obtain a field distribution which showed good mirror symmetry relative to a vertical midplane. Of still greater importance than this, however, was the finding that the $\mathbf{i}\times\mathbf{H}$ force on the Cotton Balance coil was very sensitive to the exact centering of the plane of the coil in the symmetry mid-plane of the magnetic field.

The Kharkov group constructed three Cotton Balance coils of different designs and with different numbers of turns of wire around the edges of the glass rectangle. In coil No. 1, all the turns were connected permanently in series. Numbers 2 and 3 consisted of only two complete turns each, which were subdivided into two halves so that either turn could be energized with current, or both connected in series. In coils 2 and 3 the single turns were each carefully made to lie in a true plane. They found that the most reproducible results were obtained with these two coils, probably because the simple geometrical shape of the turns permitted definition of a true mid-plane for the current flow in a sharper way than for the coil No. 1. They also discovered a sensitive test for the correct positioning of the coil in the gap. When the plane of symmetry of current flow in the coil coincided correctly with the plane of symmetry of the field in the gap, the coil would hang freely from its one-point suspension without twisting at the time its current was turned on. A

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[124] H. Capptuller, Z. Instrumentenk. **69**, 191 (1960).

[125] B. M. Yanovskii, N. V. Studentsov, and T. N. Tikhomirova, Izmeritel. Tekhn. **1959**, No. 2, p. 39; B. M. Yanovskii and N. V. Studentsov, Izmeritel. Tekhn. **1962**, No. 6, p. 28.

[126] G. K. Yagola, V. I. Zingerman, and V. N. Sepetyi, Izmeritel. Tekhn. **1962**, No. 5, p. 24.

light-lever of several meters was used to ensure high sensitivity in this test.

Great care was exercised with the balance and force-weighing procedure. Because of the weight of the Cotton Balance with its heavy glass frame the balance must necessarily carry a heavy dead load relative to the actual force to be measured. This implies a long-period system. The weighing was done by adding or subtracting weights on the same arm as that which supported the coil. Because of the long period and consequent long interval required for each weighing it was important to ensure that the length ratio of the two balance arms did not change because of unequal thermal expansion during the weighing, and great care was therefore taken to provide accurate automatic maintenance of equal temperature on the two sides by means of thermocouple-controlled electrical heaters.

By rejecting the earlier data taken with Coil No. 1 and using only data from the last two coils of superior construction, a mean result was obtained whose standard deviation, based on mean-square deviations of the individual runs from the mean, was much smaller than when measurements with Coil No. 1 were included, and whose value furthermore agreed even more satisfactorily with that obtained by Bender and Driscoll and by Vigoureux by the weak-field method.

The primary motivation for the precision measurements of the gyromagnetic ratio of the proton in the various national standards laboratories is the opportunity such measurements offer as fundamental, reproducible standards by which the "maintained" standards (in terms of which all secondary standards in each country are calibrated) can be compared and related to absolute units in terms of force and energy. Since the determination of γ_p by Bender and Driscoll, R. L. Driscoll at the U.S. National Bureau of Standards has, as a tentative procedure, been maintaining the restandardized NBS absolute ampere not only by the customary method involving banks of standard cells and standard resistors, but also by means of the precision solenoid. The results give reason to believe that this latter method may be the more reliable of the two for maintenance of constancy. It of course implies that the solenoid and its environment, both magnetic and thermal, must be maintained unchanged with greatest care.

This, however, in no way removes the difficulties involved in the problem of *standardization* of the absolute ampere. Driscoll and Cutkosky have made an absolute calibration of the NBS standards by two methods: with the current balance and with the Pellat dynamometer. The results of these two methods differ slightly; this difference is an example of the sort of difficulty encountered at present in comparing the various determinations of γ_p made in different parts of the world. Yagola, Zingerman, and Sepetyi[127] have pointed out that if one uses the absolute ampere expressed in terms of mean results of the current balance and the Pellat dynamometer one obtains for γ_p:

Bender and Driscoll,	26 751.18;
Vigoureux,	26 751.15;
Yagola, Zingerman, Sepetyi,	26 751.31.

On the other hand, if we use the absolute ampere determined by Driscoll by means of *the ampere balance* only, i.e., dropping the determination with the Pellat dynamometer, we obtain (but with a significantly increased error assignment)

Bender and Driscoll,	26 751.23;
Vigoureux,	26 751.20;
Yagola, Zingerman, Sepetyi,	26 751.26.

Although the uncertainty which exists with regard to the intercalibration of electrical units between East and West makes it difficult to introduce the Russian results into our least-squares adjustment in a completely unambiguous manner, the work of Kharkov is of great value since it establishes the following two points quite clearly: (a) A suspicion that there might be some fundamental reason for the apparent disagreement between the results of the strong- and weak-field methods (aroused by the discrepancy between items 1 and 4 of Table VIII) now seems well put to rest. (b) The careful study of potential sources of error from field distribution and other causes in the strong-field method have demonstrated how and why the pioneer work of Thomas *et al.* could have been subject to sufficient systematic error to explain its discrepancy relative to Bender and Driscoll.

(7) *Sommerfeld's Fine-Structure Constant, α*

Triebwasser, Dayhoff, and Lamb[128] have measured the frequency separation of the $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ levels in deuterium. This famous measurement is still the best source of information available for determining the Sommerfeld fine-structure constant, α. The most recent theoretical formula for this frequency shift has been given by Layzer,[129,130] accurate to terms of order $\alpha^7 mc^2$ in the energy.

$$E=\frac{\alpha^2}{16}R_\infty c\left[\frac{M}{M+m}\right]^3 \times\left[2\frac{\mu_e}{\mu_0}\frac{M+m}{M}-1+\tfrac{5}{8}\alpha^2-2\frac{\alpha^3}{\pi}\ln 137+\cdots\right], \quad (17)$$

where M is the mass of the nucleus and m the mass of

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[127] G. K. Yagola, V. I. Zingerman, and V. N. Sepetyi (private communication).

[128] S. Triebwasser, E. S. Dayhoff, and W. E. Lamb, Jr., Phys. Rev. **89**, 98 (1953).

[129] A. J. Layzer, Phys. Rev. Letters **4**, 580 (1960).

[130] R. P. Feynman, "The Present Situation in Quantum Electrodynamics," Solvay Conference Jubilee, 1961 (unpublished).

the electron. Taking the frequency separation as 10971.59±0.10 Mc $\sec^{-1}$ and the Rydberg constant as 109737.31 cm^{-1} we obtain for α^{-1} the value

$$\alpha^{-1}=137.0388\pm0.0006.$$

In order to achieve the full accuracy available in this experiment it was necessary to develop a complete theory of line shape of the transition so that the energy difference between the two levels could be determined in the presence of natural width and Doppler broadening. The measurements were made on deuterium rather than on hydrogen in order to reduce Doppler broadening by using the heavier nucleus. Because of these precautions, it was possible to measure the transition to an error which corresponds to less than $\frac{1}{100}$ of the linewidth. Some questions have, however, been raised as to the possibility of systematic errors which might have been present in the experiment at this level of precision. These doubts, although not fully justified, have been inspired by the disagreement between the value of the fine-structure constant determined from these measurements and the values of that constant as deduced from the hyperfine structure splitting in hydrogen.

Instead of measuring the frequency of the fine-structure splitting in hydrogen at low magnetic field strengths, Robiscoe[131] at the University of Chicago (now at Yale) has measured the Lamb Shift of the $n=2$ level in hydrogen by measuring the magnetic field at which the levels $^2S_{\frac{1}{2}}(m_J=-\frac{1}{2},\ m_I=-\frac{1}{2})$ and $^2P_{\frac{1}{2}}(m_J=\frac{1}{2},\ m_I=-\frac{1}{2})$ cross each other. Robiscoe's measurement of the Lamb Shift is 0.3 Mc/sec larger than the value measured by Triebwasser, Dayhoff, and Lamb. If we combine this with Lamb's measurement of the $S_{\frac{1}{2}}P_{\frac{3}{2}}$ interval we would then infer an increase of 27 ppm in the total fine-structure interval. This would imply a decrease in α^{-1} of 13.5 ppm or 0.0018 and would lead to a value

$$\alpha^{-1}=137.0370.$$

Robiscoe is now engaged in rebuilding his apparatus in order to increase the ultimate accuracy of the measurements, and plans also to extend the investigation to deuterium as well as hydrogen in order to make a more direct comparison with Lamb's results.

(8) *Hyperfine Splitting in Hydrogen*

The hydrogen hfs splitting is expressed by the formula[130]

$$\Delta\nu=\tfrac{16}{3}\alpha^2R_\infty c\frac{\mu_p}{\mu_0}\frac{\mu_e}{\mu_0}\frac{M}{M+m}\times[1+\tfrac{3}{2}\alpha^2-(\tfrac{5}{2}-\ln 2)\alpha^2-X\alpha(m/M)], \quad (18)$$

wherein X represents a correction factor for the finite extension of the electromagnetic field "inside" the proton.

TABLE IX. Measurements of the hyperfine-splitting frequency in hydrogen from 1947 to 1962.

Authors	$\Delta\nu$ in kc $\sec^{-1}$	Date
1. Nafe and Nelson[a]	1420410.±6.	1947
2. Prodell and Kusch[b]	1420405.73±0.05	1955
3. Wittke and Dicke[c]	1420405.72±0.04	1956
4. Kleppner, Goldenberg, and Ramsey[d]	1420405.751±0.004[g]	1962
5. Pipkin and Lambert[e]	1420405.7383±0.0060[g]	1962
6. Crampton, Kleppner, and Ramsey[f]	1420405.751800±0.000028	1963

[a] J. E. Nafe and E. B. Nelson, Phys. Rev. **73,** 718 (1948).
[b] A. G. Prodell and P. Kusch, Phys. Rev. **79,** 1009 (1950); **88,** 184 (1952); **100,** 1188 (1955).
[c] J. P. Wittke and R. H. Dicke, Phys. Rev. **96,** 530 (1954); **103,** 620 (1956).
[d] D. Kleppner, H.M. Goldenberg, and N.F. Ramsey, Appl. Opt. **1,** 55 (1962).
[e] F. M. Pipkin and R. H. Lambert, Phys. Rev. **127,** 787 (1962).
[f] S. B. Crampton, D. Kleppner, and N. Ramsey, Phys. Rev. Letters **11,** 338 (1963).
[g] Corrected to ^{133}Cs Standard (see Table XVI).

The experimental measurements of the hyperfine splitting in H are perhaps the most precise physical measurements ever made. Their results are listed in Table IX. In spite of accuracies approaching 2 parts in 10^{11} the applicability of the data for our purpose is vitiated by the uncertainty in the theoretical formula. A calculation of the proton field structure factor X, by Iddings and Platzman,[132] based on a rather literal interpretation of the Hofstadter form factor for the proton structure plus additional correction terms representing the effects of virtual-photon production calculated by Zwanziger[133] and by Layzer,[134] yields a value of α some 26 ppm higher than that obtained from the measurements of the deuterium fine-structure separation. No way is known of assigning a numerical uncertainty to the value $\alpha^{-1}=137.0352$, which is computed from the hfs data in this way, because of our ignorance of the structure of the internal proton field.[135]

(9) *Hyperfine Splitting in Muonium*

In order to avoid the present uncertainties from this ill-known nucleon-structure correction, and as a check on the value of α deduced from fine-structure splitting, the hyperfine splitting in muonium has been measured

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[131] R. T. Robiscoe, Phys. Rev. **138,** A22 (1965).

[132] C. K. Iddings and P. M. Platzmann, Phys. Rev. **113,** 192 (1959).

[133] D. E. Zwanziger, Bull. Am. Phys. Soc. **6,** 514 (1961).

[134] A. J. Layzer, Bull. Am. Phys. Soc. **6,** 514 (1961).

[135] Hope is now held forth that the proton field structure correction factor may be computed from empirically observed data on elastic and inelastic scattering of high-energy electrons by protons.

by V. W. Hughes *et al.*[136–139] No uncertainties as to field-form corrections, such as those for the hf splitting in hydrogen are believed to be present for muonium since there is strong evidence that the muon, like the electron, is a Dirac particle with the conventional electrodynamic coupling.

In the most recent work, the Nevis synchrotron of Columbia University provided a longitudinally polarized beam of μ^+ which was stopped in argon gas the pressure of which was varied in different runs from 10 up to 68 atm. The stopped particles formed polarized muonium by electron capture. A microwave-induced transition between the two high-field states, $(m_j, m_\mu) = (\frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, -\frac{1}{2})$ (where m_j and m_μ are the magnetic quantum numbers of the electron and the muon, respectively) changed the angular distribution of the decay positrons emitted by the muonium, notably near 0° (forward) and 180° (backward) directions. The positrons were observed at fixed microwave frequency by plotting the ratio of decay positrons to stopped mesons as a function of applied magnetic field.

The argon stopping gas perturbs the experiment, producing a fractional change in the measured value of $\Delta\nu_M$ proportional, to first order, to the argon gas density. By working over a range of pressures this effect could be extrapolated to zero. The most recent experimental result, after the pressure-shift correction is

$$\Delta\nu_M = 4463.15 \pm 0.06 \text{ Mc sec}^{-1} (\pm 13 \text{ ppm}).$$

The theoretical formula for the splitting, $\Delta\nu_M$, in muonium,

$$\Delta\nu = \tfrac{16}{3}\alpha^2 R_\infty c(\mu_\mu/\mu_p)(\mu_p/\mu_e)(\mu_e/\mu_0)^2(1+m_e/m_\mu)^{-3} \times (1+\epsilon_1+\epsilon_2)(1-\delta_\mu), \quad (19)$$

where

$$\epsilon_1 = -(1 - \ln 2)\alpha^2,$$

$$\epsilon_2 = -(8\alpha^3/3\pi) \ln \alpha (\ln \alpha - \ln 4 + \tfrac{281}{480}),$$

and

$$\delta_\mu = (3\alpha/\pi)(m_e/m_\mu) \ln (m_\mu/m_e),$$

along with numerical values previously given for R_∞, c, μ_e/μ_0, and μ_p/μ_e can be reduced to the numerical expression:

$$\Delta\nu_M = 2.632936.10^7 \alpha^2 (\mu_\mu/\mu_p) \text{ Mc sec}^{-1}.$$

We can calculate α from this using the value $\mu_\mu/\mu_p = 3.18338 \pm 0.00004$ for the ratio of the muon magnetic moment to the proton magnetic moment which has been measured by Hutchinson *et al.*[140] In this way we obtain the value

$$\alpha^{-1} = 137.0388 \pm 0.0013.$$

This value coincides with the value of α resulting from the fine-structure measurements of Lamb *et al.* on deuterium and gives assurance, provided Eq. (19) is valid, that this value of the fine-structure constant is to be preferred to the uncertain value $\alpha^{-1} = 137.0352$ calculated from the hydrogen hyperfine-structure splitting with its somewhat questionable proton structure factor corrections. Alternatively, the agreement here with the deuterium fine-structure measurement may be taken instead as a verification, to within the accuracy of the experiment, of the validity of the identification of the muon as a Dirac particle whose only essential distinction from the electron is its mass.

Although some degree of uncertainty may be associated with the procedure of extrapolation in the reduction of the experimental data, the results furnish us with comforting reassurance that our decision for the 1963 adjustment to retain the Lamb α and reject the hydrogen hfs data has not been contradicted by this later work.

(10) The Electron Magnetic Moment Anomaly, $\mu_e/\mu_0 - 1$

The work of Wilkinson and Crane[38] who have measured the g factor of the free electron by measuring directly the frequency difference between the electron cyclotron frequency and the electron spin-precession frequency, has already been mentioned [Sec. 2.4(3)]. In this admirably beautiful experiment, 100-keV electrons in 0.2-μsec bunches move parallel to a magnetic field and strike a gold foil. Electrons scattered at right angles by the foil are partially polarized. The scattered electrons are trapped in the magnetic field and held spiralling in it for a measured time, up to 1.9 msec. The bunch is then released from the trap and allowed to strike another gold foil. The cross section for 90° scattering by this second foil is dependent upon the final direction of polarization of the electrons. This cycle is repeated 500 times per second. A plot of the intensity vs trapping time is a cosine curve whose frequency is the difference between the orbital frequency and the spin-precession frequency:

$$\omega = B\left(\frac{2\mu_e}{\hbar} - \frac{e}{mc}\right) = \frac{Be}{mc}\left[\frac{\mu_e}{\mu_0} - 1\right]. \quad (20)$$

Thus, the small anomaly, $a = \mu_e/\mu_0 - 1$, is measured *directly*. The final result is

$$a = (\alpha/2\pi) - 0.328(\alpha^2/\pi^2) + \cdots = 0.001159622 \pm 0.000000027, \quad (21)$$

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[136] K. Ziock, V. W. Hughes, R. Prepost, J. Bailey, and W. Cleland, Phys. Rev. Letters **8**, 103 (1962).

[137] V. W. Hughes, Bull. Am. Phys. Soc. **118**, 33 (1963); *Proceedings of the International Conference on Nucleon Structure* (Stanford University, 1963), edited by R. Hofstadter and L. I. Schiff (Stanford University Press, Stanford, 1964).

[138] R. Prepost, J. Bailey, W. Cleland, M. Eckhause, and V. W. Hughes, Bull. Am. Phys. Soc. **9**, 81 (1964).

[139] W. E. Clelland, J. M. Bailey, M. E. Eckhause, V. W. Hughes, R. M. Mobley, R. Propost, and J. E. Rothberg, Phys. Rev. Letters **13**, 202 (1964).

[140] D. P. Hutchinson, J. Menes, G. Shapiro, and A. M. Patlach, Phys. Rev. **131**, 1351, 1362 (1963).

with a relative precision for a of ± 23 ppm and for μ_e/μ_0 of ± 27 parts in 10^9. If we equate this observed value to the theoretical expression, neglecting terms of order $(\alpha/\pi)^3$ and higher, we obtain

$$\alpha^{-1} = 137.0381 \pm 0.0032,$$

in good accord with the value obtained from the Lamb *et al.* measurement of the deuterium fine-structure separation. Since we do not know the numerical coefficient of the α^3/π^3 term in the theoretical expansion for a of Eq. (21), this test is unfortunately inconclusive. If one postulates $\alpha^{-1} = 137.0388$ exactly, Eq. (21) would imply a coefficient of $(\alpha/\pi)^3$ equal to 0.4 ± 2.1; on the other hand, using the value $\alpha^{-1} = 137.0352$ from the hfs data in hydrogen, this coefficient would be -1.9 ± 2.1. Equation (21) is therefore not precise enough to distinguish between the two values of α or to provide any information on the third-order term in the theoretical formula for the magnetic moment anomaly.

The various experimental information on the numerical value of α are shown in Fig. 6.

(*11*) *The Faraday Constant*

For more than 30 years it has been realized that the work on the Faraday[141–144] done early in this century using the silver coulometer might be in error. In 1929, R. T. Birge[13] had arrived at significantly different values of e/m depending on whether he computed that constant from electron-beam deflection experiments or by so-called "spectroscopic methods." The more accurate of the two spectroscopic methods was based on the difference between the Rydberg constants, R_{He} and R_H, which yields the atomic mass of the electron. The value of e/m is then determined by dividing the Faraday constant (from electrochemical measurements) by the "spectroscopic" atomic mass of the electron. The direct measurement of e/m from the deflection of electrons in electric and magnetic fields (which does not depend on the value of the Faraday constant) gave a value of e/m which was 0.45 ± 0.12 percent higher. This aroused the first suspicion[145] of a possible systematic error in the early measurements of F. Another reason for suspecting errors in the early work was that the results by the two methods, that of the silver voltameter and that of the iodine coulometer, disagreed by about 220 ppm. In the cited paper it was suggested that the trouble with the earlier electrochemical determinations of F might perhaps be due to a change in average atomic weight of the electrodeposited silver through selective deposition of the two, nearly equally abundant, isotopes ^{107}Ag and ^{109}Ag. This doubt seems to have been completely removed in the course of the recent, 1960, redetermination.

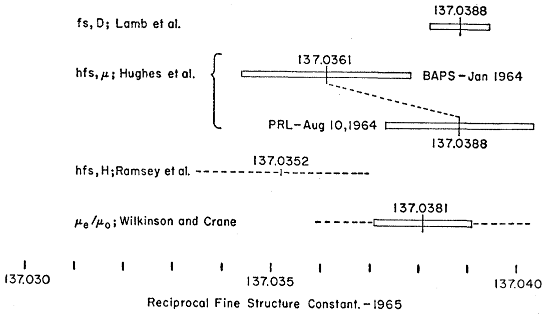

FIG. 6. Measurements of the fine-structure constant. Bars represent one standard deviation experimental uncertainty. Dashed lines are intended to indicate the existence of theoretical uncertainties to which no clearly defined limits can be set.

The early work on the Faraday was directed more toward obtaining reproducibility of the weighed deposit of silver than toward obtaining values of absolute significance because the objective was primarily one of establishing and reproducing an arbitrary fiducial standard of electrical current.[144]

The absolute value of the Faraday, F, is important for our knowledge of the fundamental constants of physics and chemistry because of its relationship to the Avogadro number and the fundamental unit of charge. It is therefore significant that the 1963 adjustment includes as one of its input data the completely new redetermination of the Faraday made by the National Bureau of Standards[146] with most careful attention to avoid systematic error. In the 1963 Adjustment the results of the older, less accurate work have been discarded.

The measurement of the Faraday by electrolysis of silver requires (1) the determination of the electrochemical equivalent of silver, and (2) determination of the mean atomic weight of the silver actually used. In order that the determination shall be meaningful in an absolute sense the following questions regarding the determination of the electrochemical equivalent must be successfully met.

(a) Is all the measured charge carried by simple Ag^+ ions? Or are there complexes? Is there electronic conduction?

(b) Does the electrolysis modify the isotopic abundance ratio, ^{107}Ag/^{109}Ag?

(c) Is there an error from "inclusions" in the silver deposited on the cathode?

(d) Has any of the silver from the cathode dissolved in the electrolyte?

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[141] E. B. Rosa and G. W. Vinal, U.S. Bur. Std. Sci. Papers **285,** 479 (1916).

[142] E. W. Washburn and S. J. Bates, J. Am. Chem. Soc. **34,** 1341, 1515 (1912).

[143] G. W. Vinal and S. J. Bates, U.S. Bur. Std. Sci. Papers **218,** 425 (1914); J. Am. Chem. Soc. **36,** 916 (1914).

[144] G. W. Vinal, "Le Voltametre à Argent," Compt. Rend., Congr. Intern. d'Électr., Paris **3,** 95 (1932).

[145] J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. **20,** 82 (1948).

[146] D. N. Craig, J. I. Hoffman, C. A. Law, and W. J. Hamer, J. Res. Natl. Bur. Std. (U.S.) **64A,** 381 (1960).

(e) Has any silver been detached from the anode by erosion rather than by electrolysis?

(f) Are there errors from impurities in the silver, especially O and H?

In most of the older work with the silver coulometer it was the silver plated onto the cathode which was weighed. One serious criticism of such work was that the deposited silver might contain "occlusions" of electrolyte (silver nitrate), nitric acid, or water, alone or in combination. Such corrections had been found to affect the Faraday determination anywhere from 40 to 160 ppm. The error from occlusions is avoided in the new work because the measurement was done by weighing the silver *lost* by electrolytic dissolution from the anode rather than the silver plated onto the cathode. This was important also in connection with question (b) above. Occlusions could play no part in electrolytic dissolution of pure silver. Furthermore, isotopic separation would presumably be eliminated, *a priori*, since silver would be uniformly dissolved electrolytically and would pass into the electrolyte in such a manner as to maintain the original isotopic composition. The possible objection that one silver isotope might go into the solution electrolytically more readily than the other so that the latter might have a selective tendency to become detached mechanically as neutral silver and fall as part of the anode "sludge" has been answered by the mass-spectroscopic abundance determinations.[147,148] Measurements of the ratio ^{107}Ag/^{109}Ag, made on the electrolytically deposited silver, produced in the process of purifying the silver to be used for the anodes, showed agreement with the ratio obtained for the silver in certified reagent-grade silver nitrate and, within the experimental uncertainty, with the ratio obtained for native silver from various sources. This is cited[146] as "conclusive evidence that no measurable isotopic separation had occurred in the electrolytic process used to purify the silver for the anodes."

An aqueous solution of perchloric acid was chosen as the electrolyte (instead of silver nitrate) because tests showed that silver is highly stable therein and that the formation of silver oxide as well as oxygen would thus be precluded. This was a precaution of value in connection with question (d) above. It was also found to be the most suitable of all electrolytes tested to insure that the simple reaction

$$\mathrm{Ag(metal)} \rightarrow \mathrm{Ag}^{+} + \epsilon$$

would proceed quantitatively without any side reactions. An auxiliary silver reference electrode for measuring the potential of the silver anode during the electrolysis provided an important means of checking that no reaction could be taking place other than the desired one.

Independent measurements were intentionally made with a considerable variation of the following five different parameters: (i) current density per unit area of anode surface, (ii) resulting anode potential, (iii) duration of run and amount of silver electrolyzed, (iv) different samples of silver for the anode, (v) different preparatory treatment of the silver samples.

The variation of current density from 0.025 to 0.150 A cm^{-2} of anode surface showed no trend in the resulting value of the electrochemical equivalent, and one reassuring conclusion from this is that if any of the coulombs measured in any of the runs were transported by any mechanism other than the presumed one, say by electronic conduction either through the solution or any other path, the effect was below the level of precision of the measurements.

It was found that the best and most reproducible results with the least amount of anode sludge were obtained with monocrystalline anodes of silver, which has been highly purified by repeated electrolysis and then prepared by vacuum metallurgy. With these precautions the electrolytic erosion of the anode occurred uniformly from all parts of the immersed surface. It is to be expected that a monocrystalline sample would be less subject to irregular erosion. In polycrystalline samples it is conceivable that some microcrystals might become detached from the anode mechanically and fall as sludge before their electrolytic dissolution was complete. After the full technique was developed, extremely little sludge was obtained.

Of the 31 silver coulometer runs, 17 were made on unpurified silver and 14 on purified silver. Many runs, especially those made with unpurified or deliberately contaminated samples, were for informative purpose and were not used as precision determinations of the electrochemical equivalent. Of the 14 runs on purified silver, 9 were made on silver that had been melted in vacuum and 5 on silver melted in hydrogen. Corrections for impurities on the 9 amounted to only 0.000001 or 0.000002 mg/C, so uncertainties in the corrections may be neglected. On the five with hydrogen treatment, corrections for retained hydrogen were necessary, amounting to 0.000027 in two cases and to 0.000010 in three cases.[149]

The mean of the nine vacuum values yielded the following value for the electrochemical equivalent of silver:

$$1.1179722 \pm 0.0000070 \text{ mg C}^{-1},$$

where the error is a statistical standard deviation. No systematic error as great as 1 ppm is believed to afflict the above value.

Since the Faraday is given by the ratio of the atomic mass to the electrochemical equivalent of silver, a pre-

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[147] W. R. Shields, D. N. Craig, and V. H. Dibeler, *Proceedings of the International Conference on Nuclidic Masses* (Hamilton), edited by H. E. Duckworth (University of Toronto Press, Toronto, 1960), p. 519; J. Am. Chem. Soc. **82,** 5033 (1960).

[148] W. R. Shields, E. L. Garner, and V. H. Dibeler, J. Res. Natl. Bur. Std. (U.S.) **662,** 1 (1962).

[149] A. G. McNish (private communication, 31 August 1961).

cise knowledge of the mean atomic mass of silver [on the scale ($^{12}C=12$)] is needed. On this scale the nuclidic masses of the two stable silver isotopes are given by the Everling, König, Mattauch, and Wapstra least-squares adjustment from mass-spectroscopic and nuclear-reaction data to standard deviations of ±110 micro mass units, i.e., fractional standard deviations of about ±1 ppm. To compute the mean atomic mass it is necessary to determine precisely the abundance ratio[150] $^{107}Ag/^{109}Ag$. Three precise determinations of this ratio by Crouch and Turnbull,[151] Shields, Craig, and Dibeler,[147] and Shields, Garner, and Dibeler[148] were considered. These three measurements were:

(a) $^{107}Ag/^{109}Ag=1.0733\pm0.0043$,

(b) $^{107}Ag/^{109}Ag=1.07547\pm0.00206$,

(c) $^{107}Ag/^{109}Ag=1.07597\pm0.00135$.

The error quoted by the respective authors in all three cases are 95% confidence limits as to statistical uncertainty added to an estimate of systematic error for the same confidence limit, that is:

$$\text{Total quoted error}=\epsilon(\text{statistical})+\epsilon(\text{systematic}).$$

Crouch and Turnbull found an unexplained mass-discrimination effect and have corrected their data for it although W. R. Shields adduces experimental evidence against such an effect. If one assumes absence of such an effect, experiment (a) results in a ratio 1.0759 in agreement with (b) and (c); because of this systematic uncertainty we have decided to reject measurement (a). A weighted average of (b) and (c), weighted inversely as the squares of their statistical errors, since both are subject to the same systematic errors, yields for $r=^{107}Ag/^{109}Ag$,

$$r=1.0759\pm0.0006.$$

The atomic mass of the isotopic mixture of silver is

$$M_{Ag}=M_{107}+(M_{109}-M_{107})/(1+r),$$

and using the Everling, König, Mattauch, and Wapstra[14] values

$$M_{107}=106.90497\pm0.00011,$$

$$M_{109}=108.90470\pm0.00011,$$

$$M_{109}-M_{107}=1.99973,$$

one obtains for the mean atomic mass of silver on the unified ($^{12}C=12$) scale

$$M_{Ag}=107.86827\pm0.00030.$$

This result is in agreement with, but is significantly more accurate than the value, (based primarily on gravimetric methods) 107.870±0.003 adopted by the IUPAC in 1961.

Using the values for the electrochemical equivalent of silver and its mean atomic weight, the value of the Faraday becomes

$$F=96485.66\pm0.66 \text{ NBS C mole}^{-1}.$$

To this must be applied a conversion factor [Sec. 2.4(7)] to express the result in absolute coulombs: 1 NBS coulomb =1.000012 absolute coulombs. Thus the final value of the Faraday on the unified scale of atomic masses is

$$F=96486.82\pm0.66 \text{ C mole}^{-1}.$$

The great care with which this remarkable redetermination of the Faraday has been carried out by the U. S. National Bureau of Standards requires detailed study of the original paper[146] for proper appreciation. Nevertheless, we feel that so much fundamental importance is attached to an accurate knowledge of the absolute value of this quantity that it is a great pity that equally careful electrochemical redeterminations, if possible by alternative methods, have not been made by other laboratories and other workers. Only by such means can the possibility of systematic errors be minimized. The Faraday constant is the only quantity entering our 1963 adjustment on which only one up-to-date measurement was available. The structure of the input data is such that all of our output values would be radically affected if, for some (presently unsuspected) reason the input value of F were found to be significantly systematically erroneous.

(*12*) *The Gas Constant*, R_0

The gas constant occupies a unique position, differing from all the others in that, too imprecisely known to qualify as an auxiliary constant, it still does not appear among the stochastic input data of our least-squares adjustment. This is because R_0 has no bearing in determining our "unknowns," α, e, N, Λ. R_0 is in fact only of importance because it contains the information from which we obtain the Boltzman constant, k, which is the conversion constant between our nominal Kelvin temperature scale and the corresponding energy per particle $k=R_0/N$. For this reason R_0 is only of use in computing some of the derived constants, those associated with thermal energy, in our final tables of output values.

The gas constant is defined by the perfect gas law, $pV=R_0T$ and is determined experimentally from the ratio of the normal molar volume V_0 of an ideal gas

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[150] This requirement might have been avoided if isotopically separated samples of one or the other of the two silver isotopes had been used as material for the anode. This however was deemed impractical. It must be recalled that it was necessary to start with a relatively large quantity of silver because of the elaborate precautions for chemical purification, repeated electrolysis, vacuum metallurgy, and finally, growing of monocrystalline anodes. Instead of this, small samples of the separated isotopes were used to prepare artificial mixtures of silver of accurately known isotopic composition and these were employed in the mass-spectroscopic abundance ratio determinations to calibrate the "bias" of the mass spectrometer.

[151] E. A. C. Crouch and A. H. Turnbull, J. Chem. Soc. **1962**, 161.

to the absolute temperature T_0 of the ice point. Precision determinations of the normal molar volume have been made by Baxter and Starkweather,[152] Batuecas,[153] Moles, Toral and Escribano,[154] and Cragoe.[155] Birge and Jenkins in a review paper[156] have given the theory connected with the determinations. The latest review of work in this field, by Batuecas[157] describes work done by him as late as 1952.

We adopted for the 1963 Adjustment a value derived from V_0 given by R. T. Birge[25] in 1941 after a study of all available information; this value is in substantial agreement with the more recent result of Batuecas:

$$V_0 = 22414.6 \pm 0.9 \text{ cm}^3 \text{ atm mole}^{-1} \text{ (Old Chemical Scale)}.$$

After conversion to the unified scale of atomic weights ($^{12}C = 12$) and to the new Kelvin temperature scale on which $T_0 = 273.15°K$ this gives

$$R_0 = V_0/T_0 = 8.31434 \pm 0.00035 \text{ J mole}^{-1} \text{ deg}^{-1}.$$

Further work by precision metrologists to obtain better values of the ideal gas constant would be very much in order; plans of this sort are under consideration at the National Bureau of Standards.[158]

(13) *Fluxoid Quantization*

The original *idea* of magnetic flux quantization is generally attributed to F. London[159] who concluded that the magnetic flux encircled by a superconducting current loop should be quantized in integer multiples of a unit $\varphi_0 = hc/e$.

Simultaneously in 1961, Doll and Näbauer[160] and Deaver and Fairbank,[161] reported clear evidence of the observation of such quantization in small ring or tube-shaped samples. Earlier in the same year Mercereau and Vant-Hull[162] had reported an unsuccessful attempt to reveal such an effect in a 1-mm-diam indium ring. The size of the flux quanta, however, turned out to be just half as large as the value, hc/e, predicted by London, a fact which is explained as a necessary consequence of the requirement that superconducting electrons circulating in the ring are paired in a collective motion of two electrons with opposite spins and opposite momenta. These entities, which obey Bose rather than Fermi statistics, have an effective charge of $2e$ and hence the true quantum of magnetic flux turns out to be

$$\varphi_0 = hc/(2e) = 2.0678 \times 10^{-7} \text{ G cm}^2. \tag{22}$$

The possibility of making practical application of this phenomenon to superconducting rings of sufficiently large dimensions to permit high precision measurement of the magnitude of the magnetic flux quantum by *actually counting* the number of them successively embraced by a superconducting ring of accurately measured cross sectional area for a field increment of accurately measured absolute intensity took shape in 1964.[163–168] One of the remarkable results of some of these experiments seems to be that we are forced to ascribe much more concrete physical reality to a *vector potential* (even in regions of space where the magnetic field is zero) than we have heretofore been accustomed to do.[169]

It now appears to be feasible[170] to consider counting the successive accretion of flux quanta within a superconducting ring of cross sectional area of order 1 cm^2. If the area of such a ring could be determined to a precision of 20 ppm or better, it should be possible to make an absolute determination of the important constant h/e to the same relative precision. This does not seem to be beyond the bounds of possibility. Techniques are known for producing polished glass or quartz cylinders of extreme precision in roundness and in straightness of the generators. The diameters of two such cylinders can be measured, if they do not differ too greatly, by using them as spacers between optically flat glass plates. The separation of the two inner surfaces of the glass plates can be determined by means similar to those used in measuring a Fabry–Perot etalon. If this could be done to a precision of 0.1 μ for glass rods 1 cm in diameter there is hope of attaining the desired general order of precision in our knowledge of the cross sectional area of the rods. These rods then would be coated with evaporated metal bands (of tin, for example) in which the oxide or other types of junctions for observing the flux quantization are provided. The external magnetic field would be supplied by one of the well-known precision solenoids such as are avail-

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[152] G. P. Baxter and H. W. Starkweather, Proc. Natl. Acad. Sci. U.S. **10**, 479 (1924); **12**, 699 (1926); **14**, 57 (1928).

[153] T. Batuecas and F. L. Casado, J. Chim. Phys. **33**, 41 (1936); F. L. Casado and T. Batuecas, Anales Real Soc. Espan. Fis. Quim. (Madrid) **48B**, 5 (1952); T. Batuecas, *ibid.* **49B**, 517 (1950); **49B**, 405 (1953).

[154] E. Moles, T. Toral, and A. Escribano, Trans. Faraday Soc. **35**, 1439 (1939).

[155] C. S. Cragoe, J. Res. Natl. Bur. Std. (U.S.) **26**, 495 (1941).

[156] R. T. Birge and F. A. Jenkins, J. Chem. Phys. **2**, 167 (1934).

[157] T. Batuecas, *Proceedings of the Second International Conference on Nuclidic Masses* (Vienna, 1963), edited by W. H. Johnson (Springer-Verlag, Vienna–New York, 1964), p. 139.

[158] A. G. McNish (private communication).

[159] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1, p. 152.

[160] R. Doll and M. Näbauer, Phys. Rev. Letters **7**, 51 (1961).

[161] B. S. Deaver, Jr., and W. M. Fairbank, Phys. Rev. Letters **7**, 43 (1961); see also, thesis, B. S. Deaver, Stanford University 1962 (unpublished).

[162] J. E. Mercereau and L. L. Vant-Hull, Bull. Am. Phys. Soc. **6**, 121 (1961).

[163] J. M. Rowell, Phys. Rev. Letters **11**, 200 (1963).

[164] J. Lambe, A. H. Silver, J. E. Mercereau, and R. C. Jaklevic, Phys. Letters **11**, 16 (1964).

[165] R. C. Jaklevic, J. Lambe, A. H. Silver, and J. E. Mercereau, Phys. Rev. Letters **12**, 159 (1964); **12**, 274 (1964).

[166] J. E. Zimmerman and J. E. Mercereau, Phys. Rev. Letters **13**, 125 (1964); **14**, 887 (1965).

[167] A. L. Kwiram and B. S. Deaver, Jr., Phys. Rev. Letters **13**, 189 (1964).

[168] J. E. Mercereau, Bull. Am. Phys. Soc. **9**, 499 (1964); **9**, 721 (1964).

[169] Y. Aharonov and D. Bohm, Phys. Rev. **115**, 485 (1959).

[170] J. E. Mercereau (private communication).

able in many national standardizing laboratories (used for standardizing the ampere and the ohm in absolute units). Precautions would have to be taken to insure sufficiently accurate parallelism of the axis of the cylinder with the externally applied field.

Such an independent new and precise source of information on the quantity h/e would be of great value for our present state of knowledge of the fundamental constants of physics. Because of the present unsatisfactory level of reliability of data on such quantities as h/e obtained from the field of x rays, we have felt obliged to reject them from our input data for the 1963 adjustment. The result of this rejection, however, as will be further discussed in Sec. 3.2, has been that the remaining stochastic data fall apart into two disconnected groups, (a) a group determining α, and (b) a group determining essentially the Faraday constant F. A great deal of highly desirable overdetermination is thus sacrificed which would be regained if we could obtain the information on h/e from cryogenics with a relative precision of order 10 or 20 ppm.

The potential value for precision metrology of these newly revealed phenomena of flux quantization will surely, we hope, not escape attention for here we have another way, independent of nuclear magnetic resonance, of defining and maintaining an electrical unit of current by means of a fundamental constant of nature.

3. DESCRIPTION OF THE 1963 ADJUSTMENT

3.1. Selection of Input Data

The experimental data which has been listed and discussed in the preceding sections are recapitulated in Table X. Here we list all of the data previously mentioned whose precision justifies them for consideration in a least-squares adjustment. This does not mean that all of this data was included in the 1963 least-squares adjustment since not all of the data was available at that time. Table X however is our basic collection of input data which must be considered if one is to attempt to determine the present "best" values of the fundamental constants.

In Table X the data are listed in 10 groups. These will be rapidly reviewed in succession, with comments on the significance of the data and its inclusion or omission from the 1962 analysis of variance. In the right-hand column those items which were retained for the analysis of variance are identified by their serial number in that survey.

1. Of the fine-structure data we have provisionally retained, in order to test its consistency with the remainder of the data, the hyperfine-structure splitting in hydrogen and the fine-structure splitting in deuterium. The error to be attached to the hfs measurement cannot reflect the accuracy of the experiment, otherwise this measurement would rank as an auxiliary constant (the most accurate one we know!). Instead, an arbitrary assignment of ± 35 kc/sec is intended to reflect the uncertainty of the theory of the effects of the finite proton structure.

2. Of the five measurements of the proton moment listed in Table VII we have rejected the second because of its low weight but kept the third item in order to test its consistency. The recent measurement of Mamyrin and Frantsuzov is listed here primarily for comparison at the moment.

3. The determination of the value of the Faraday by the cooperative efforts of a group of electrochemists and a group of mass spectroscopists at the U.S. National Bureau of Standards is the only measurement of comparable precision available to us.

4. Of the measurements of the gyromagnetic ratio of the proton listed in Table VIII only the first, fourth, and fifth were retained for the analysis of variance. The others were omitted primarily because of a lack of detailed information concerning the basis for calibration of the electrical units in absolute terms at the time of the analysis. The first item was retained with the hope that one might clearly distinguish between the inconsistent strong field and weak field measurements. In the past year the additional data from Yagola and his co-workers have plausibly explained the source of this discrepancy.

5. Only the first three results were available in 1962. All of the earlier measurements are of poorer reliability.

6. Because of the uncertainty in the wavelengths of Mo $K\alpha_1$ and Cu $K\alpha_1$ the available data on $N\Lambda^3$ was grouped into two classes depending upon which x-ray line was used as the ultimate calibration line. Each of these then actually refers to a different definition of the x-unit.

7. The annihilation-radiation measurement by Knowles was not included in the least-squares analysis of variance because it was apparent that the x-ray data as a whole was suspect. Knowles' measurement could then stand alone as the only valid determination of the conversion factor Λ.

8. None of these data were available for the analysis of variance.

9. The gas constant is uncoupled from the remainder of the data and does not contribute to the analysis of variance.

10. The magnetic moment of the muon (or the muon mass) contributes a new dimension to the constants space of our analysis. It appears only in connection with the muonium hfs.

(1) Rejection of Data

Whether a given item of data should be rejected from a least-squares adjustment simply and solely because the item is an "outlying" one is a question which merits a little discussion. By an "outlying" item we mean, in the case of an ordinary weighted average of observations on a single stochastic quantity, an item

TABLE X. Recapitulation of experimental data on fundamental constants.

Group	Description	Numerical value	Comments	Item number in analysis of variance
1.	Fine-structure data			
1a.	Hyperfine-structure separation in hydrogen	1 420 405 751.800±0.028 sec^{-1}	Ramsey *et al.*, error increased to 35 kc sec^{-1} to allow for theoretical uncertainty	1.
1b.	Hyperfine splitting in muonium	4 463.15±0.06 Mc sec^{-1}	Hughes *et al.*	
1c.	α^{-1}, anomalous moment of electron	137.0381±0.0032	Wilkinson and Crane	
1d.	Fine-structure splitting in deuterium	10 971.59±0.10 Mc sec^{-1}	Lamb *et al.*, error increased to 0.50 Mc sec^{-1} for preliminary analysis	2.
1e.	Lamb shift in hydrogen	1 058.07±0.10 Mc sec^{-1}	Robiscoe, preliminary	
2.	Proton magnetic moment (free proton)			
2a.		2.792906±0.000056	Boyne, Franken	3.
2b.		2.79287±0.00002	Mamyrin, Frantsuzov	
2c.		2.792757±0.000025	Sommer, Thomas, Hipple	4.
2d.		2.79277±0.00007	Sanders *et al.*	5.
3.	Faraday constant	9648.682±0.066 emu	US-NBS	6.
4.	Gyromagnetic ratio of proton (corrected for diamagnetism)			
4a.		26 751.92±0.08	Bender, Driscoll (weak field)	7.
4b.		26 751.90±0.20	Yagola *et al.* (strong field)	
4c.		26 751.88±0.08	Vigoureux (weak field)	8.
4d.		26 750.80±0.30	Yanovskii *et al.* (weak field)	
4e.		26 753.4±0.6	Thomas, Driscoll, Hipple (strong field) (earlier value, 26752.8±0.25 used for analysis of variance)	9.
5.	Conversion factor, x-units to milliangstroms			
5a.		1.002020±0.000035	Bearden (1931, Cu 1537.396)	10.
5b.		1.002110±0.000075	Bearden (1935, Cu 1537.396)	11.
5c.		1.002011±0.000033	Bäcklin (1935, Al 8322.18)	12.
5d.		1.002050±0.000045	Bearden (1964, Cu 1537.370 recomputation of 5a.)	
5e.		1.002050±0.000029	Edlen, Svensson (recomputed for Cu 1537.370)	
6.	Siegbahn–Avogadro number			
6a.		6060.18±0.32×10^{20}	Smakula, Straumanis, Table V (Cu $K\alpha_1$ 1537.396, error increased)	13.
6b.		6059.72±0.33	Various authors, Table V (Mo $K\alpha_1$ 707.831, error increased)	14.
6c.		6060.08±0.24	Bearden, Ref. 81 (W $K\alpha_1$ 208.5770)	
6d.		6060.13±0.15	Henins and Bearden, Ref. 77 (W $K\alpha_1$ 208.5770)	
7.	Annihilation radiation			
7a.		24.21216±0.00075 x-units	J. W. Knowles, positrons in H_2O	
7b.		24.21373±0.00033 x-units	J. W. Knowles, positrons in Ta (both values corrected to W $K\alpha_1$ 208.5770)	
8.	Short-wavelength limit, $V\lambda_s$			
8a.		12 373.09±0.40	Spijkerman, Ref. 101	
8b.		12 373.1±1.5	Hagström, Ref. 100 (both values corrected to W $K\alpha_1$ 208.5770)	
9.	Gas constant R_0			
9a.		8.3144±0.00035	Adopted value, based on Birge, Ref. 25,	
9b.		8.3144±0.0003	Batuecas, Ref. 157	
10.	Magnetic moment of muon, μ_μ/μ_p	3.18338±0.00004	Ref. 140	

whose value lies so remotely from the densest part of the cluster of observed values as to arouse our suspicion that it may be systematically erroneous. The slightly more complicated case of a least-squares adjustment of overdetermined data bearing on the determination of "best" values for several stochastic variables (the "unknowns") is the exact analog of the simpler case, merely generalized from one-dimensional to multidimensional space. In order to represent an overdetermined set of n equations in m unknowns, $n>m$, we may think of a cartesian reference frame in the m space with one axis for each unknown. Then each input datum and its equation determines a surface in this space and one expects all n of these surfaces to intersect nearly in a single point of the space. Variation of the numerical input datum moves the surface in a direction normal to itself. Since the numerical input has an assigned error estimate attached to it corresponding to each observational equation, there is actually not just one mathematical surface but a region of space centered on the surface, a fuzzy domain of uncertainty having a thickness and density distribution determined by the assigned standard deviation. The different surfaces may be oriented in a great variety of ways in this m-dimensional space. It is these fuzzy surfaces then which intersect nearly in a common point of the m space. If the fuzzy surfaces intersect in such a way that there exists a region of the space which is common to all of the (ill-defined) surfaces, then the experimental data are all mutually consistent, but if one of the surfaces is "outlying," then the point which represents the consensus of a majority of the input data equations fails to lie inside regions of the structure of that surface well enough to avoid the suspicion that the corresponding input datum is perhaps afflicted with systematic error. In such a case, with most of the data acceptably mutually consistent and only a small minority outlying in character, we still have a satisfactorily clear-cut situation. Much less satisfactory situations in which outlying data are less self-evident can easily be imagined. So far all we wish to emphasize is that, whether we are concerned with weighted averaging in one variable or in many, the same principles apply and the same common-sense idea of an outlying datum is also applicable.

The question we wish to discuss now regards the validity of rejecting data at all, just because they are outlying. We come to the point immediately. The validity of rejection depends on how outlying the datum is relative (a) to the precision attached to it individually and (b) to the precision attached to the weighted average of the remainder of the group from which it is proposed for rejection. Thus it is clear that in order to answer meaningfully the question as to whether it is valid to reject a datum, we must have *a priori* information concerning the estimated precision of all the data in the group. We practically never make a measurement without having some *a priori* preconception (it may be vague or it may be more precise) as to what precision to expect of our methods, our apparatus, and our skill as observers. Looked at from one viewpoint, life may be said to be nothing else but a succession of these *a priori* judgments followed and checked by *a posteriori* conclusions.

In the discussion to follow, we shall refer to two measured values (of purportedly the same quantity) as being "mutually significantly discrepant" if the difference between the two values is large in comparison to the estimated standard deviation of that difference. To apply the criterion we must clearly have *a priori* information, i.e., estimates of the standard errors, σ_1 and σ_2, of each of the two discrepant measurements. Assuming the two measurements to be the results of error-statistically independent observations, then the standard deviation of their difference is $\sigma_D=(\sigma_1^2+\sigma_2^2)^{\frac{1}{2}}$. We take the stand in the error analysis of this article that it is incorrect, and in fact misleading, to include in a weighted average (with weights proportioned inversely as the squares of the standard-deviation estimates of the items being averaged) quantities that exhibit significant discrepancy by the above criterion. Clearly if two measurements of the same quantity differ by several times as much as the assigned estimates of precision lead us to expect they should, one or both of the precision estimates must be unreliable and it is meaningless in calculating the average to attach weights to the measurements based on these estimates. If the precision estimates, on the other hand, are correct then at least one of the measurements must contain a systematic error (or at least a rare statistical fluctuation) and again it would be inappropriate to form a weighted average. In such cases, one or both of the items ought to be rejected. We must, in such circumstances, do our best to try to locate the *physical cause* of the unreliability. Elimination on the mere grounds that an item appears to be *outlying* relative to a remaining group is in our opinion far less satisfactory than finding a valid reason in the methods of measurement or in the interpretation of the result. The outlying position of the value may, however, be a valuable clue calling our attention to the need for further, still more critical examination of the work.

There are of course also ways (for example the chi-squared test) of measuring the over-all compatibility or consistency of a group of measurements either of a single stochastic variable or of an overdetermined set of observational equations bearing on several such variables. R. T. Birge[171] was the first to emphasize the importance of such methods to physics in his early analytical reviews of the fundamental constants by pointing out that there are in fact *two* independent criteria for estimating the error to be attached to the weighted average value of a quantity for which a

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[171] R. T. Birge, Phys. Rev. **40**, 207 (1932).

number of independently measured values are available, the "criterion of internal consistency" and the "criterion of external consistency." Suppose that we have n independent determinations of a single stochastic quantity x_i. Each result has an estimated standard deviation σ_i. We attach weights w_i in inverse proportion to the squares of the errors, so that $w_i=k/\sigma_i^2$ and form the weighted average value $\langle x\rangle$ by the usual rule

$$\langle x\rangle=\sum w_i x_i/\sum w_i. \tag{23}$$

By the criterion of *internal consistency* we calculate the standard deviation to attach to the weighted mean using the rule that the weight of the mean is the sum of the weights of the individual items from which it was derived. The error σ_I of the weighted mean value by internal consistency is therefore given by

$$\sigma_I^2=k/\sum w_i. \tag{24}$$

The error of the weighted mean by *external consistency* is calculated from the residues, $\Delta_i=x_i-\langle x\rangle$, by which each of the individual items differs from the mean. The error by external consistency, σ_E, is given by

$$\sigma_E^2=\sum w_i\Delta_i^2/(n-1)\sum w_i. \tag{25}$$

Thus, the error of the mean by *internal* consistency is the *expected error the mean value ought to have* if the distribution of the values of the items around the mean were a purely random one consistent with the errors σ_i assigned to the items, whereas the error by *external* consistency is a measure based upon how much the individual items really did deviate from the mean value. For this reason σ_I is often referred to as the *a priori* error and σ_E, as the *a posteriori* error. Birge pointed out that the ratio $R=\sigma_E/\sigma_I$ is a useful measure of the overall consistency or compatibility of the set of values $[x_i]$. If r is of the order of unity, then we can conclude that the test reveals no strong evidence of systematic errors being present. In other words, the values of the n items (which purport to be observations of the same quantity) cluster together as closely as one would expect in view of the magnitudes of their *a priori* assigned errors, σ_i. If r is notably greater than unity, then strong suspicion is aroused that one or more of the items is systematically erroneous or that the *a priori* error estimates were too small.

The ratio R is closely related to the statistic "chi squared" introduced by R. A. Fisher.[172] If we divide each residue, $\Delta_i=x_i-\langle x\rangle$, by the *a priori* error, σ_i, of the item, we obtain the "normalized residue." The sum of the squares of the normalized residues is χ^2

$$\chi^2=\sum_{i=1}^{n}[(x_i-\langle x\rangle)/\sigma_i]^2, \tag{26}$$

$$R^2=\chi^2/(n-1). \tag{27}$$

In the more general case of a least-squares adjustment to determine m stochastic unknowns given n input equations of observation $(n>m)$, Eq. (27) is only slightly changed to read

$$R^2=\chi^2/(n-m). \tag{28}$$

The meaning of the number 1 in the denominator of Eq. (27) can be understood as follows: It is there because the formula applies to the case of a single stochastic variable. In mathematical statistics, this quantity, $n-1$ or $n-m$, is called "the degrees of freedom" and the rule is given that "the expectation value of χ^2 is equal to the number of degrees of freedom," which is the same as saying that if no systematic errors are present, we expect Birge's R to be equal to unity. Fisher has computed tables of the χ^2 distribution[173] from which, given the number of degrees of freedom of the least-squares adjustment, one can obtain the probability that χ^2 shall have a value equal to or greater than a tabulated value χ_0^2 (always, of course, assuming that systematic errors are absent).

Birge's ratio test or the χ^2 test are designed to answer the question whether or not a set of stochastic data is consistent, i.e., compatible. Now suppose that the answer is, with high probability, negative. We then are confronted with the problem of what to do about it; how to identify if possible, the items of data likely to be responsible for the trouble. We admit that statistics is powerless to do this *with indubitable certainty*, but we feel, nevertheless, that it may sometime be capable of furnishing valuable clues as to where to look for trouble. The only sure way of locating a source of systematic error is of course to find its cause either in the physical methods of measurement employed, in the methods of reducing the data, or in the correctness of the theoretical interpretation. The problem of seeking for what is likely to be wrong with a least-squares adjustment, which input items are likely to be those whose elimination would restore compatibility with the smallest sacrifice of data, leads us to the problem of "analysis of variance."

The present situation regarding the available data on the constants, fraught as it is with many incompatibilities, requires rejection of some of the more suspect data. A blind least-squares averaging of obviously incompatible data is an incorrect and unjustifiable misuse of the method of least-squares since if the data are incompatible it is clear that the *a priori* assigned errors of at least some of our input data are too small and we know therefore that our data must be incorrectly weighted.

The moment one starts rejecting discrepant data, however, one runs the risk of introducing personal

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[172] R. A. Fisher, *Statistical Methods for Research Workers* (Oliver and Boyd, Ltd., Edinburgh, Scotland, 1932).

[173] R. A. Fisher, *loc. cit.*, Table III. More extensive tables exist; M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U.S. Government Printing Office, Washington, D. C., 1964), Applied Mathematics Series, AMS-55, pp. 978–985.

bias. Under such circumstances the best we can do is to analyze as thoroughly as the circumstances warrant the results of utilizing all the items of available data and also various judiciously chosen subsets of these items, and to present the results of these analyses. We then indicate our own preferred selection and give a complete table of output values based upon this. Those who prefer other selections are thus left free to arrive at their own conclusions.

Such a program, in which a considerable list of more or less discrepant data is broken down into subgroups for least-squares analyses is often referred to as "an analysis of variance." Suppose one has n independent observational data leading to n equations in m unknowns ($m<n$). From these data, one adjustment with n equations in m unknowns can be made. Then n different adjustments can be formed consisting of subsets with $n-1$ equations, subsets in each of which a different one of the original n equations has been omitted. Next, we can omit, from the original set, pairs of equations and thus form $n(n-1)/2$ subsets, each consisting of $n-2$ equations. This process may be continued down to the point where each subset comprises only one more equation than the number of unknowns. Beyond this point, overdetermined least-squares solutions cannot be formed.

The 14 equations with which we must deal, formed from the data of Table X, are however far from being of the most general form. They are only of six different *kinds*, that is to say, the experimentally measured quantities are to be equated to only six different functions of the four unknowns; several of these kinds of equations have two or three representatives corresponding to measurements of the same physical quantity by different people, different methods, or both. They also exhibit a further degeneracy in that the proton moment, the gyromagnetic ratio, and the Faraday form a subset in which any pair taken together determines the third. We shall call this the "cozonal set."[174] In spite of these degeneracies there are still, however, several thousand overdetermined sets which could be formed from our 14 equations if we wished to explore all possible combinations. We have instead used an approach in which we successively eliminate those input data which exhibit the largest departures from fit with the general consensus, and after each such rejection re-examine all of the remaining data as regards its measure of compatibility. In this way we have carried out some 160 least-squares analyses of various possible subsets of the input data. This cannot, therefore, be said to constitute a *complete* analysis of variance, but we believe it to be probably complete enough to furnish the reader with a fair picture of the state of knowledge of the constants at the close of 1962 and thus to furnish the basis from which we made the choices of selections and rejections for the 1963 adjustment.

(2) *Readjustments of A Priori Input Error Assignments*

Certain of our groups of data in Table X exhibit marked inconsistencies local to the group. In the simple case where all the items in a group are merely different measurements of *the same quantity*, we have a one-dimensional problem in which it is fairly easy by simple inspection to spot the outstandingly discrepant item or items. Consider, for example, the three measurements of μ_p/μ_n which yielded the following results (corrected for diamagnetism):

Boyne and Franken (1961),	2.792906±0.000056;
Sommer, Thomas, and Hipple (1951),	2.792757±0.000025;
Sanders, Dellis, and Turberfield (1961),	2.792770±0.000070.

The last two of these results are in satisfactory agreement, well within the standard deviation of their difference, but the first differs from the second by 53.2±20.5 ppm, a discrepancy of more than twice its own standard deviation. Eventually, we shall reject Boyne and Franken's result for reasons explained in Sec. 2.5(5), reasons related to the experiment itself, but for the purpose of the present analysis of variance we wish to retain all such discrepant data to test their consistency and so we are forced to proceed on the hypothesis that the apparent discrepancies are in fact compatible, and hence that the assigned *a priori* errors of the input quantities were too small. This calls for readjustment of the *a priori* error assignments of some or all of such items of discrepant data. In the absence of any other guiding information, we have decided to adopt the policy, in such a case, of expanding the error measures of the subset of moderately discrepant data in proportion to their original magnitudes by multiplying their errors by a common factor of such size as to yield a χ^2 for the subset reasonably close to its expectation value. We have seen above that the expectation value of χ^2 is $n-m$, the number of degrees of freedom, which we shall designate by f. Since the standard deviation of χ^2 is $(2f)^{\frac{1}{2}}$, we should try to pick an expansion factor which will make χ^2 fall reasonably inside the range, $f-(2f)^{\frac{1}{2}}<\chi^2<f+(2f)^{\frac{1}{2}}$.

We wish to emphasize that this minor local "doctoring" of the *a priori* error assignments within small subgroups where a discrepant datum is obvious because all items are of the same kind is purely a provisional device for the purpose of the analysis of variance. In the final least-squares adjustment, the "undoctored" *a priori* errors of all the items to be retained are those which will be used. In justification of this provisional doctoring procedure, consider for the moment what the

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[174] Three or more differently oriented planes which are parallel to a common axis are said to be "cozonal." Such a set of three planes does not determine a point in 3-space; instead, the planes, intersecting in pairs, give three parallel lines.

result would be if we did not expand the error assignments in the small subset just described. The contributions to the χ^2 of the entire adjustment, or of any large subset of the entirety, of which this small set of three input items happened to be a part, would be notably increased by the larger squared residuals r_i^2, coming from this internally inconsistent subset alone. This would increase the measure of incompatibility of the entire adjustment *as a whole* and necessitate an expansion of the error measures by the criterion of external consistency *of all of the output values*. When it is apparent from the start, however, that the cause of the incompatibility lies in one small subset of the input data, it makes little sense to pretend to ignore this fact and spread the effects of such incompatibility over the entire adjustment. What we are doing by such "doctoring" is in reality to make the picture appear more compatible than in fact it really is by relieving the small local strains in the structure where we already know these exist. If even after this, the analysis of variance shows that certain of the data still remain discrepant, we shall feel that the finger of suspicion of systematic error points even more strongly at such data. At this stage we are merely seeking *clues* as to the whereabouts of error, not *proof*.

(3) *Measures of Incompatibility*

The problem of spotting likely trouble-makers among items of input data of a least-squares adjustment when the overdetermined system is multivariate is slightly more difficult. The methods we use here have proven convenient. No rigor can be claimed for these methods since they do not *prove* that the items selected as suspect are afflicted with systematic error. There is a real value, however, in seeking tests which may reveal that the elimination of a relatively small minority of input data leaves the remainder of the overdetermined system far more consistent, especially if subsequent examination of the physical methods of measurement used in obtaining that suspected minority of input data strongly support our suspicion that they are likely to be systematically erroneous.

We have explained in Sec. 3.1(2) the meaning of the terms "residue" and "normalized residue." In what follows we shall designate the normalized residue of the ith input datum by r_i. In the absence of systematic errors, the expectation value of r_i^2 for each datum is unity.

The analogy between a least-squares adjustment and an overdetermined mechanical structure consisting of elastic members is a valuable one to consider; the more rigid elastic members correspond to the determinations of high accuracy to which greater statistical weight must be attached. Because the individual input data suffer from errors, the overdetermined set of equations is, however, more or less incompatible, and the analogous situation in the case of the mechanical structure results in different amounts of elastic energy stored in the various members. The squared normalized residual, r_i^2, then may be thought of as the contribution to the total elastic energy of strain, χ^2, contributed by the ith datum when the system has found equilibrium at its minimum energy state, i.e., when the condition of least-squares has been satisfied. Large contributions, those for which $r_i^2 \gg 1$, lead us to suspect that a systematic error was present in that datum or that too small an *a priori* or "internal" error (i.e., from information "internal" to that particular datum) had been assigned to it. This test is valuable as a rough indication. However, we must recall that the removal of a suspect item in the adjustment may well result in a new and completely different redistribution of the strain energy among the remaining items, a redistribution indicative of a quite different interpretation regarding *which* items are responsible for the strain.

Another criterion of strain is $r_i'^2$. This is the analog of the elastic energy required to stretch the rejected ith datum back into forced accord with the value of that datum implied by the remainder of the adjustment as the latter stands after rejection of the ith datum. Still a third useful measure is the difference between the experimental value and the least-squares-adjusted value relative to the standard error *of this difference*. These criteria require closer examination.

In order better to clarify the discussion and its symbols we recall that our tests will consist in examining the results of removing one item of the input data, the ith, either from the adjustment as a whole or from some subset thereof. Since we have four unknowns, $x_1, \cdots, x_4$, the observational input equation associated with the ith datum will, in general, in its final linearized form look like this:

$$a_{i1}x_1+a_{i2}x_2+a_{i3}x_3+a_{i4}x_4-\epsilon_i \overset{\prime}{=} y_i, \qquad (29)$$

wherein the a's are the exactly known numerical coefficients of the unknowns, the x's. The sum of the first four terms in the left-hand member is the function of the unknowns to which this particular equation refers and we shall speak of it for brevity simply as "the function," or the ith function. The last term in the left-hand member, ϵ_i, is the small residue (to be determined by the least-squares procedure) required to balance this equation when the least-squares adjusted values, resulting from the adjustment of the *entire* initial set or subset of observational data under consideration, have been substituted for the x's. We define $r_i = \epsilon_i/\sigma_i$.

The least-squares adjustment is a procedure for selecting a set of values for the x's such as to minimize the sum of squares of all the r_i and it is this minimum value which we call χ^2. y_i in Eq. (29) is the ith datum. It is the numerical value resulting from the experimental measurement after appropriate reduction with the use of exactly known auxiliary constants and σ_i is the *a priori* standard deviation assigned to y_i on the basis of information internal to the particular experiment.

It is our object to compare the results available from two least-squares analyses, one which includes the ith datum, the other which deletes it. Since in what follows the ith item is the only one the effect of whose insertion or removal is to be discussed, we shall, for simplicity, drop the subscript i from here on. Let us designate by y_0 the experimental value of the ith datum y_i and by σ_0 the *a priori* assigned standard-deviation error of y_0. Let us designate by y_1 the numerical value of the function $a_{i1}x_1+a_{i2}x_2+a_{i3}x_3+a_{i4}x_4$ when the least-squares adjusted values of the x's from the solution of the entire initial set or subset have been substituted therein. Let us designate by y_2 the value of this function when the least-squares adjusted values of the x's from the solution of the *remainder* of the initial set or subset *after rejection of the ith item* have been substituted into the function. Let σ_1^2 and σ_2^2 be the variances of y_1 and y_2. Since y_2 is the value of an experimental quantity calculated from a set of data from which that specific experiment has been deleted, we might call this the "indirect" value (i.e., the value implicit in the remainder of the equations), although the appropriateness of the term can be questioned if the set contains *other* direct determinations of the same quantity.

We define then the normalized residues, r and r', for the original set and for the deleted set as follows:

$$r=(y_0-y_1)/\sigma_0, \tag{30}$$

$$r'=(y_0-y_2)/\sigma_0. \tag{31}$$

Now we can compute a relationship between the quantities y_1 and σ_1^2 on the one hand, and the quantities y_0, y_2, σ_0^2, and σ_2^2 on the other hand, by the application of simple statistical rules for uncorrelated quantities because y_0 and y_2 have independent error distributions.

Since y_1 is the weighted average of y_0 and y_2, that is to say, the weighted average of the directly observed value y_0 and the so-called "indirect" value implicit in all the rest of the data (after deletion of the item y_0), we can write

$$\sigma_1^{-2}=\sigma_0^{-2}+\sigma_2^{-2}; \quad \text{or} \quad \sigma_1^2=\sigma_0^2\sigma_2^2/(\sigma_0^2+\sigma_2^2) \tag{32}$$

and

$$y_1=\sigma_1^2(y_0/\sigma_0^2+y_2/\sigma_2^2). \tag{33}$$

From the last four equations it is easy to show that

$$r'/r=(\sigma_0^2+\sigma_2^2)/\sigma_0^2=\sigma_2^2/\sigma_1^2 \tag{34a}$$

and that

$$\sigma_1^2/\sigma_0^2=(r'-r)/r', \tag{34b}$$

$$\sigma_2^2/\sigma_0^2=(r'-r)/r. \tag{34c}$$

We must remember that y_0 and y_2 are error-statistically independent quantities while y_0 and y_1 are not, since the least-squares solution y_1 is computed from data that includes y_0. The variance of the difference y_0-y_2 can be written immediately as $\sigma_0^2+\sigma_2^2=(r'/r)\sigma_0^2$, but the variance of the difference y_0-y_1 must be computed by first expressing y_0-y_1 in terms of y_0-y_2. When this is done we then find that this variance is $(\sigma_0^2+\sigma_2^2)(r/r')^2$ or $\sigma_0^2-\sigma_1^2=(r/r')\sigma_0^2$. We thus have:

$$(\text{variance of } y_0-y_2)=\sigma_{02}^2=(r'/r)\sigma_0^2, \tag{35a}$$

$$(\text{variance of } y_0-y_1)=\sigma_{01}^2=(r/r')\sigma_0^2. \tag{35b}$$

A result which may be at first somewhat surprising, but which is actually obviously necessary, is that the difference, y_0-y_1, divided by its standard deviation is equal to y_0-y_2 divided by *its* standard deviation. This is readily verified using Eqs. (30) and (31). Hence, either expression can be used as a measure of the consistency of the experimental measurement y_0 with the remainder of the data.

$$(y_0-y_1)/\sigma_{01}\equiv(y_0-y_2)/\sigma_{02}=(rr')^{\frac{1}{2}}. \tag{36}$$

It is clear that rr' is the squared normalized residual associated with the addition of one experimental datum to the least-squares adjustment. Let χ^2 be the sum of the squared normalized residuals of the least-squares adjustment without this datum. It follows that

$$\chi^2=\chi^{2\prime}+rr'. \tag{37}$$

In keeping with our analogy of an elastic structure we can make a direct physical interpretation of rr'. Firstly, we recognize that the normalization of the residuals renders them equally valid analogues of either the stress (force) or strain (elongation) in a member of the structure (the reciprocity theorem of elasticity). Thus r can be regarded as a measure of the initial stress in the member before it is removed from the structure, and r' as a measure of the change in length upon removal. Then rr' is twice the additional elastic energy of strain. A part of this energy was stored in the member and a part in the rest of the structure.

Figure 7 is intended to illustrate this situation with a concrete physical analog.

In the upper two sketches we represent, on the left, a complete least-squares adjustment by a system of six coupled springs, all under tension, and on the right the same system after one of the springs has been uncoupled. The five springs which remain coupled are still under some tension, i.e., still have some remaining stored elastic energy, though *less* than before. To simplify the discussion and its illustration, in the lower sketch we next replace the five coupled springs by a single equivalent spring having the same elastic force-constant per unit deflection. The unstressed length y_0 of the helical spring on the left represents the ith datum, the datum the effect of whose rejection from the total system (or addition to the remaining system) is what we are interested in studying. The helical spring on the right is the equivalent of the remainder of the system and stands therefore for the remaining $n-1$ input data

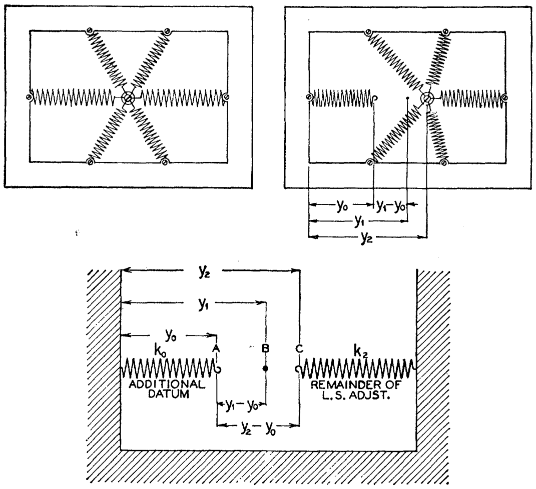

FIG. 7. Mechanical analog to illustrate the effect of removing an item of data from a least-squares adjustment. The total adjustment is represented by the system of six coupled springs in the upper left-hand figure, all of which are under tension. The left-hand spring is uncoupled and the system relaxes to the configuration shown in the upper right-hand figure. There still remains stored elastic energy in the five coupled springs, but *less* than before. In the lower figure the system of five coupled springs has been replaced, for simplicity of explanation, by a single elastically equivalent spring.

equations. The distance y_2 represents the value of the quantity y, implied by the solution of the remainder of the system of equations so that y_2-y_0 represents the residual (unnormalized) by which the ith datum disagrees with the value implicit in the remainder of the system. Each spring has a stiffness constant, which measures its force per unit deflection; k_0 being this constant for the left-hand spring, k_2 for the right-hand spring. If the square of the normalized residue is to be equated to the energy stored in the spring then it is clear that we must identify k_i with $2/\sigma_i^2$. As they stand in the figure, uncoupled, both springs are in their lowest state of stored elastic energy. (The system represented by the right-hand spring is in fact of course more complicated than shown and consists of $n-1$ elastic elements in equilibrium.) It therefore already contains stored elastic energy which we shall not disturb. Now let us deflect the springs so as to couple the ends A and C together. Let B represent the position which the two coupled ends assume when equilibrium is reached. In this new state the total gain in stored elastic energy is

$$\Delta E=\tfrac{1}{2}k_0(y_1-y_0)^2+\tfrac{1}{2}k_2(y_2-y_1)^2. \tag{38}$$

The establishment of equilibrium (with the spring ends joined at B) means that, at that position, E is a minimum (the analog of the condition of least squares), and, holding y_0 and y_2 constant, if we set $dE/dy_1=0$ we see that this is of course exactly the same condition as equating the forces of the two deflected springs, namely,

$$\tfrac{1}{2}k_0(y_1-y_0)=\tfrac{1}{2}k_2(y_2-y_1). \tag{39}$$

Eliminating k_2 between these last two expressions one readily obtains

$$\Delta E=\tfrac{1}{2}k_0(y_1-y_0)(y_2-y_0). \tag{40}$$

ΔE is the additional energy stored in both springs when they are in their mutually equilibrated state with their ends coupled. It is the analog of the increase in χ^2 caused by adding the ith datum to the system. Expressing k_0 in terms of its equivalent, $2/\sigma_0^2$, clearly reduces Eq. (40) to

$$\Delta E=\Delta\chi^2=(y_1-y_0)(y_2-y_0)/\sigma_0^2=rr', \tag{40a}$$

which is identical in significance to Eq. (37).

We see thus that r, r', and their product rr' all contain valuable information pertinent to the compatibility or incompatibility of a given item of data with the remainder of an adjustment. We shall base our arguments regarding consistency of the data therefore on a discussion of the magnitudes r, r', and rr'.

(4) *Discussion of the Analysis of Variance*

The 14 input items which together form the basis of our analysis are those which are so indicated in Table X. With the help of our auxiliary constants, each datum can be used to form an equation involving four unknowns, which we shall take to be α, e, N, and Λ. It should be borne in mind that these variables merely form the *coordinate system* for our description of the four-dimensional function-space of our problem and other variables functionally related to these could serve equally well; the specific choice of variables is immaterial. In some of our calculations, in fact, we have used as alternative variables α^{-1}, α^3/e, F, and Λ.

The 14 equations in 4 unknowns are nonlinear, each being reducible to the form of a product of powers $\alpha^h e^i N^j \Lambda^k$, equated to a stochastic number A, the result of a physical measurement. The familiar theory of least-squares with its implied invariance to linear transformations applies only to linear systems. The method of perturbations employed in order to linearize our equations and the justification for terminating the Taylor expansion of the equations at the linear terms has been explained along with the complete least-squares procedure in many previous papers,[1,9,145,175–177] and need not therefore be re-explained in detail here. We call the new set of equations the "linearized" set of observational equations, thus distinguishing them from the "primitive" set.

The least-squares adjustment of the full set of 14

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[175] J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. **25**, 691 (1953).
[176] E. R. Cohen, Nuovo Cimento Suppl. **6**, 110 (1957).
[177] J. W. M. DuMond, IRE Trans. Instr. **I-7**, 136 (1958).

Table XI. Least-squares analysis, 14 equations, 4 variables (degrees of freedom=10; $\chi^2=27.02$, $R=1.644$). Fourteen different least-squares adjustments are represented here. Each line gives r_i, $\chi^{2\prime}$, $(\chi^2-\chi^{2\prime})/r_i^2$, r_i', and r_ir_i' for a different adjustment in each of which all items of data are present *except* the one named in the column labelled "Item deleted." Each of these 14 adjustments has 13–4=9 degrees of freedom and the expectation value of its $\chi^{2\prime}$, in the absence of any but random incompatibilities, should be 9. At the top is given the χ^2 for the 10-degrees-of-freedom least-squares adjustment in which all 14 items are used.

Item deleted	r_i	$\chi^{2\prime}$	$(\chi^2-\chi^{2\prime})/r_i^2$	r_i	r_ir_i'
1. Hyperfine structure	1.24	22.47	2.95	3.66	4.54
2. Fine structure	−0.48	26.73	1.23	−0.59	0.28
3. μ (Boyne, Franken)	2.31	21.29	1.07	2.48	5.73
4. μ (Sommer, Thomas, Hipple)	−0.79	26.07	1.52	−1.20	0.95
5. μ (Sanders *et al.*)	−0.10	27.01	1.00	−0.10	0.01
6. Faraday	−0.02	27.01	2.50	−0.50	0.001
7. γ (Bender, Driscoll)	−0.37	26.77	1.84	−0.68	0.25
8. γ (Vigoureux)	−0.87	25.62	1.84	−1.60	1.39
9. γ (Thomas, Driscoll, Hipple)	3.40	14.88	1.05	3.57	12.13
10. Λ (Bearden, 1931)	−1.31	25.01	1.17	−1.53	2.01
11. Λ (Bearden, 1935)	0.59	26.65	1.03	0.61	0.36
12. Λ (Bäcklin, 1935)	−1.66	23.71	1.20	−1.99	3.31
13. $N\Lambda^3$ (Cu $K\alpha$)	1.42	23.61	1.69	2.40	3.41
14. $N\Lambda^3$ (Mo $K\alpha$)	−0.01	27.02	2.00	−0.02	0.0002

equations with their errors modified as indicated in Table X leads to the following solution:

$$1/\alpha=137.0373\pm0.0014,$$

$$e=(4.80313\pm0.00014)\times10^{-10}\text{ esu},$$

$$N=(6022.33\pm0.18)\times10^{20}\text{ mole}^{-1},$$

$$h=(6.62592\pm0.00033)\times10^{-27}\text{ erg sec},$$

$$m=(0.910934\pm0.000027)\times10^{-27}\text{ g},$$

$$\Lambda=1.002066\pm0.000014,$$

where the errors are computed on the basis of internal (*a priori*) consistency. The value of χ^2 for this solution, however, is 27.02, to be compared with an *a priori* expectation value of 10, so that the ratio R is 1.644. Purely on a statistical basis the probability is only 0.002 that a value of χ^2 as large as this could occur by chance, and hence we are justified in examining the data further to see if we can discover any discrepancies, and if we can identify the source of this large value of χ^2.

In order to explore this matter, we carry out 14 least-squares adjustments, each one deleting one specific item from the set of 14 equations to give all possible combinations of 13 equations. The results of these calculations are presented in Table XI. In this table the first column lists the one item which has been deleted to give a system of 13 equations in 4 variables. The second column gives the normalized residual of that datum in the full least-squares analysis. The sum of the squares of the residuals of this column is just χ^2. When a specific datum is deleted, the value of χ^2 for this 13-item system will, of course, be reduced; these values are listed as $\chi^{2\prime}$ in column 3. By the deletion of an item y_i, from our set we certainly reduce χ^2 by r_i^2, but we do even more than that because the remainder of the system is also allowed to relax to a state of lower strain. Hence we will always have $\chi^2-\chi^{2\prime}\geq r^2$. The amount by which this relationship is an inequality rather than an equality represents also a measure of consistency of the data, and this measure is listed in column 4. The normalized residual of the deleted variable from the least-squares solution of the censored set r' is given in each case in column 5. The square of the difference between the experimental datum and the value implied by all of the remainder of the data, divided by the variance of this difference, is denoted by $rr'=\chi^2-\chi^{2\prime}$ in column 6.

It is immediately apparent that item 9, the gyromagnetic ratio measurement of Thomas, Driscoll, and Hipple, is the single most discrepant item, followed by the proton moment measurement of Boyne and Franken, and the hyperfine-structure calculations of Iddings and Platzmann. We also see in this table that the value of $N\Lambda^3$ for Mo $K\alpha_1=707.831$ x-units is apparently the most consistent of all items. Such a conclusion should be made cautiously, however, for as we shall see, this agreement is an accidental result of the fact that this item (14) lies in between the value of item 13 (the Cu $K\alpha$ data) and the indirect value of $N\Lambda^3$ computed from the other twelve. We have:

Indirect (1−12),	6058.796±0.461;
Cu $K\alpha$(13),	6060.184±0.321;
Weighted mean,	6059.731±0.264;
Mo $K\alpha$(14),	6059.725±0.327.

If we use smaller errors for the two $N\Lambda^3$ values (i.e., if we do not arbitrarily expand the errors by the factor of 3 which we had introduced to compensate for the obvious inconsistency of these data), we obtain a value for χ^2 of 36.13, with the Mo data contributing 3.46 and

Table XII-a. Least-squares analysis, 13 equations, 4 variables. Cu $K\alpha$ data for $N\Lambda^3$ deleted, Mo $K\alpha$ data retained; degrees of freedom=9; $\chi^2=24.76$, $R=1.659$. (See Table XI for general explanation.)

Item deleted	r_i	$\chi^{2'}$	$(\chi^2-\chi^{2'})/r_i^2$	r_i	$r_i r_i'$
1. Hyperfine structure	1.20	20.76	2.77	3.33	4.00
2. Fine structure	−0.50	24.45	1.24	−0.62	0.31
3. μ (Boyne, Franken)	2.31	19.04	1.07	2.48	5.72
4. μ (Sommer, Thomas, Hipple)	−0.79	23.80	1.53	−1.21	0.95
5. μ (Sanders *et al.*)	−0.10	24.75	1.00	−0.10	0.01
6. Faraday (NBS)	−0.02	24.76	2.00	−0.04	0.0008
7. γ (Bender, Driscoll)	−0.37	24.51	1.81	−0.67	0.25
8. γ (Vigoureux)	−0.87	23.38	1.82	−1.59	1.38
9. γ (Thomas, Driscoll, Hipple)	3.40	12.61	1.05	3.57	12.15
10. Λ (Bearden, 1931)	−1.24	23.05	1.11	−1.37	1.70
11. Λ (Bearden, 1935)	0.64	24.36	1.00	0.64	0.41
12. Λ (Bäcklin, 1931)	−1.59	21.92	1.13	−1.79	2.84
14. $N\Lambda^3$ (Mo $K\alpha$)	0.45	20.91	18.95	8.52	3.84

the Cu data contributing 5.76 to this sum. The corresponding values of rr' are 6.61 and 11.37.

If we delete the Cu $K\alpha$ data for $N\Lambda^3$ (and use the smaller error for the Mo $K\alpha$ data) we obtain a set of 13 equations, which, treated in the same manner as the 14 equations for Table XI, give us the results shown in Table XII-a. In comparison are the data of Table XII-b, which is similar to Table XII-a except that here we retain the Cu $K\alpha$ data (with its original error) and delete the Mo $K\alpha$ data. The residuals of Table XII-a are, in general, comparable to the corresponding residuals of Table XII-b. This is particularly true for the ratio r_i'/r_i. The tables clearly demonstrate that the $N\Lambda^3$ data which is introduced into our analysis does not have a large influence on the consistency patterns for the rest of the data, but on the other hand, 95% of the strain "energy" introduced into the structure by including either $N\Lambda^3$ result is due to the distortion away from the equilibrium position determined by the remainder of the data, and only 5% of this strain is ascribable to the displacement of the $N\Lambda^3$ value from the consensus. Furthermore, the Cu $K\alpha$ data introduces approximately twice as much strain as the Mo $K\alpha$ data (Cu data: $\Delta\chi^2=8.61$, $r_i'=168.1$; Mo data: $\Delta\chi^2=3.84$, $r_i'^2=72.6$).

Because of the large values of $r_i'^2$, we are probably justified in deleting *all* of the $N\Lambda^3$ data from our analysis. If we do so, however, the direct (ruled-grating) measurements of Λ are no longer connected in any way with the other variables. Furthermore, items 3 to 9 can all be expressed in terms of the two variables Ne and α^3/e. The value of χ^2 for this system can be decomposed into a sum of three terms: $\chi^2=\chi_1^2+\chi_2^2+\chi_3^2$. The first term represents the two equations determining α and gives $\chi_1^2=1.03$, $R=1.01$; the second term represents a system of seven equations in the two unknowns, Ne and α^3/e, and gives $\chi^2=18.40$, $R=1.92$. The mutual consistency of the seven equations in two unknowns is independent of the value of α determined from the remainder of the data. The adjusted value of the electronic charge e is affected, however, in direct proportion to the change in α^3. The adjusted

Table XII-b. Least-squares analysis, 13 equations, 4 variables. Mo $K\alpha$ data for $N\Lambda^3$ deleted, Cu $K\alpha$ data retained; degrees of freedom=9; $\chi^2=29.52$, $R=1.811$. (See Table XI for general explanation.)

Item deleted	r_i	$\chi^{2'}$	$(\chi^2-\chi^{2'})/r_i^2$	r_i'	$r_i r_i'$
1. Hyperfine structure	1.56	22.79	2.77	4.32	6.74
2. Fine structure	−0.31	29.40	1.23	−0.38	0.12
3. μ (Boyne, Franken)	2.32	23.73	1.07	2.49	5.78
4. μ (Sommer, Thomas, Hipple)	−0.76	28.64	1.53	−1.16	0.88
5. μ (Sanders *et al.*)	−0.09	29.51	1.00	−0.09	0.008
6. Faraday (NBS)	−0.07	29.50	2.18	−0.16	0.012
7. γ (Bender, Driscoll)	−0.39	29.24	1.85	−0.72	0.28
8. γ (Vigoureux)	−0.89	28.05	1.84	−1.64	1.46
9. γ (Thomas, Driscoll, Hipple)	3.39	17.43	1.05	3.56	12.09
10. Λ (Bearden, 1931)	−1.80	25.93	1.11	−1.99	3.59
11. Λ (Bearden, 1935)	0.36	29.38	1.03	0.37	0.13
12. Λ (Bäcklin, 1931)	−2.18	24.18	1.12	−2.45	5.34
13. $N\Lambda^3$ (Cu $K\alpha$)	0.66	20.91	19.55	12.97	8.61

TABLE XIII. Least-squares analysis, 7 equations, 2 variables; degrees of freedom=5; $\chi^2=18.40$, $R=1.918$. (See Table XI for general explanation.)

Item deleted	r_i	$\chi^{2\prime}$	$(\chi^2-\chi^{2\prime})/r_i^2$	r_i	$r_i r_i'$
3. μ (Boyne, Franken)	2.28	12.82	1.07	2.45	5.58
4. μ (Sommer, Thomas, Hipple)	−0.86	17.28	1.52	−1.31	1.12
5. μ (Sanders *et al.*)	−0.12	18.38	1.00	−0.12	0.014
6. Faraday (NBS)	0.09	18.38	2.44	0.22	0.02
7. γ (Bender, Driscoll)	−0.32	18.21	1.82	−0.58	0.19
8. γ (Vigoureux)	−0.82	17.17	1.84	−1.51	1.23
9. γ (Thomas, Driscoll, Hipple)	3.42	6.14	1.05	3.59	12.26

output values for the least-squares analysis with the $N\Lambda^3$ data omitted are:

$$1/\alpha=137.0360\pm0.0014,$$

$$e=(4.80326\pm0.00016)\times10^{-10}\text{ esu},$$

$$N=(6022.16\pm0.20)\times10^{20}\text{ mole}^{-1},$$

$$\Lambda=1.002024\pm0.000023,$$

$$h=(6.62623\pm0.00036)\times10^{-27}\text{ erg sec},$$

$$m=(0.910960\pm0.000030)\times10^{-27}\text{ g}.$$

The large value of χ^2 for the subset of seven equations in two unknowns justifies us in looking further for a cause of this discrepancy, since a value as large as $\chi^2=18.40$ should occur by chance with a probability of less than $\frac{1}{400}$. We therefore carried out an additional set of seven least-squares adjustments which, similar to the adjustments of Table XI, result from deleting one of the input data. (See Table XIII.) The results of this analysis are quite similar to the results of that table indicating that the deletion of the x-ray data has not greatly affected the over-all structure of the remaining inconsistencies. Particularly striking is the insensitivity of the ratio $r_i'/r_i=(\chi^2-\chi^{2\prime})/r_i^2$ to the deletion of the x-ray data. A comparison of the weights of the output values of N with and without the x-ray data on $N\Lambda^3$ indicates that this latter datum, although it represents the "traditional" approach to the determination of the Avogadro constant, has only one-fifth the weight of the nuclear magnetic resonance data. Thus we lose very little in rejecting the x-ray data.

The largest incompatibility which still remains after the x-ray data are deleted is exhibited by item 9 (Thomas, Driscoll, and Hipple's determination of the gyromagnetic ratio γ). This item by itself contributes approximately two-thirds of the total strain of the system. The second largest contribution to the strain is item 3 (Boyne and Franken's measurement of μ), which is responsible for more than one-fourth of the total.

If we now delete item 9 from our system we can generate the results shown in Table XIV. The total χ^2 of 6.14 is based on six equations in two variables and hence yields a consistency measure $R=1.24$. From the final column of Table XIV we see that the largest discrepancy is associated with item 3, the measurement by Boyne and Franken of the proton magnetic moment. This item by itself contributes 5.80 to the total χ^2 of 6.14 for the subset of items 3 to 8. If Boyne and Franken's measurement is deleted, the value of χ^2 for five equations in two unknowns is reduced to $\chi^2=0.34$ ($R=0.336$) and we obtain:

$$1/\alpha=137.0360\pm0.0014,$$

$$e=(4.80327\pm0.00015)\times10^{-10}\text{ esu},$$

$$N=(6022.16\pm0.20)\times10^{20}\text{ mole}^{-1},$$

$$h=(6.62626\pm0.00036)\times10^{-27}\text{ erg sec},$$

$$m=(0.910964\pm0.000030)\times10^{-27}\text{ g},$$

$$F=9648.70\pm0.05\text{ emu/mole},$$

$$\Lambda=1.002024\pm0.000023.$$

The data are now highly consistent; for a normal distribution of data, a value of χ^2 as small as 0.34 would be expected by chance with only 5% probability. Of

TABLE XIV. Least-squares analysis, 6 equations, 2 variables; degrees of freedom=4; $\chi^2=6.14$, $R=1.239$. (See Table XI for general explanation.)

Items deleted	r_i	$\chi^{2\prime}$	$(\chi^2-\chi^{2\prime})/r_i^2$	r_i'	$r_i r_i'$
3. μ (Boyne, Franken)	2.32	0.34	1.08	2.50	5.80
4. μ (Sommer, Thomas, Hipple)	−0.76	5.26	1.53	−1.16	0.88
5. μ (Sanders *et al.*)	−0.08	6.13	1.12	−0.09	0.007
6. Faraday (NBS)	0.19	6.05	2.42	0.46	0.09
7. γ (Bender, Driscoll)	0.21	6.06	1.91	0.40	0.08
8. γ (Vigoureux)	−0.29	5.97	1.93	−0.56	0.16

course, this is a misleading statement, our data having been strongly censored to remove all of those items which would contribute to a large value of χ^2, and hence we should expect the χ^2 of our censored system to be considerably smaller than the value which would be expected for an uncensored set.

We have carried out a relatively violent censoring of our initial input data in order to achieve the set of fundamental constants just listed. We have, however, obtained this censored set as the logical result of successive tests of consistency of the data.

We see throughout these tests clear-cut evidence of strong incompatibility with the remaining consensus of information on the constants exhibited by the following items:

3. Boyne and Franken's determination of μ_p/μ_n;
9. Thomas, Driscoll, and Hipple's determination of γ;

13, 14. The weighted mean value of $N\Lambda^3$ derived from the crystal lattice spacings measured with the Mo $K\alpha_1$ line or the Cu $K\alpha_1$ line.

We summarize the numerical results of our least-squares adjustments in Table XV. In this table we can see the effect of the various deletions on the adjusted values of several physical constants. All of these results which contain data on $N\Lambda^3$ (items 13 and 14), as well as the fine-structure items, 1 and 2, are computed with the expanded scale of errors required for consistency among individual items. It should be borne in mind that the value of the Avogadro number given here comes entirely from items 2, 4, 5, 6, 7, and 8 of Table X and does not involve the "direct" measurement of $N\Lambda^3$ from XRCD data, which has been deleted from this final adjustment. The above value of $\Lambda = 1.002024 \pm 0.000023$ rests entirely on the three direct determinations of the wavelength of Cu $K\alpha$ radiation with flat-ruled gratings, items 10, 11, and 12 in Table X, and involves a *definition* of the x-unit in terms of the assumed value 1537.396 x-units for Cu $K\alpha_1$. Two of these three direct determinations of Λ (item 10, by Bearden, and item 12, by Bäcklin) were made by recording on a photographic plate the direct beam, the specularly reflected beam, and the diffracted beams of the Cu $K\alpha_1$ emission line in different orders. We have already discussed [Sec. 2.5(1)] the problems inherent in the precise characterization of x-ray line shapes from a photographic image, and it is perhaps significant that the third experimental determination of Λ (item 11), which achieved collimation by means of a two-crystal spectrometer rather than a slit system, yields a considerably larger value. The grating reflection occurs between the two-crystal reflections; the first crystal reflection determined the direction of the beam incident on the grating, the second the directions of the direct, reflected, and diffracted beams. In this case one might be more ready to suppose that the observed

Table XV. Summary of results. Least-squares output values from various choices of input data.

	χ^2	$1/\alpha$	e	h	m	N	Λ
Full set (14 equations)	36.13	137.0375±0.0014	4.80310±0.00014	6.62585±0.00032	0.910929±0.000027	6022.37±0.18	1.002075±0.000011
Delete item 14	29.52	137.0378±0.0014	4.80307±0.00014	6.62579±0.00032	0.010923±0.000027	6022.40±0.19	1.002083±0.000011
Delete item 13	24.76	137.0372±0.0014	4.80314±0.00014	6.62594±0.00032	0.010936±0.000027	6022.32±0.19	1.002063±0.000011
Delete items 13 and 14	20.92	137.0360±0.0015	4.80326±0.00015	6.62623±0.00036	0.910960±0.000030	6022.16±0.20	1.002024±0.000023
Delete items 9 and 14	17.43	137.0378±0.0014	4.80308±0.00014	6.62581±0.00032	0.910926±0.000027	6022.39±0.24	1.002083±0.000011
Delete items 9 and 13	12.61	137.0372±0.0014	4.80314±0.00014	6.62595±0.00032	0.910938±0.000027	6022.31±0.23	1.002064±0.000011
Delete items 3, 9, 14	11.42	137.0378±0.0014	4.80308±0.00014	6.62582±0.00032	0.910927±0.000027	6022.41±0.24	1.002083±0.000011
Delete items 9, 13, 14	8.66	137.0360±0.0015	4.80327±0.00015	6.62626±0.00036	0.910963±0.000030	6022.14±0.20	1.002024±0.000023
Delete items 3, 9, 13	6.67	137.0372±0.0014	4.80315±0.00014	6.62596±0.00032	0.910939±0.000027	6022.32±0.24	1.002063±0.070011
Delete items 3, 9, 13, 14	2.86	137.0360±0.0015	4.80327±0.00015	6.62626±0.00036	0.910964±0.000030	6022.16±0.20	1.002024±0.000023
Delete items 1, 3, 9, 13, 14	0.34	137.0388±0.0031	4.80298±0.00033	6.62559±0.00076	0.910908±0.000062	6022.52±0.41	1.002024±0.000023

diffracted line profile approximated the natural profile and that the peak of this observed profile could, with some degree of assurance, be identified with the same wavelength as that observed in the measurements of lattice spacings for determining $N\Lambda^3$.

Because of these considerations and the uncertainties they involved, we decided to reject the three direct determinations of Λ (items 10, 11, 12) from the input data of our final 1963 least-squares adjustment. When uncertainties concerning the crystal determinations of $N\Lambda^3$ have been clearly resolved, the best means of obtaining information on Λ is a computation of the quotient of $N\Lambda^3$ by the least-squares adjusted best value of N, i.e., the value of N based on items 2, 4, 5, 6, 7, and 8. Let us call this value **N**. It is well to recall here, as explained in an earlier section, that a definite meaning can only be attached to $\Lambda=\lambda_g/\lambda_s$ if we define λ_s less ambiguously than in terms "of the standard grating constant of purest calcite." If we compute Λ from $[N\Lambda^3/\mathbf{N}]^{\frac{1}{3}}$, then we obtain a numerical value for Λ such that wavelengths λ_s are *by definition* measured in terms of an "*x*-unit" which has been defined by the numerical value assigned to the x-ray wavelength used to determine the lattice spacing of the crystal.

TABLE XVI. Defined values and equivalents.

Meter (m)	1650763.73 wavelengths of the unperturbed transition $2p_{10}$–$5d_5$ in ^{86}Kr
Kilogram (kg)	Mass of the international kilogram
	Astronomical
Second (s)	1/31 556925.9747 of the tropical year at 12^{h}ET, 0 January, 1900 (yr$=365^{\mathrm{d}}5^{\mathrm{h}}48^{\mathrm{m}}\,45^{\mathrm{s}}.9747$)
	Physical
	9192631770 cycles of the hyperfine transition (4, 0→3, 0) of the ground state of ^{133}Cs unperturbed by external fields
Degree Kelvin (°K)	In the thermodynamic scale, 273.16°K = triple-point of water T (°C) $=$ T (°K) $-$ 273.15 (freezing-point of water, 0.0000±0.0002°C)
Unified atomic mass unit (u)	1/12 the mass of an atom of the ^{12}C nuclide
Standard acceleration of free fall (g_n)	9.80665 m s^{-2} 980.665 cm s^{-2}
Normal atmosphere (atm)	101325 N m^{-2} 1013250 dyn cm^{-2}
Thermochemical calorie (cal$_{\mathrm{th}}$)	4.184 J 4.184×10^7 erg
Int. Steam Table calorie (cal$_{\mathrm{IT}}$)	4.1868 J 4.1868×10^7 erg
Liter (l)	0.001000028 m^3 (recommended by CIPM 1950) 1000.028 cm^3
Inch (in.)	0.0254 m 2.54 cm
Pound (avdp.)	0.45359237 kg
(lb)	453.59237 kg

Until such time as an international agreement is reached by defining unambiguously, in the operational sense, a unit in terms of which to intercompare all the x-ray emission-line wavelengths, we shall be unceasingly plagued with this difficulty. But improvement in the definitions and conventions is only a start. These must be followed by a careful and extensive program of remeasurements of most x-ray wavelengths in order to be sure that they have been properly defined in terms of these conventions (see Table XVI).

Specifications of the lattice spacing of a species of crystal is a poor way of defining a unit for measuring x-ray wavelengths, but this does not invalidate the use of the lattice spacing of a given crystal as a transfer unit for the accurate measurement of wavelength ratios. A careful study of all the experimental parameters which may affect the wavelength values so determined must also be made. We must not ignore the fact that x-rays have applications in nuclear spectroscopy and meson physics; precision in this field ought as far as possible to keep pace with the increasing level of precision in the whole of physics.

3.2. The Least-Squares Adjustment of 1963

The rejections of data discussed in the preceding sections leave us with six input items involving three unknowns, α, e, and N. These are as follows:

Stochastic input data used in 1963 Adjustment.

fs separation in D (Lamb *et al.*)	10971.59±0.10 Mc sec^{-1}
Magnetic moment of proton in nuclear magnetons (Sommer *et al.*)	2.792757±0.000025
Magnetic moment of proton in nuclear magnetons (Sanders *et al.*)	2.792770±0.000070
Faraday constant–silver (NBS)	9648.682±0.066 C mole^{-1}
Gyromagnetic ratio of the proton (Bender *et al.*)	26751.92±0.08 sec^{-1} G^{-1}
Gyromagnetic ratio of the proton (Vigoureux)	26751.88±0.08 sec^{-1} G^{-1}

For the fine structure separation in deuterium we have now returned to the original (unexpanded) standard error which is based on the evaluation of the accuracy of the experimental data. Having demonstrated that the fine-structure data is more consistent than the hydrogen hfs value, we no longer need to retain the expanded error assignment.

These data combined as explained earlier with the

TABLE XVII. General physical constants. Least-squares adjusted output values of 1963. The digits in parentheses following each quoted value represent the standard deviation error in the final digits of the quoted value as computed on the criterion of internal consistency. The unified scale of atomic weights is used throughout ($^{12}C=12$). C = coulomb; G = gauss; Hz = hertz; J = joule; N = newton; T = tesla; u = unified nuclidic mass unit; W = watt; Wb = weber.

Constant	Symbol	Value	Unit	
			mksA	cgs
Speed of light in vacuum	c	2.997925(1)	$\times 10^{8}$ m s^{-1}	$\times 10^{10}$ cm s^{-1}
Gravitational constant	G	6.670(5)[a]	10^{-11} N m^{2} kg^{-2}	10^{-8} dyn cm^{2} g^{-2}
Elementary charge	e	1.60210(2) 4.80298(7)	10^{-19} C	10^{-20} emu 10^{-10} esu
Avogadro constant	N_A	6.02252(9)	10^{26} kmole^{-1}	10^{23} mole^{-1}
Mass unit	u	1.66043(2)	10^{-27} kg	10^{-24} g
Electron rest mass	m_e	9.10908(13) 5.48597(3)	10^{-31} kg 10^{-4} u	10^{-28} g 10^{-4} u
Proton rest mass	m_p	1.67252(3) 1.00727663(8)	10^{-27} kg u	10^{-24} g u
Neutron rest mass	m_n	1.67482(3) 1.0086654(4)	10^{-27} kg u	10^{-24} g u
Faraday constant	F	9.64870(5) 2.89261(2)	10^{4} C mole^{-1}	10^{3} emu 10^{14} esu
Planck constant	h $h/2\pi$	6.62559(16) 1.054494(25)	10^{-34} J s 10^{-34} J s	10^{-27} erg s 10^{-27} erg s
Fine-structure constant $2\pi e^2/hc$	α $1/\alpha$	7.29720(3) 137.0388(6)	10^{-3}	10^{-3}
Charge-to-mass ratio for electron	e/m_e	1.758796(6) 5.27274(2)	10^{11} C kg^{-1}	10^{7} emu 10^{17} esu
Quantum of magnetic flux	hc/e h/e	4.13556(4) 1.379474(13)	10^{-11} Wb	10^{-7} G cm^{2} 10^{-17} esu
Rydberg constant	R_∞	1.0973731(1)	10^{7} m^{-1}	10^{5} cm^{-1}
Bohr radius	a_0	5.29167(2)	10^{-11} m	10^{-9} cm
Compton wavelength of electron	h/m_ec $\lambda_C/2\pi$	2.42621(2) 3.86144(3)	10^{-12} m 10^{-13} m	10^{-10} cm 10^{-11} cm
Electron radius	$e^2/m_ec^2=r_e$	2.81777(4)	10^{-15} m	10^{-13} cm
Thomsen cross section	$8\pi r_e^2/3$	6.6516(2)	10^{-29} m^{2}	10^{-25} cm^{2}
Compton wavelength of proton	$\lambda_{C,p}$	1.321398(13)	10^{-15} m	10^{-13} cm
	$\lambda_{C,p}/2\pi$	2.10307(2)	10^{-16} m	10^{-14} cm
Gyromagnetic ratio of proton	γ $\gamma/2\pi$	2.675192(7) 4.25770(1)	10^{8} rad s^{-1} T^{-1} 10^{7} Hz T^{-1}	10^{4} rad s^{-1} G^{-1} 10^{3} s^{-1} G^{-1}
(Uncorrected for diamagnetism H_2O)	γ' $\gamma'/2\pi$	2.675123(7) 4.25759(1)	10^{8} s^{-1} T^{-1} 10^{7} HzT^{-1}	10^{4} rad s^{-1} G^{-1} 10^{3} s^{-1} G^{-1}
Bohr magneton	μ_B	9.2732(2)	10^{-24} J T^{-1}	10^{-21} erg G^{-1}
Nuclear magneton	μ_N	5.05050(13)	10^{-27} J T^{-1}	10^{-21} s G^{-1}
Proton moment	μ_p μ_p/μ_N	1.41049(4) 2.79276(2)	10^{-26} J T^{-1}	10^{-23} erg G^{-1}
(Uncorrected for diamagnetism in H_2O sample)		2.79268(2)		
Gas constant	R_0	8.31434(35)	J deg^{-1} mole^{-1}	10^{7} erg deg^{-1} mole^{-1}
Boltzmann constant	k	1.38054(6)	10^{-23} J deg^{-1}	10^{-16} erg deg^{-1}
First radiation constant $(2\pi hc^2)$	c_1	3.74150(9)	10^{-16} W m^{2}	10^{-5} erg cm^{2} s^{-1}
Second radiation constant (hc/k)	c_2	1.43879(6)	10^{-2} m deg	cm deg
Stefan–Boltzmann constant	σ	5.6697(10)	10^{-8} W m^{-2} deg^{-4}	10^{-5} erg cm^{-2} s^{-1} deg^{-4}

[a] The universal gravitational constant is not, and cannot in our present state of knowledge, be expressed in terms of other fundamental constants. The value given here is a direct determination by P. R. Heyl and P. Chrzanowski, J. Res. Natl. Bur. Std. (U.S.) **29**, 1 (1942).

auxiliary constants (Table III) permit us to form an overdetermined set of equations in α, e, and N having three degrees of freedom. The set in fact, as we have already pointed out, breaks up into two independent sets, since the last five items contain only two unknowns and provide no implicit additional information on the value of α, which is defined entirely from the first item. The adjustment of these equations by least squares leads to the following set of recommended best values of the physical constants as of 1963:

$$1/\alpha = 137.0388 \pm 0.0006,$$
$$e = (4.80298 \pm 0.00006) \times 10^{-10}\ \text{esu},$$
$$h = (6.62559 \pm 0.00015) \times 10^{-27}\ \text{erg sec},$$
$$m = (9.10908 \pm 0.00013) \times 10^{-28}\ \text{g},$$
$$N = (6022.52 \pm 0.09) \times 10^{-20}\ \text{mole}^{-1}\ (^{12}\text{C} = 12).$$

The χ^2 for this adjustment in three degrees of freedom has the very low value of 0.34. This corresponds to a Birge ratio of errors-by-external to errors-by-internal consistency of only 0.33.

It must be remembered however that this results from a nonrandom set of input equations, a set indeed which has been radically *censored* (purged of "outlying" items). The *variance* in χ^2 is $2f = 6$. Thus, although the expectation value of R^2 is 1, the standard deviation of this ratio is ± 0.82, so that the smallness of the observed value, 0.10, is of little significance[178] except to say that the indicated compatibility of this overdetermined set of equations is reassuring. We have used the criterion of *internal* consistency for computing the errors in all of our output values, this being the one which in this case yields the larger errors.

Table XVIII. Energy conversion factors.

1 electron volt	$= 1.60210(2) \times 10^{-19}$ J $= 1.60210(2) \times 10^{-12}$ erg $= 8065.73(8)\ \text{cm}^{-1}$ $= 2.41804(2) \times 10^{14}\ \text{s}^{-1}$
$V\lambda$	$= 12398.10(13) \times 10^{-8}$ eV cm
1 eV per particle	$= 11604.9(5)$ °K $= 23061(1)\ \text{cal}_{\text{th}}\ \text{mole}^{-1}$ $= 23045(1)\ \text{cal}_{\text{IT}}\ \text{mole}^{-1}$
1 amu	$= 931.478(5)$ MeV
Proton mass	$= 938.256(5)$ MeV
Neutron mass	$= 939.550(5)$ MeV
Electron mass	$= 511006(2)$ eV
Rydberg	$= 2.17971(5) \times 10^{-11}$ erg $= 13.60535(13)$ eV
Gas constant, R_0	$= 8.31434 \times 10^{7}\ \text{erg mole}^{-1}\ \text{deg}^{-1}$ $= 0.082053\ \text{liter atm mole}^{-1}\ \text{deg}^{-1}$ $= 82.055\ \text{cm}^3\ \text{atm mole}^{-1}\ \text{deg}^{-1}$ $= 1.9872\ \text{cal}_{\text{th}}\ \text{mole}^{-1}\ \text{deg}^{-1}$ $= 1.9858\ \text{cal}_{\text{IT}}\ \text{mole}^{-1}\ \text{deg}^{-1}$
Standard volume of ideal gas V_0	$= 22413.6\ \text{cm}^3\ \text{mole}^{-1}$

Table XIX. Variance matrix and correlation coefficient matrix of 1963 adjustment. Variances are given, in units of (ppm)^2, on and below the major diagonal. Correlation coefficients are given in italics above the diagonal. Since there are in fact only three variables in the adjustment these matrices are degenerate and are only of rank 3.

	α	e	N	h	m	F
α	21	*0.96*	*−0.88*	*0.95*	*0.88*	0
e	62	199	*−0.93*	*0.99*	*0.97*	*−0.06*
N	−62	−204	240	*−0.93*	*−0.93*	*0.41*
h	104	336	−346	569	*0.98*	*−0.08*
m	62	212	−222	362	237	*−0.12*
F	0	−5	35	−10	−10	30

In the preceding sections we have made clear just what rejections of available data we have made before forming the final set of input equations for the 1963 adjustment. We have also given for each rejected item our reasons for these rejections which were of two kinds, (a) those based on doubts as to the reliability of the experimental method or the method of reducing and interpreting the data, and (b) those based on the outlying character of the item, i.e., its inconsistency relative to the general consensus of the total data available for adjustment. This leaves others who may wish to use our work free to judge whether or not we have chosen wisely, and to modify our results or form other least-squares adjustments which they may deem preferable.

In Tables XVII and XVIII we list a number of the more frequently useful constants and conversion factors which we have computed with the use of the least-squares adjusted output values of our 1963 adjustment. Wherever necessary, of course, these values are combined with the auxiliary constants of Table III. The uncertainties attached to all the numerics in Tables XVII and XVIII are the standard deviations computed from the variance matrix of Table XIX. As we have already explained, the output values of a least-squares adjustment, in general, have correlated error distributions. Therefore, when further numerical values are to be computed, using formulae (functions) which involve two or more of these output values, care must be taken to use the generalized formula of error propagation in computing the error of the function in question. Table XIX gives the variance matrix

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[178] The expectation value of R may also be computed. Its value is 0.92 and the standard deviation is 0.39.

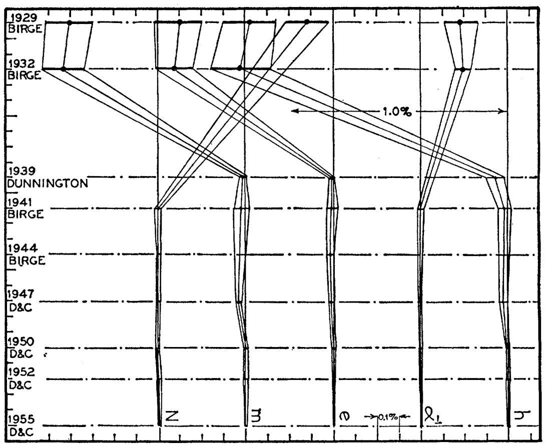

FIG. 8. History of our knowledge of h, α^{-1}, e, m, and N from 1929 to 1955.

and the correlation coefficient matrix appropriate to our 1963 least-squares adjustment. This table is the direct result of the least-squares adjustment based on its errors by the criterion of internal consistency, the criterion which in the present case yields the larger errors. The final adjustment had only three unknowns and a 3 by 3 matrix would therefore suffice but for greater convenience in use, in addition to the original three unknowns, α, e, N, we have augmented the matrix to include also h, m, F. Because, however, there are in fact only three statistically independent variables involved in the problem these matrices are degenerate and are only of rank 3.

3.3. Comparison of the 1963 Results with Previous Evaluations

We show in Figs. 8 and 9, a complete history of fluctuations in our knowledge of five of the fundamental constants over an interval of 34 years. The magnitudes of these fluctuations have changed in scale so enormously since the early work of R. T. Birge in 1929, when systematic errors of the order of one percent or larger were being found and eliminated, down to the present level of fluctuations of several parts per million, that it is necessary to depict the history of these fluctuations with two separate graphs with a scale change of 10 between them.

The principal changes in the input data for 1963 relative to 1955 which are responsible for the changes of approximately two standard deviations in most of the constants between these two dates, are (1) the much more accurate value of the Faraday published in 1960, (2) the much more accurate value of the gyromagnetic ratio of the proton (Bender and Driscoll) and the elimination of the systematically erroneous Thomas, Driscoll, and Hipple value of that constant, (3) the elimination of all of the x-ray data giving $N\Lambda^3$, and h/e data from the short-wavelength limit of the continuous x-ray spectrum.

3.4. Present Status of the Constants (1965)

With the publication of Bearden's "Table of X-Ray Wavelengths"[81] it is now possible to re-evaluate the x-ray data on the basis of a consistent definition of the x-unit. The available data of Table X has therefore been reconsidered in light of this and a series of additional least-squares adjustments were carried out in 1965. For this analysis we retained the deuterium fine-structure measurement and the muonium hyperfine-structure measurement (items 1b and 1d) from group 1. Item (1a) was rejected because of the theoretical uncertainties and because of its previously demonstrated inconsistency (admittedly a somewhat circular argument); item (1c), Wilkinson and Crane's measurement, was omitted because of its low weight and (1e) Robiscoe, because of its preliminary character and because, as a measurement of the fine-structure splitting, it must rely on the $P_{\frac{3}{2}}$–$S_{\frac{1}{2}}$ separation which is already included in the data in (1a). The inclusion of the muonium data (1b) requires that the magnetic moment of the muon or equivalently the relative mass of the muon be also considered. Thus, our calculation must now include five variables (α, e, N, Λ, and m_μ).

The purpose of the calculation was to try to distinguish between certain discrepancies in the data. Thus, the data on the magnetic moment of the proton fall into two groups. The important question to be answered is whether the high value, characterized by

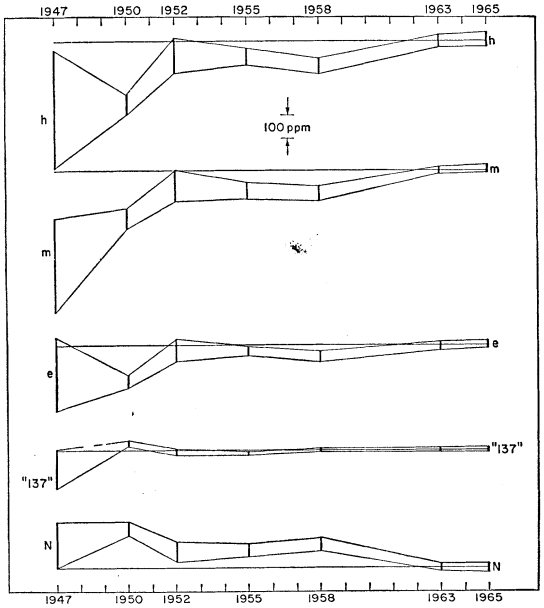

FIG. 9. History of our knowledge of h, α^{-1}, e, m, and N from 1947 to 1965.

either Boyne and Franken or by Mamyrin and Frantsuzov or the low value characterized by either Sommer *et al.* or by Sanders *et al.* is the more nearly correct. We therefore introduced these four items into the least-squares adjustment as two separate equations, one representing the "high" data (2.792880 ± 0.00003), the other representing the "low" data (2.792763 ± 0.00003).

Similarly, because of the good agreement between items 4a, b, c on the gyromagnetic ratio of the proton only a single equation was written to represent the average value of all three measurements. The less precise data (4d and 4e) were omitted.

The measurement of the Faraday (group 3) was introduced without further modification.

From group 5 (the conversion factor from x-units to milliangstroms) we kept only Edlen and Svensson's re-evaluation of Tyren's 1940 measurements and Bearden's re-evaluation of his own 1931 data.

Of the various measurements of the Siegbahn Avogadro constant ($N\Lambda^3$) we include 6c (Bearden's very thorough and careful measurements on $CaCO_3$) and 6d (Bearden and Henin's measurements on Si). We have also Smakula's measurements of several crystals as reported in Table V but with Straumanis' high LiF data omitted. Smakula's data only yields $N\Lambda^3 = 6060.08 \pm 0.11 \times 10^{20}$ on the basis of λ Cu $K\alpha_1 = 1537.396$; when this is reduced to the W $K\alpha_1$ standard (λ Cu $K\alpha_1 = 1537.370$) we obtain

$$N\Lambda^3 = 6060.38 \pm 0.11 \times 10^{20}$$

$$(\text{Smakula, Cu } K\alpha_1 = 1537.370).$$

Bearden's measurement is worth special notice here. A careful study was made of the impurity content of the calcite crystals and correlated density measurements of the crystals with chemical determinations of various metallic impurities. Bearden was able to demonstrate with reasonable accuracy that metallic impurities are predominantly interstitial in the calcite crystal. All of the crystal samples could then be extrapolated to the density of pure calcite (one could equivalently also use the measured density of the crystal, but correct the molecular weight for the measured impurity content).

From this data we then constructed 16 equations in 5 unknowns. The value of chi squared for this system was $\chi^2 = 24.18$. For 11 degrees of freedom this gives $R = 1.48$, and the statistical tables tell us that the probability of a value as large or larger than this is only slightly larger than 1%. If we successively delete items we find that no deletion except the "high" proton moment (Boyne and Franken, and Mamyrin and Frantsuzov) decreases chi squared below 18.8. With the "high" moment equation deleted, however, we obtain a chi-squared value of 12.71 so that, for 10 degrees of freedom, we have $R = 1.075$. The values of the constants computed for this case are in excellent agreement with the 1963 adjustment. The differences are in all cases less than one-third of a standard deviation. This is not at all surprising; the main effect of this adjustment is the determination of the value of the conversion factor Λ since as we pointed out earlier the "traditional" determination of Avogadro's number is less precise than the value determined from nuclear resonance data. The inclusion of the x-ray data then gives

$$\Lambda = 1.002080 \pm 0.000006 \ (\text{W } K\alpha_1 = 208.5770 \ x\text{-units}).$$

One of the primary reasons for the current interest in a least-squares analysis only two years after a similar study is to attempt to clarify the uncertainties surrounding the value of the fine-structure constant. If therefore we perform a least-squares adjustment which deletes from consideration the three so-called "direct" measurements of the fine structure constant, that is, the fine-structure separation in deuterium, the hyperfine structure in hydrogen and the hyperfine structure in muonium, we can achieve a least-squares adjustment of the constants which yields

$$\alpha^{-1} = 137.0367 \pm 0.0022,$$

$$\Lambda = 1.002093 \pm 0.000015.$$

This value of α falls between the deuterium fine-structure and the hydrogen hyperfine-structure values and agrees well with the earlier value reported by Hughes *et al.* from muonium hfs[137] shown in Fig. 6, although of course Hughes' later value presumably supercedes the earlier one. It should not be inferred that this calculation implies that the muonium fine-structure measurement is the more nearly correct, since the experimental uncertainties are such that the standard deviation interval overlaps the values of all these determinations.

The over-all picture of the values of the fundamental constants over the past eighteen years is shown in Fig. 9. This figure is an extension of Fig. 8, but, because of the increased precision which has been achieved in the last two decades as compared to the previous two, the scale of Fig. 9 has had to be enlarged by a factor of 10. The variations are expressed in terms of relative deviations from the "recommended" values of the 1963 adjustment[179] which are given here in Table XVII. The values for 1965 shown here include all of the data discussed in the preceding paragraphs. If the direct fine-structure data is omitted, the value of α^{-1} is decreased by 15 ppm, but the standard deviation increases from 5 ppm to 16 ppm. Similarly, e and m are increased 44±50 ppm relative to the 1963 values and

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[179] A. G. McNish, Natl. Bur. Std. Tech. News Bull. (October 1963), p. 175; J. Opt. Soc. Am. **54,** 281 (1964); Phys. Today **17,** 48 (1964).

N is decreased by almost exactly the same amount. Planck's constant h is increased 71 ppm above the "recommended" value, but here also the standard deviation increases from 25 to 84 ppm so that all the variations still lie within the assigned error range.

We may therefore conclude that the 1963 "recommendation" need not be altered by the newer data which have become available in the last two years and that the uncertainties in our knowledge of the fundamental constants are smaller than they have been in the past. Errors and discrepancies indeed still exist, but these are inevitable and will serve as the basis on which to improve experimental techniques and theoretical descriptions.

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