Analysis of Variance of the 1952 Data on the Atomic Constants and a New Adjustment, 1955*

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The 1952 data used by DuMond and Cohen in an evaluation of the atomic constants are analyzed for the presence of systematic errors by a variance analysis performed by an electronic digital computer. For simplicity the velocity of light is treated as a fixed constant of known value and there remain then eleven linear equations in four unknowns subject to least-squares adjustment. Least-squares adjustments of 219 over-determined subsets of these equations have been made and χ^2 has been evaluated for each such subset. An analysis of these data indicates that small systematic errors are most likely to exist in the following input data: (1) The determination of the Faraday by the silver voltameter. (2) The determination of the cyclotron resonance frequency of the proton by the inverse cyclotron method of Bloch and Jeffreys. (3) Certain of the higher voltage determinations of h/e by the continuous x-ray quantum limit. In descending order of magnitude of discrepancy from the remaining data on the constants are the determinations of (a) Felt, Harris, and DuMond made at 24 500 volts, (b) Bearden and Schwarz at 19 600 volts,

(c) Bearden and Schwarz and also Bearden, Johnson, and Watts in the region between about 10 kv and about 6 kv. An analysis of the various observations taken by these observers at different voltages reveals a possible systematic trend when discrepancy is plotted against either voltage or window width in volts. Conjectures to account for the effect are discussed.

The modifications called for by this analysis yield a new 1955 adjustment in which χ^2 is smaller than it was for the November, 1952 adjustment. The new $\chi^2=3.25$ is satisfactorily close to its expected value, 3. Thanks to the fact that the error measures adopted in the November, 1952 adjustment for the output values were conservatively based on the criterion of external consistency, the changes in the values occasioned as a result of the present analysis are all well within those estimated limits. A welcome effect of this new adjustment is that the adjusted output value of λ_g/λ_s, the conversion factor from Siegbahn's x-units to milli-angstroms, now lies much closer to the input value. A new table of constants and conversion factors is presented.

I. INTRODUCTION

IN an article[1] published in 1953 (herein designated as DC 53) two of us, from carefully selected high precision measurements of quantities related to the atomic constants, formed an over-determined set of 13 equations in the following five unknowns; the fine-structure constant, α, the velocity of light, c, the electronic charge, e, Avogadro's number N, and the conversion factor, λ_g/λ_s, from x-units (Siegbahn) to milli-angstroms. By the method of least squares this set was then solved for the "best" values of these unknowns. In that paper it was noted that χ^2, the measure of the incompatibility of such an over-determined set of equations, turned out to be considerably larger than its expected value which is just the number of degrees of freedom of the set, namely eight. This could as stated at that time, be ascribed either to the estimated error measures of the input data having been chosen too small or to the presence of unsuspected systematic errors in certain of the input data. In DC 53, in addition to the complete set of 13 equations, three subsets called Cases II, III, and IV (see Table III, page 702 of that paper) were also subjected to least-squares analysis. In these subsets different groups of the equations were omitted to see if such omissions might yield values of χ^2 more nearly in line with statistical expecta-

tion. No very conclusive evidence of systematic error could be drawn from these groups, but it was realized that this exploration of the consistency measures of subgroups was very far from being exhaustive. At that time the labor of performing a completely exhaustive survey of χ^2 for all possible over-determined subsets of the 13 equations would have delayed the publication of the results unduly. For this reason the measure used to fix the standard deviations of all of the output values in DC 53 was based on external rather than internal consistency so as to reflect in the error measures the incompatibility of the 13 equations on which the adjusted values were based.

We have not been satisfied however with this compromise and have felt that further efforts should be made to uncover, if possible, evidence for systematic errors in some of the data of the 13 equations which were used in DC 53. It was decided therefore to attack the problem by a form of analysis of variance. In such an analysis a large number of overdetermined subsets are subjected to least-squares adjustment and χ^2 is determined for each. Inspection of these data may then lead to the desired clues regarding the where-abouts of systematic errors.

Least-squares adjustments are very laborious, particularly if they are carried through to an evaluation of χ^2. The task of making an exhaustive exploration of all of the significant subsets of the 13 observational equations of DC 53 and obtaining a value of χ^2 for each

would be prohibitive by hand. Digital computers are on the other hand well adapted to just such work.

In order to minimize the expense both for programming and for time on the computer it was decided to eliminate one unknown, the velocity of light, c, from the least-squares adjustment treating this quantity instead as a fixed known auxiliary constant. Reference to Table IV, page 704 of DC 53, giving the error matrix and the matrix of correlation coefficients, shows that c is much more weakly correlated to the other unknowns than any of the rest and its retention in the variance analysis would therefore have been expensive and practically valueless.

II. THE MEASURE OF CONSISTENCY, χ^2

As explained in DC 53 the experimental data comprising the measured values of some 14 physical quantities, six of which are so accurately known as to be appropriately treated as auxiliary fixed constants, are combined to form 13 equations [(8.1) to (8.13), page 701] in the five primary unknowns α, c, e, N, and λ. ($\lambda = \lambda_g/\lambda_s$, the conversion factor between x-units in Siegbahn's scale and milliangstrom units.) Each of these equations is of the form of a simple product of powers of the primary unknowns

$$\alpha^i c^j e^k \cdots = A(1-r) \qquad (1)$$

equated to A, the numeric which results from the physical measurement. If we were to put true values of the variables, α, c, e, etc., into the left-hand side of this equation we would, in general, not obtain the number, A, since it is the result of measurement and therefore subject to error. We must include the factor $(1-r)$ in order that the equation shall be valid. The quantity, r, is the actual relative error in the measured quantity, A, and is, of course, beyond our ken. Let there be n equations of the type (1) above, each with its exponents i_μ, j_μ, etc., its numeric A_μ, and its relative error r_μ. As explained in DC 53, the theory of least squares leads to the conclusion that if the error distributions for the various physical measurements, A_μ, are Gaussian and have estimated standard deviations (root-mean-square deviations), σ_μ, the best choice for the set of r_μ, i.e., that set whose probability of occurrence is maximum, is the choice which minimizes the sum

$$Q = \sum_{\mu=1}^{n} \frac{r_\mu^2}{\sigma_\mu^2}. \qquad (2)$$

This is the "least-squares" condition: The n equations (1) can be thought of as solved for the residues, r_μ, written as functions of the unknowns α, c, e, etc., and we seek that set of values for the unknowns which minimizes the sum of the squares of the quotients of each residual divided by its standard deviation.

If the distributions of the errors of measurement are other than Gaussian the condition of Maximum Likelihood as expressed above is too specialized, but it has

been shown[2] that independent of any assumptions about the shapes of the distribution curves of errors save only that the standard deviations, σ_μ, exist (i.e., are finite) in each case, the least-squares condition (2) above is equivalent to the condition that the resultant solution shall be that set which has minimum root-mean-square deviations.

For convenience in effecting the least-squares adjustment, the system of equations of type (1) is "linearized." We adopt origin values α_0, c_0, e_0, etc., which have been chosen sufficiently close to our expected solution that any set of values α, c, e, etc., in which we are likely to be interested will differ from these individual origin values by only small relative amounts; that is α_0, c_0, e_0 are so chosen that $x_\alpha = (\alpha - \alpha_0)/\alpha_0$, $x_c = c - c_0/c_0 \cdots$ are always small, and we then express the experimental measurements in terms of these dimensionless variables x_α, x_c, x_e, etc. To each type of experimental determination of a function such as Eq. (1) there corresponds a hyperplane

$$i_\mu x_\alpha + j_\mu x_c + k_\mu x_e + \cdots = a_\mu - r_\mu, \qquad (3)$$

which is tangent to the curved surface typified by Eq. (1). The constant, a_μ, is defined as $(A_\mu - A_{\mu 0})/A_{\mu 0}$, in which $A_{\mu 0}$ is the value of the function (1) when the origin values α_0, c_0, e_0, etc., are inserted in the left member. The orientation of this plane in the hyperspace depends on the exponents i_μ, j_μ, $k_\mu \cdots$ of (1) i.e., on the coefficients i_μ, j_μ, k_μ of (3), while the origin distance of the plane depends on a_μ. The entire status of our knowledge regarding the "best" values of α, c, e, etc., to fit the data is contained in the way these various planes intersect each other to define some compromise point, taking into consideration the relative reliability of the positioning of each plane, i.e., the magnitude of the standardard error σ_μ. The function, Q, of Eq. (2) which is to be minimized is an expression of the second degree in the variables x_α, x_c, x_e, etc., and the minimum condition is obtained by equating to zero each of the partial derivatives of Q taken with respect to each variable in turn. It is easy to show that this process is equivalent to the following simple recipe for forming the so-called "normal equations": Write down the system of n observational equations, (1), omitting the residue, r_μ, in each case. Assign to each equation a weight

$$p_\mu = C/\sigma_\mu^2, \qquad (4)$$

where the constant C may have any convenient numerical value. To obtain the normal equation for a given variable (i.e., the one which expresses the condition that the partial derivative of Q with respect to that variable shall vanish), multiply each of the linearized observational equations (with r_μ omitted) by the coeffi-

[2] E. R. Cohen, Revs. Modern Phys. **25**, 709 (1953); E. Whittaker and G. Robinson, *Calculus of Observations* (Blackie and Sons, Ltd.), fourth edition, p. 224; R. L. Plackett [Biometrika **36**, 458 (1949)] has traced the origins of the generalized theorem of least squares for non-normal distributions to Gauss, Laplace, and Markoff.

cient of the variable in question in that equation and by the weight assigned to that equation and add these individual expressions together to give a single "normal" equation. Repeat for each variable, and in this way construct a set of q simultaneous equations for the q unknown quantities, x_α, x_c, x_e etc.

The solution is completed by inserting the values obtained for the x's into the original set of observational equations and finding the associated residuals; the values of the residuals computed using the solution of the normal equations we shall denote as R_μ (a number) to be distinguished from r_μ which is a function of the unknowns x_α, x_c, $x_e \cdots$. The minimum value of the quadratic expression Q, Eq. (2), is χ^2, the measure of consistency of the set of n observational equations. χ^2 now can be computed.

$$\chi^2 = \sum (R_\mu^2/\sigma_\mu^2). \tag{5}$$

The expectation value of χ^2 is $n-q$. This difference $n-q$ is called the number of "degrees of freedom" of the over-determined set of observational equations. Thus, taking as an example the set of 13 linearized observational equations in five unknowns which formed the basic data of DC 53 [designated as Eqs. (8.14) to (8.26), page 702 of that paper] the value of χ^2 for the set was 52.1 while the expected value was $13-5=8$. The ratio $r_e/r_i = [\chi^2/(n-q)]^{\frac{1}{2}}$ is the generalization to multi-dimensional space of R. T. Birge's[3] ratio of the measures of external and internal consistency. In the above example r_e/r_i was 2.55. This means that the error measures to be associated with the least-squares adjusted output values of x_α, x_c, x_e etc., must be scaled up, from the expected a priori values which one would assign to them calculated on the basis of the estimated σ_μ's of the input quantities, a_μ, by this factor r_e/r_i in order to reflect the incompatibility of the observational equations with each other. If r_e/r_i is significantly greater than unity this can mean either that the estimated σ_μ's of the input data were chosen too small or that the input data contain systematic errors.

The method of computing the error measures and correlation coefficients of the output x's from the inverse of the normal equation matrix is explained in detail in DC 53 (Sec. 4) and will therefore not be repeated here.

R. A. Fisher has tabulated[4] the values for which the probability, ϵ, that χ^2 shall be greater than, or equal to, χ_0^2 takes particular values $\epsilon=0.99$, $0.98\cdots0.001$ for different numbers of degrees of freedom, $m=1$, $2\cdots30$. This table is reproduced here for the first eight degrees of freedom (see Table I).

Reference to this table shows that the probability of getting χ^2 as great as or greater than 52.1 for the case of 8 degrees of freedom is less than 0.001.

The object of our analysis was then to determine χ^2 for a large number of significant subsets of the equations

[3] R. T. Birge, Phys. Rev. 40, 213 (1932).
[4] See Table XIV in Fisher's Statistical Methods for Research Workers (Oliver & Boyd Ltd., Edinburgh).

TABLE I. Values of χ^2 as function of ϵ and m.[a]

Degrees of freedom m	0.99	0.98	0.95	ϵ 0.90	0.80	0.70	0.50
				χ_0^2			
1	0.000	0.001	0.004	0.016	0.064	0.148	0.455
2	0.020	0.040	0.103	0.211	0.446	0.713	1.386
3	0.115	0.185	0.352	0.584	1.005	1.424	2.366
4	0.297	0.429	0.711	1.064	1.649	2.195	3.357
5	0.554	0.752	1.145	1.610	2.343	3.000	4.351
6	0.872	1.134	1.635	2.204	3.070	3.828	5.348
7	1.239	1.564	2.167	2.833	3.822	4.671	6.346
8	1.646	2.032	2.733	3.490	4.594	5.527	7.344

Degrees of freedom m	0.30	0.20	0.10	ϵ 0.05	0.02	0.01	0.001
				χ_0^2			
1	1.074	1.642	2.706	3.841	5.412	6.635	10.827
2	2.408	3.219	4.605	5.991	7.824	9.210	13.815
3	3.665	4.642	6.251	7.815	9.837	11.341	16.268
4	4.878	5.989	7.779	9.488	11.668	13.277	18.465
5	6.064	7.289	9.236	11.070	13.388	15.086	20.517
6	7.231	8.558	10.645	12.592	15.033	16.812	22.457
7	8.383	9.803	12.017	14.067	16.622	18.475	24.322
8	9.524	11.030	13.362	15.507	18.168	20.090	26.125

[a] Table I is abridged from Table III of Fisher: "Statistical Methods for Research Workers," published by Oliver and Boyd, Ltd., Edinburgh, by permission of the author and publishers.

of observation. Since the number of subsets is large, it seemed desirable to plan the work in such a way that the digital computer would automatically explore the subsets according to prearranged rules. We shall now explain briefly what equations were used, how they were coded, and the manner in which the computer program was carried out.

III. SETUP OF THE SYSTEM OF EQUATIONS FOR THE ANALYSIS OF VARIANCE

The 13 linearized equations of observation (8.14) to (8.26) in DC 53 (page 702) are written in five unknowns x_1 to x_3 which correspond in the order named to the primitive variables, α, c, e, N, and $\lambda(\lambda=\lambda_g/\lambda_s)$. We drop Eqs. (8.14) and (8.15) and substitute a fixed value for x_2, namely

$$x_2 = 9.98 \pm 1.0 \text{ (ppm)}. \tag{6}$$

This is the unknown which corresponds to the velocity of light and the value here chosen corresponds to fixing that velocity at

$$c = 299793.0 \pm 0.3 \text{ km sec}^{-1} \tag{7}$$

in accord with results obtained by Bergstrand and also by Froome. This leaves us with a set of 11 equations in 4 unknowns corresponding to the primitive variables α, e, N, and λ. In the present paper we shall designate the linearized unknowns with symbols x_1 to x_4 defined as follows:

$$\alpha = \alpha_0(1+10^{-5}x_1); \quad \alpha_0 = 0.007297000 \tag{8}$$

$$e = e_0(1+10^{-5}x_2); \quad e_0 = 4.802200 \times 10^{-10} \tag{9}$$

$$N = N_0(1+10^{-5}x_3); \quad N_0 = 0.6025000 \times 10^{24} \tag{10}$$

$$\lambda = \lambda_0(1+10^{-5}x_4); \quad \lambda_0 = 1.0020200. \tag{11}$$

TABLE II. Observational equations, sources of data and coding numbers.

Kind number	Equation serial number	Equation (The x's are parts in 10^{5})	Weight	Description of experimental source	Eq. ref. DC 53
0	1	$x_4 = 0$	0.11	$\lambda_g/\lambda_s = 1.002020$	(6.8)
1	1	$x_3 + 3x_4 = 3.5$	0.07	$N\lambda^3$ (Birge's average)	(6.12)
2	1	$x_1 \quad\quad = 4.0$	4.92	Dayhoff fine structure splitting in deuterium	(6.13)
3	1	$3x_1 - x_2 \quad = -2.3$	0.19	Thomas, Driscoll, and Hipple, gyromagn. ratio of proton	(6.7)
4	1	$x_2 + x_3 = 11.1$	0.58	Iodine ⎫ Faraday by electrochemistry	(6.3)
4	2	$x_2 + x_3 = 2.2$	0.25	Silver ⎭	(6.4)
5	1	$-3x_1 + 2x_2 + x_3 = 24.9$	0.08	Bloch and Jeffries, inverse cycl. ⎫ Mag. mom. of proton	(6.5)
5	2	$-3x_1 + 2x_2 + x_3 = 13.5$	0.83	Sommer, Thomas, and ⎬ Hipple, omegatron ⎭	(6.6)
6	1	$-x_1 + x_2 \quad - x_4 = -11.6$	0.04	Felt, Harris, and DuMond ⎫ Short wavelength	(6.9)
6	2	$-x_1 + x_2 \quad - x_4 = -3.4$	0.06	Bearden, Johnson, and Watts ⎬ limit of continuous	(6.10)
6	3	$-x_1 + x_2 \quad - x_4 = -5.6$	0.015	Bearden and Schwarz ⎭ x-ray spectrum	(6.11)

These x's must not be confused with those of DC 53 both because the subscripts are differently associated with the primitive unknowns, and because these new x's represent relative deviations from the origin values in parts per hundred thousand instead of parts per million.

In Table II we show the 11 equations in four unknowns which form the object of our analysis of variance. The equations are grouped into "kinds," each kind of equation determining a particular linear combination of the unknowns. At the left appear two code numbers which label these equations as follows: The first column gives the code number designating the "kind" of equation. When there is more than one equation of a given kind these are distinguished from each other by a second code number appearing in the second column. It will be noted that there is only one equation of each of the first four kinds. There are two equations belonging to each of the next two kinds; and the last kind has three equations. In Table II on the right of each observational equation the experiment which yielded the corresponding information is briefly described. (In almost every equation other experimental measurements of much higher accuracy than the one named may also have been involved in determining the numeric, but the one named is in each case the only one which contributes materially to the estimated uncertainty of that equation.) On the extreme right in Table II appears the equation number as it appeared in DC 53. The reader is referred to these equation numbers in that article for a fuller discussion of the sources of data and references to the original articles.

The primary purpose of the entire investigation is, of course, to try to select a subset of the equations of Table II from which the most reliable adjusted values of the four unknowns can be deduced. Let us call this our A objective. A common sense approach would then be to search for a subset, which determines all four unknowns and whose χ^2 is the smallest. Care must be taken in evaluating the significance of these values of χ^2 since they are computed from sets which have been specially selected and not randomly chosen. Thus, it is not strictly correct to use Fisher's table (Table I) to evaluate the probability of an observed value of χ^2 for these sets, but one would tend to give more weight to the sets with the greatest number of degrees of freedom because such sets repose on a broader experimental base.

A closely related secondary objective is to try to locate which, if any, of the 11 equations of Table II are likely to have systematic errors. We shall call this our B objective. One way of doing this is to examine those subsets whose χ^2's are much larger than the expected value to see if the presence of certain equations in such sets and their absence in other sets with smaller χ^2's may be used as evidence that those equations have systematic errors. A still better way (which we shall call the "method of increments to χ^2") is to make an exhaustive investigation of the effect on χ^2 of adding a specified equation to each and every subset not already containing that equation. The new subset will have one more degree of freedom than the original one but, if the new χ^2 exceeds that of the old subset by much more than unity, one has an indication that the equation so added may contain a systematic error, or that its accuracy has in some other way been overestimated.

For the present analysis of variance, 219 subsets of the equations listed in Table II were selected and the χ^2 was determined for each. The selection rules for the first 171 subsets were chosen with the A objective chiefly in mind and with the idea of economizing on computing machine time. The following were the rules for selection of these subsets:

(a) Not more than one equation of any one kind should be included in any one set, and (b) with this restriction, all sets should be examined which over-determine all the unknowns. The first 171 subsets examined, Tables III, IV, and V exhaust all the possibilities under these rules of selection. Admittedly this is not an exhaustive or complete analysis of variance however since (a) it omits all over-determined subsets containing two or more equations of the same kind which were excluded under the (a) selection rule, and

(b) the form of the equations in Table II is such that certain over-determined subsets exist which do not over-determine all four unknowns. [Table V(a) lists 48 subsets of this latter type.] Before discussing the reason for adopting these selection rules we shall first explain the symbols used to identify particular subsets because this terminology facilitates the discussion.

The computer symbol used for identifying a particular subset of the equations of Table II is a number with one digit for each kind of equation. Each digit is the serial number of the equation of the corresponding kind included in the set, the *position* of the digit indicating the kind number. A zero in any position means that that kind has been omitted altogether. The set symbol 1110203 thus indicates inclusion in the set of the first equations of kinds 0, 1, and 2, omission of kind 3, inclusion of the second equation of kind 4, omission of kind 5, and inclusion of the third equation of kind 6. It is also convenient to designate groups of sets according to the *kinds* of equations excluded or included without specific reference to which equation of any given kind is to be selected. Thus the set with symbol 1110203 belongs to the group designated by the group symbol [1110101].

Consider now the rule that not more than one equation of any one kind should be included in the subsets to be examined. We can examine all the subsets satisfying this rule and belonging to a specified group, for example the group [1110111]. There will surely be one of these subsets whose χ^2 is the smallest, say the set 1110123. As far as our A objective is concerned, once we have found this subset there seems little information of value likely to be gained by considering subsets in which one or more additional equations of any one of the kinds are added since such subsets will surely have greater χ^2. Such subsets must however be considered if we are to apply the method of increments to χ^2 exhaustively.

The restriction (b) to examine (subject to the first selection rule) only those sets which determine all of the unknowns eliminates from consideration certain degenerate subsets. This restriction was also obviously framed with reference to our A objective.

After the calculations of χ^2's for the 171 selected subsets were completed, Professor John Tukey of Princeton University (to whom we are much indebted for valuable advice and guidance) pointed out that the B objective would be best served by accumulating as much statistical evidence as possible for or against the likelihood of systematic error in any given equation of Table II. To do this quite exhaustively by examining the increments in χ^2 resulting from the addition of a given equation to *all* subsets, we should have evaluated χ^2 for many subsets which we had not considered.

Fortunately however the evidence we have obtained, though admittedly only partial, seems quite sufficiently clear-cut to satisfy both A and B objectives.

IV. METHODS WITH DIGITAL COMPUTER

The major calculations described in this paper were carried out on the Electrodata Datatron digital computer. The program was designed to carry out least-squares adjustments on sets of linear equations in either four or five unknowns, and to derive χ^2 for the adjusted values. The normal equations were solved by inverting the (real symmetric) normal matrix, C, using the Gauss-Doolittle method given by Dwyer (1951).[5] The unknowns $x_1 \cdots x_4$ which we shall symbolize with the vector, $\mathbf{x}$, were then obtained by solving

$$C^{-1} \cdot \mathbf{k} = \mathbf{x}_0, \tag{12}$$

where $\mathbf{k}$ is the "normal vector" consisting of the numerical constants forming the right-hand members of the normal equations. The precision of $\mathbf{x}_0$ was improved by iterating:

$$\Delta \mathbf{k}_i = k - C \cdot \mathbf{x}_i \tag{13}$$

$$\mathbf{x}_{i+1} - \mathbf{x}_i = C^{-1} \cdot \Delta \mathbf{k}_i. \tag{14}$$

In general two cycles of iteration reduced all elements of $\Delta \mathbf{k}_i$ to less than the tolerance of 0.0001. (For both the x's and the k's one unit represents a relative deviation from the origin value of 1 part in 10^5.)

It was found to be economical to compute χ^2 from χ_0^2, the sum of normalized residues for $x=0$, by using

$$\chi^2 = \chi_0^2 - \mathbf{k} \cdot \mathbf{x}. \tag{15}$$

Provision was made so that all of C, $\mathbf{k}$, C^{-1}, and $\mathbf{x}$ could, if desired, be printed as they were obtained so that the adjusted values, variances and covariances of the unknowns could be found for any set of equations. In a survey of a large number of sets, however, this printing was omitted because it would have required 30 seconds for each set as against 12 seconds for the calculations and for printing χ^2 with the group of digits identifying the set.

A great deal of preliminary labor was eliminated by preparing, not a detailed list of equations for each set, but the single list of 11 equations of Table II and building into the program means by which sets would be selected automatically according to the prearranged selection rules (a) and (b) explained in the last section.

A list was prepared by hand, giving all sets of kinds (i.e., all "groups") of equations satisfying the selection rule (b), namely the sets must over-determine all the unknowns. For each set of kinds the machine generated all the sets of equations required and calculated χ^2 for each set as it was generated, printing only the set symbol and the value of χ^2. The more interesting of these cases, as judged by examining the χ^2's were then reexamined in greater detail. Provision was made for a slight modification in the program so that the machine would calculate for a hand-prepared list of particular sets of equations (the interesting ones to be reexamined)

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[5] P. S. Dwyer, *Linear Computations* (John Wiley and Sons, Inc., New York, 1951), p. 191.
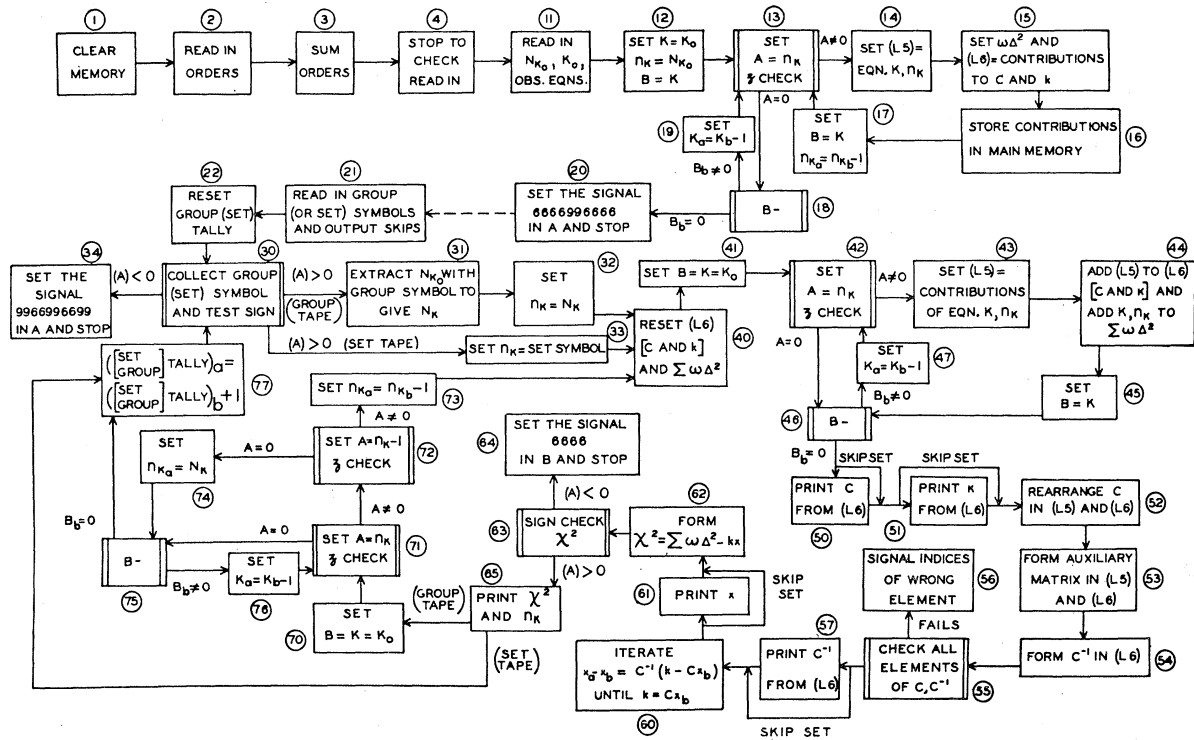
FIG. 1. Block diagram of the steps in machine computations of χ^2. It will be noted that certain operations of printing can be bypassed, see blocks 50, 51, 57, 61. This was done to save computer time on the first exploratory run in which only the set symbol and χ^2 were printed for each set. Later the more interesting sets, as judged by the χ^2's, could be printed out in full detail as regards the C and C^{-1} matrices and the $\mathbf{k}$ and $\mathbf{x}$ vectors.

all the pertinent data and print the complete results: normal matrix, normal vector, inverse matrix, adjusted values of the unknowns, χ^2, and set symbol.

As already stated, χ^2 was computed and printed for 171 sets, covering all cases under selection rules (a) and (b). From these, 26 sets were selected for recomputation with complete printing out of all details. At a later date the 48 additional sets of Table V(a) were computed. These are the sets which, though over-determined, fail to over-determine all four unknowns.

The entire work of checking the code to be fed into the machine, as well as performing the calculations for the first 171 sets, examining the χ^2's for the interesting

TABLE III. Equations in 3 degrees of freedom.

χ^2	Designation of Eq. set
13.71	1111223
19.34	1111222
26.91	1111221
25.21	1111213
30.66	1111212
38.14	1111211
03.25	1111123
07.71	1111122
15.01	1111121
11.29	1111113
17.33	1111112
24.92	1111111

cases, and recalculating and printing the details occupied somewhat less than a "block" of time (6 hours). The net time expended in calculation and printing was only a little over one hour.

A full account of the computer program, including the complete code and a detailed flow sheet is given in a Special Technical (A.E.C) Report [No. 18, Contract AT(04–3)–63] now available for private circulation. We reproduce here in Fig. 1 a block diagram of the steps in machine computation. The code is designed for the use of anyone wishing to perform similar variance analyses in as many as 50 equations of 10 kinds in 5 unknowns.

V. RESULTS OF THE VARIANCE ANALYSIS

Subject to the selection rules (a) and (b) the equations of Table II yielded 12 subsets of 3 degrees of freedom, 64 subsets of 2 degrees of freedom, and 95 subsets of 1 degree of freedom. We list here, in Tables III, IV, and V, the sets in 3, 2, and 1 degrees of freedom, respectively.

We shall abbreviate the words "degrees of freedom" with the symbol d.f. and shall refer to the χ^2's of a whole class of those sets containing a given kind of equation and a given equation of that kind by writing the kind number in parenthesis after the symbol χ^2 with the equation number as its subscript. Thus $\chi^2(6_3)$ refers to the class of all χ^2's of sets containing equation number (3)

TABLE IV. Equations in 2 degrees of freedom.

χ^2	Designation of Eq. set	χ^2	Designation of Eq. set	χ^2	Designation of Eq. set	χ^2	Designation of Eq. set
09.34	1110223	04.44	1111013	02.72	0111123	11.27	1011113
16.29	1110222	11.46	1111012	06.99	0111122	16.07	1011112
24.05	1110221	19.20	1111011	14.24	0111121	22.92	1011111
16.99	1110213	03.96	1111203	10.47	0111113	08.78	1101223
27.10	1110212	05.91	1111202	16.35	0111112	09.28	1101222
35.04	1110211	12.04	1111201	23.90	0111111	13.45	1101221
03.22	1110123	03.08	1111103	13.00	1011223	20.23	1101213
07.55	1110122	06.78	1111102	19.11	1011222	20.77	1101212
14.81	1110121	13.72	1111101	26.34	1011221	24.96	1101211
08.50	1110113	10.93	0111223	24.50	1011213	01.59	1101123
16.80	1110112	16.17	0111222	30.48	1011212	02.65	1101122
24.57	1110111	23.66	0111221	37.63	1011211	07.48	1101121
03.09	1111023	22.43	0111213	03.24	1011123	08.86	1101113
07.33	1111022	27.55	0111212	06.65	1011122	10.41	1101112
14.55	1111021	34.95	0111211	13.11	1011121	15.65	1101111
		10.33	1111220	00.44	1111120		
		21.75	1111210	07.52	1111110		

of the sixth kind (the last equation in Table II). Inspection of Table III shows that, in every 3 d.f. case,

$$\chi^2(6_3) < \chi^2(6_2) < \chi^2(6_1),$$

there being four such triplets for comparison. Exactly the same statement is true in every 2 d.f. case, there being among these 20 triplets for comparison. In the 1 d.f. cases the same statement can be made for 27 out of the 29 triplets. The remaining two exceptional triplets are listed in Table VI.

The evidence seems strong, therefore, that the third equation of kind 6 yields better consistency in nearly every instance than the second equation of this kind, and that the second equation of this kind yields better consistency than the first.

A similar inquiry as regards the two equations of kind 5 leads to the conclusion that, in all six cases of 3 d.f., all 29 cases of 2 d.f., and in 29 out of a total of 33 cases of 1 d.f., Eq. (5_2) yields lower χ^2 than Eq. (5_1). Also, as regards the two equations of kind (4), it appears that (4_1) gives lower χ^2 than (4_2) in all six cases of 3 d.f., in 24 cases out of 26 of 2 d.f., and in 15 cases out of 33 of 1 d.f. Tables VII and VIII show the few exceptions to the very strong trends we have described.

The evidence for the trend, $\chi^2(4_1) < \chi^2(4_2)$, is admittedly not quite as strong as for the other two trends because of the rather large number of exceptions (18) in the 1 d.f. cases. Of these 1 d.f. exceptions 15 are actual reversals of the trend and three are stalemates in which χ^2 is unchanged by going from Eq. (4_1) to Eq. (4_2). The trend is so strongly indicated in the 3 d.f. and 2 d.f. cases, to which we attach much more significance however, that we believe it is quite clearly indicated.

Having now arrived at the conclusion that, among

TABLE V. Equations in 1 degree of freedom.

χ^2	Designation of Eq. set	χ^2	Designation of Eq. set	χ^2	Designation of Eq. set	χ^2	Designation of Eq. set
02.17	1110023	07.58	1010223	05.25	1110220	00.36	1111020
04.73	1110022	16.21	1010222	10.25	1110210	00.17	1111010
11.08	1110021	23.80	1010221	00.43	1110120	01.60	0111203
04.42	1110013	14.15	1010213	02.82	1110110	03.40	0111202
10.09	1110012	26.99	1010212	03.08	1111003	09.42	0111201
17.35	1110011	34.80	1010211	05.89	1111002	02.63	0111103
00.00	1110203	03.22	1010123	11.94	1111001	06.26	0111102
00.05	1110202	06.45	1010122	0.271	0111023	13.19	0111101
00.49	1110201	12.79	1010121	06.89	0111022	03.08	1011203
00.70	1110103	08.26	1010113	14.10	0111021	05.89	1011202
00.70	1110102	15.56	1010112	04.34	0111013	11.94	1011201
02.97	1110101	22.70	1010111	11.45	0111012	03.08	1011103
04.01	0110223	00.87	1100223	19.19	0111011	05.89	1011102
10.81	0110222	01.21	1100222	03.08	1011023	11.94	1011101
18.55	0110221	05.12	1100221	05.89	1011022	00.35	1101203
07.93	0110213	01.80	1100213	11.94	1011021	00.31	1101202
19.96	0110212	03.00	1100212	03.08	1011013	03.08	1101201
27.99	0110211	07.92	1100211	05.89	1011012	01.56	1101103
02.72	0110123	01.59	1100123	11.94	1011011	02.54	1101102
06.93	0110122	02.64	1100122	01.58	1101023	07.27	1101101
14.15	0110121	07.48	1100121	02.60	1101022	02.27	1111200
06.13	0110113	02.78	1100113	07.36	1101021	00.42	1111100
15.12	0110112	05.06	1100112	04.13	1101013		
22.96	0110111	10.76	1100111	07.46	1101012		
				13.52	1101011		

TABLE V(a). χ^2 for additional sets violating selection rule (b).

07.73	0011223	07.73	1001223
07.73	0011222	07.73	1001222
07.73	0011221	07.73	1001221
19.12	0011213	19.12	1001213
19.12	0011212	19.12	1001212
19.12	0011211	19.12	1001211
00.00	0011123	00.00	1001123
00.00	0011122	00.00	1001122
00.00	0011121	00.00	1001121
06.78	0011113	06.78	1001113
06.78	0011112	06.78	1001112
06.78	0011111	06.78	1001111
07.73	0101223	07.73	0111220
07.73	0101222	19.12	0111210
07.73	0101221	00.00	0111120
19.12	0101213	06.78	0111110
19.12	0101212	07.73	1011220
19.12	0101211	19.12	1011210
00.00	0101123	00.00	1011120
00.00	0101122	06.78	1011110
00.00	0101121	07.73	1101220
06.78	0101113	19.12	1101210
06.78	0101112	00.00	1101120
06.78	0101111	06.78	1101110

the equations of kinds 4, 5, and 6, those which give almost invariably the lowest χ^2's are (4_1), (5_2), and (6_3), we now call attention to perhaps the most significant result of all which is the fact that, among the 12 sets of 3 d.f. in Table III (no kinds omitted), by far the best χ^2 is associated with the set 1111123. The expected value of χ^2 for all these sets is 3 and χ^2 (1111123) = 3.25 is in strikingly good agreement with this, whereas the χ^2 of all other 11 sets is much larger ranging from 7.71 to 38.14. Interpolation in Table I shows that the odds are about 35 to 65 for getting χ^2 in excess of this value, 3.25. It seems to us that this set, 1111123, is therefore a satisfactory answer to our A objective.

We cannot claim in this discussion to have made the most exhaustive possible efforts in the direction of our B objective, the accumulation of all possible evidence for or against the liklihood of systematic error being present in each of the 11 equations. To make such a complete search it would be desirable to explore the effect on χ^2 of adding each of the 11 equations in turn to all sets not already containing that equation, and our present computer program has not covered enough cases to permit this.

Table V(a) gives χ^2 for 48 interesting subsets of equations which are exceptions to selection rule (b) in that, although they are over-determined by 1 degree of freedom, none of them over-determines all the unknowns. This situation arises because the 48 sets of Table V(a) all contain equations of kinds 3, 4, and 5 which are not algebraically independent. These three

TABLE VI. Exceptions to the rule, $\chi^2(6_3) < \chi^2(6_2) < \chi^2(6_1)$.

$\chi^2(6_3)$	$\chi^2(6_2)$	$\chi^2(6_1)$
$\chi^2(1101203)=0.35$	$\chi^2(1101202)=0.31$	$\chi^2(1101201)=3.08$
$\chi^2(1110103)=0.70$	$\chi^2(1110102)=0.70$	$\chi^2(1110101)=2.97$

equations are of the following form:

$$3x_1 - x_2 = a_3$$
$$x_2 + x_3 = a_4$$
$$-3x_1 + 2x_2 + x_3 = a_5.$$

If we add the first and third equations and subtract the second the result is

$$0 = a_3 - a_4 + a_5,$$

and the numerical values of the a's will in general fail to satisfy this relationship.

We see from Table V(a) that the 48 sets can be grouped into four classes each characterized by a different value of χ^2, which is determined by the choice of the equations of kinds 4 and 5. Those sets which contain (4_1) and (5_1) yield $\chi^2 = 6.78$; those which contain (4_1) and (5_2) yield $\chi^2 = 00.00$ (more accurately this value is 0.00122); those which contain (4_2) and (5_1) yield $\chi^2 = 19.12$; and $(4_2,)$ (5_2) yield $\chi^2 = 7.73$. The explanation of this lies in the fact that from equations of the kinds 3, 4, and 5 we can only evaluate $3x_1 - x_2$ and $x_2 + x_4$ and we still need two other equations to complete a just-determinate solution for our four unknowns. Thus in all these

TABLE VII. Exceptions to the rule, $\chi^2(5_2) < \chi^2(5_1)$.

$\chi^2(5_2)$	$\chi^2(5_1)$
$\chi^2(1011023)= 3.08$	$\chi^2(1011013)= 3.08$
$\chi^2(1011022)= 5.89$	$\chi^2(1011012)= 5.89$
$\chi^2(1011021)=11.94$	$\chi^2(1011011)=11.94$
$\chi^2(1111020)=00.36$	$\chi^2(1111010)=00.17$

sets, which are 1 degree of freedom systems, the fourth and fifth equations (the ones beside 3, 4, and 5 which we choose) do not contribute to the over-determinateness. The χ^2 value is determined entirely by the consistency of the over-determined set of 3, 4, 5. If this triplet of equations were consistent, $a_3 - a_4 + a_5$ should be zero and hence the inconsistency is measured by the square of the residue $(a_3 - a_4 + a_5)^2$. If the standard deviations of the a's are σ_3, σ_4, and σ_5 then we have

$$\chi^2 = \frac{(a_3 - a_4 + a_5)^2}{\sigma_3^2 + \sigma_4^2 + \sigma_5^2}.$$

The very low value, χ^2 $(4_1,5_2) = 0.00122$ is a result of the excellent agreement between the following experimental values: The proton magnetic moment of Sommer, Thomas, and Hipple

$\mu' = 2.792685 \pm 0.000030$

(before diamagnetic correction),

the gyromagnetic ratio of the proton of Thomas, Driscoll, and Hipple

$$\gamma = 26752.3 \pm 0.6 \text{ sec}^{-1} \text{ gauss}^{-1},$$

the atomic mass of the proton (regarded in our analysis

as a fixed auxiliary constant)

$$M_p = 1.007593,$$

and the Faraday constant measured with the iodine coulometer of Vinal and Bates

$$F = 9652.15 \pm 0.13 \text{ emu (g mole)}^{-1} \text{ (physical scale)}.$$

The iodine value of F is to be compared with the value computed from γ, M_p and μ'

$$F = \gamma M_p / \mu' = 9652.16 \pm 0.25.$$

We thus have strong corroborative evidence that the iodine Faraday is more likely to be correct than the silver Faraday, and hence that Eq. (4_1) is to be preferred to Eq. (4_2).

If we now utilize our selected best set of equations, 1111123, we obtain the least-squares solution given in

TABLE VIII. Exceptions to the rule $\chi^2(4_1) < \chi^2(4_2)$.

$\chi^2(4_2)$	$\chi^2(4_1)$
2 degrees of freedom	
$\chi^2(1111202) = 5.91$	$\chi^2(1111102) = 6.78$
$\chi^2(1111201) = 12.04$	$\chi^2(1111101) = 13.72$
1 degree of freedom	
$\chi^2(1110203) = 0.00$	$\chi^2(1110103) = 0.70$
$\chi^2(1110202) = 0.05$	$\chi^2(1110102) = 0.70$
$\chi^2(1110201) = 0.49$	$\chi^2(1110101) = 2.97$
$\chi^2(1100223) = 0.87$	$\chi^2(1100123) = 1.59$
$\chi^2(1100222) = 1.21$	$\chi^2(1100122) = 2.64$
$\chi^2(1100221) = 5.12$	$\chi^2(1100121) = 7.48$
$\chi^2(1100213) = 1.80$	$\chi^2(1100113) = 2.78$
$\chi^2(1100212) = 3.00$	$\chi^2(1100112) = 5.06$
$\chi^2(1100211) = 7.92$	$\chi^2(1100111) = 10.76$
$\chi^2(0111203) = 1.60$	$\chi^2(0111103) = 2.63$
$\chi^2(0111202) = 3.40$	$\chi^2(0111102) = 6.26$
$\chi^2(0111201) = 9.42$	$\chi^2(0111101) = 13.19$
$\chi^2(1101203) = 0.35$	$\chi^2(1101103) = 1.56$
$\chi^2(1101202) = 0.31$	$\chi^2(1101102) = 2.54$
$\chi^2(1101201) = 3.08$	$\chi^2(1101101) = 7.27$
$\chi^2(1011203) = 3.08$	$\chi^2(1011103) = 3.08$
$\chi^2(1011202) = 5.89$	$\chi^2(1011102) = 5.89$
$\chi^2(1011201) = 11.94$	$\chi^2(1011101) = 11.94$

Table IX. The result, $\chi^2 = 3.25$, yields for the ratio of the scales of error by external and internal consistency the very satisfactory value

$$r_e/r_i = [\chi^2/(n-q)]^{\frac{1}{2}} = 1.04.$$

Table X lists the error elements by external consistency (which now differ insignificantly from those by internal consistency).

It is to be noted that the adjusted values of the unknowns yielded by this new adjustment differ from those of DC 53 by amounts which are entirely inside the standard error ranges of the 1953 adjustment. The new standard errors are however considerably smaller than those of DC 53.

VI. DISCUSSION OF THE REJECTED EQUATIONS

Possible Sources of Systematic Error

We have rejected from our new adjustment the equations (4_2), (5_1), (6_1), and (6_2) because of the strong

TABLE IX. Least-squares solution of the set 1111123.

L.S. adjusted values of linearized unknowns (in ppm)	L.S. adjusted values of primitive variables	Change in ppm from DC 53
$x_1 = 39.2$	$\alpha = 7.29728 \times 10^{-3}$	3
	$\alpha^{-1} = 137.0373$	-3
$x_2 = 137.2$	$e = 4.80286 \times 10^{-10}$ esu	-4.9
$x_3 = -23.7$	$N = 6.02486 \times 10^{23}$ (g mole)$^{-1}$ Phys.	22.3
$x_4 = 19.4$	$\lambda_g/\lambda_s = 1.002039$	-23.5

probability, which our variance analysis has raised, of their containing systematic errors. These equations correspond respectively to (4_2), the determination of the Faraday by the silver voltameter, (5_1), the measurement of the magnetic moment of the proton by the inverse cyclotron method of Bloch and Jeffreys, (6_1) the x-ray continuous spectrum quantum limit determination of the conversion constant from wavelengths in x-units (Siegbahn scale) to quantum energy in electron volts ("h/e" experiment) at 24.5 kv by Felt, Harris, and DuMond, and (6_2) the same experiment at 10 and 6 kev by Bearden, Johnson, and Watts.

The fact that the Faraday determinations by the electrolysis of iodine are in better accord with the consensus of the data on the atomic constants than are the Faraday determinations using silver has been realized and pointed out now for many years. The reason is still obscure. Both determinations were made long before the existence of isotopes was suspected. The fact that natural iodine is an isotopically pure substance while silver has two isotopes in nearly equal abundance has been often suggested as possibly having a bearing on this but the work at the U. S. National Bureau of Standards undertaken by Craig and Hoffman to clear up these questions seems so far to be inclusive. The discrepancy here is nearly four times the value to be expected from the estimated standard errors of the measurements.

The results of our analysis of variance indicate that the discrepancy of 114 ppm between the inverse cyclotron measurements at Stanford University by Bloch and Jeffreys and the "omegatron" measurements at the

TABLE X. Error elements by external consistency for 1111123.

	Error matrix, $v_{ij} = \sigma_i \sigma_j r_{ij}$ (in ppm^2)			
	α	e	N	λ_g/λ_s
α	21.52	62.50	-60.60	17.70
e	62.50	373.2	-480.0	139.6
N	-60.60	-480.0	726.0	-210.6
λ_g/λ_s	17.70	139.6	-210.6	204.2
	Standard errors σ_i (in ppm)			
	4.65	19.30	26.9	14.5
	Correlation coefficients r_{ij}			
α	1.000	0.697	-0.485	0.263
e	0.697	1.000	-0.922	0.500
N	-0.485	-0.922	1.000	-0.538
λ_g/λ_s	0.263	0.500	-0.538	1.000

TABLE XI. X-ray quantum limit determinations.

Experimenters	Nominal voltage	a (volts)	$hc^2/(e\lambda_g/\lambda_s)$	Discrepancy (ppm)	Discrepancy (volts)	Remarks
BJW[a]	6112	0.27	12370.8	-116	-0.7 ± 0.4	W target
BS[b]	8050	0.37	12371.9	-28	-0.2 ± 0.5	Cu target
BS[b]	8050	0.37	12371.0	-101	-0.8 ± 0.5	{3 observations Mo, Ta, Au targets
BS[b]	8050	0.37	12370.1	-174	-1.4 ± 0.5	W target
BS[b]	9860	0.47	12370.1	-174	-1.7 ± 0.5	{2 observations Cu, Ni targets
BJW[a]	10168	0.48	12371.2	-80	-0.8 ± 0.6	W target
BS[b]	19600	0.96	12371.9	-28	-0.6 ± 1.1	W target, W fil.
BS[b]	19600	0.96	12370.1	-174	-3.4 ± 1.1	W target, Ox. Cath.
FHD[c]	24500	6.0	12370.0	-177	-4.3 ± 1.3	W target, W fil.

[a] Bearden, Johnson, and Watts, Phys. Rev. **81**, 70 (1951).
[b] J. A. Bearden and Guenter Schwarz, Phys. Rev. **79**, 674 (1950).
[c] Felt, Harris, and DuMond, Phys. Rev. **92**, 1160 (1953).

United States National Bureau of Standards by Sommer, Thomas, and Hipple on the magnetic moment of the proton, should be resolved in favor of the omegatron results. This conclusion has recently been corroborated at the Clarendon Laboratory, Oxford University, England, where D. J. Collington, A. N. Dellis, J. H. Sanders, and K. C. Turberfield have repeated the inverse cyclotron measurement, using instead of "dees" a straight-sided central conductor connected to the rf supply and two grounded outer segmental conductors. Their result (uncorrected for the diamagnetism of the proton resonance sample) is

$$\mu_p' = 2.79273\pm0.00004 \text{ nuclear magnetons,}[6]$$

which differs from the omegatron value by only 16 ppm, an amount which is well within the probable error of the difference. Great care was taken to eliminate from the construction of the apparatus all material which was sufficiently magnetic to disturb the field in the region of the proton orbit by as much as 5 ppm. These workers state that most samples of brass tested had an unacceptably high susceptibility. The presence of slightly magnetic materials might well account for the low result obtained in the Stanford experiments.

The measurements of the short wavelength limit of the continuous x-ray spectrum have been made over a sufficiently wide range of voltages to permit a conjecture as to the cause of discrepancy. The measurements published by Bearden, Johnson, and Watts, hereafter designated as BJW were performed at two different voltages and those of Bearden and Schwarz, hereafter designated as BS were made at four different voltages. As a result the voltage resolving power of the two-crystal spectrometer these workers used was different for these different voltages, the half-width at half-maximum height of the spectral "window" expressed in volts being greater at the higher voltages. The work of Felt, Harris, and DuMond (FHD) done at the highest voltage of all had a still wider spectral window width in volts.

[6] J. H. Sanders (private communication, May 4, 1955); see also Letter to the Editor by Collington, Dellis, Sanders, and Turberfield, Phys. Rev. **99**, 1622 (1955).

Table XI lists these different experimental results in order of increasing voltage. The first point of maximum bending of the observed isochromat (or spectral intensity curve) was assumed in all this work as the true location of the quantum limit. As we shall see, the results cast some doubt on the exact validity of this assumption. Each experimental determination is actually aimed at measuring the quantum energy-wavelength conversion factor, $V_0\lambda_0$, relating energy, V_0, in volts to the corresponding x-ray wavelength λ_0 on the Siegbahn scale in x-units;

$$V_0\lambda_0 = hc^2/(e\lambda_g/\lambda_s) \qquad (16)$$

then permits calculation of the universal constant, h/e, provided the constants c and λ_g/λ_s are given. (In
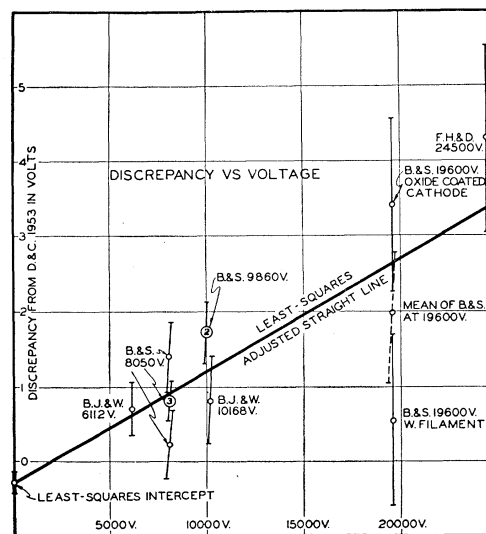

FIG. 2. Eleven determinations of the quantum limit of the continuous x-ray spectrum measured at six different applied voltages. If we assume as an arbitrary reference a constant value of the voltage-wavelength conversion factor (the value of DC 53) the ordinates in this figure represent in volts how much the position of the observed first point of maximum bending in the intensity curve differed from the calculated position, while the abscissae give the applied voltages at which the determinations were made. The choice of a straight line for the least-squares fit to the points is purely hypothetical.

FIG. 3. Eleven determinations of the quantum limit of the continuous x-ray spectrum measured at six different applied voltages. Here the same data as those of Fig. 2 are plotted as ordinates, but the abscissae are the half-widths at half maximum height of the spectrometer window curve in each case. The choice of a straight line for the least-squares fit to the points is purely hypothetical.
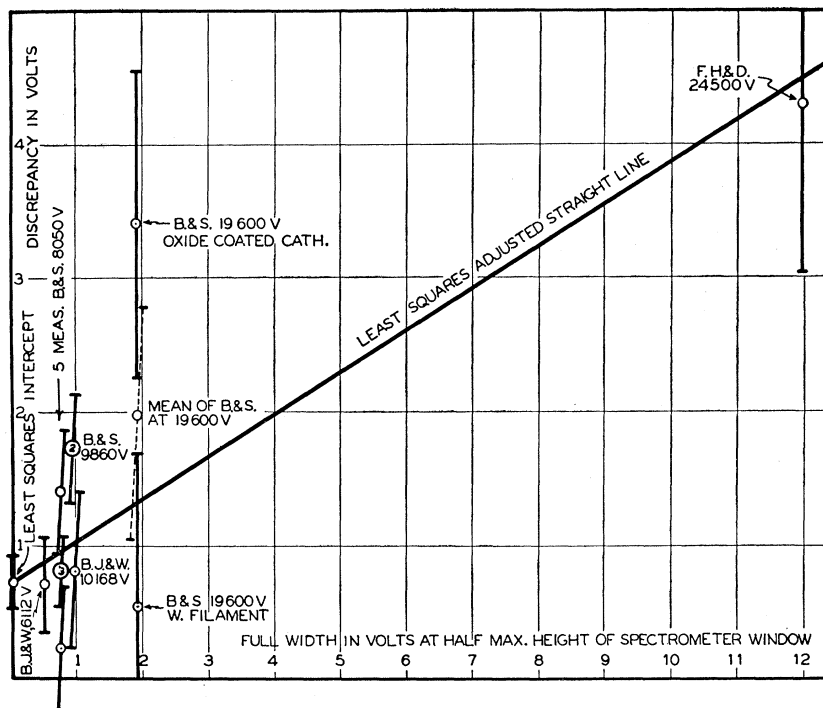
this equation e is expressed in absolute electrostatic units, V in absolute electromagnetic units.)

The column labeled "a (volts)" gives the half-width at half-maximum height of the spectrometer "window" curve. The column labeled "$hc^2/(e\lambda_g/\lambda_s)$" gives the observed value of the voltage-wavelength conversion factor. The point of maximum bending is used as the criterion to determine the threshold. The columns labelled "discrepancy" give the relative and absolute deviations of each experimentally determined voltage threshold from the value required to give the DC 53 least-squares adjusted value for $hc^2/(e\lambda_g/\lambda_s)=12372.2$ kilovolts x-units.

Because the different experimenters listed in Table XI used different values for the constants c and λ_g/λ_s to calculate their results as to h/e we have recomputed and listed what they actually measured before these constants were ntr ioduced, namely the conversion factor $V_0\lambda_0$ from volts to x-units. If no systematic or random errors were present the result as to this conversion factor should be the same at all voltages, but instead there seems to be a systematic trend toward higher values of $V_0\lambda_0$ as one goes toward higher voltages. We take our least-squares adjusted value (DC 53)

$$hc^2/(e\lambda_g/\lambda_s)=12372.2 \text{ kv } x\text{-units} \qquad (17)$$

as an arbitrary reference against which to compare these results. The columns in Table XI marked "discrepancy" give the difference, expressed in parts per million and also in volts, between the observed quantum threshold position (first point of maximum bending) and the calculated position based on Eq. (17). The

column marked a gives the calculated half-width at half-maximum height, expressed in volts, of the spectra-"window" curve or acceptance band of the spectroml eter. Figure 2 exhibits the discrepancy from the reference value as a function of voltage and Fig. 3 shows the same quantity as a function of spectral window half-width, a.

Our present conjecture is that the cause of systematic error may reside in the method used for locating the true threshold from the experimentally observed x-ray intensity curves. This supposition is based on the fact that the systematic trend exhibited in Fig. 2 and Fig. 3 seems to indicate an increasing discrepancy or systematic error either with increasing voltage at which the experiment is performed or with increasing spectral window width. In Fig. 4 we reproduce one of the isochromats from the FHD determination on which we have marked at A, the point of maximum bending and at B, the point at which the quantum threshold should occur to accord with the value of Eq. (17). The variation of about 3.7 volts exhibited by the least-squares adjusted line of Fig. 3 is the same order as this separation between points A and B of Fig. 4. So much care was taken in the matter of both voltage and wavelength measurements in the FHD determination (about which one of us had direct knowledge) that it is very hard to believe so large a discrepancy could be the result of errors in these measurements.

Figure 5 shows how the point A of maximum bending in Fig. 4 was determined by plotting the third derivative of the isochromat and locating its zero point. The third derivative was obtained by means of a numerical
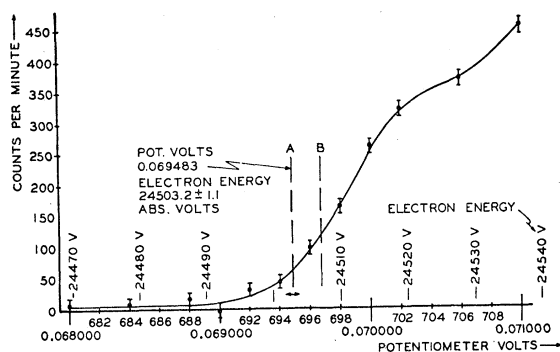
FIG. 4. One of the isochromats taken at 24.5 kv by FHD. The position, A, marks the point of maximum bending, determined by the method of Fig. 5, and the arrows indicate the estimated uncertainty in locating this position while the position B is the calculated position of the quantum limit based on the least-squares-adjusted best value of the voltage-wavelength conversion factor from the DC 53 adjustment.

interpolation method using points at equidistant abscissa spacings on the smoothed curve of Fig. 4. The method is of course no more precise than the smoothing of the curve is reliable, and the assigned error in Fig. 5 was based on variations in the location when the curve was smoothed by different people. This same error spread is shown in Fig. 4 by the arrows on either side of the abscissa location A.

In the case of all the experiments listed in Table XI, save those of BJW, the method of isochromats was used. This consists ideally in monochromatizing an x-ray beam and measuring the continuous spectrum intensity associated with the selected wavelength as a function of the voltage applied to the x-ray tube. The resulting curve is called an isochromat. (In the case of BJW the voltage was fixed and the wavelength variable, but this difference is of no consequence.) In practice the "monochromatization" will actually consist of selection from the continuous spectrum by a monochromator whose band pass curve has a sharp peak at some determined wavelength with asymptotic decay on either side. The dynamical theory of x-ray reflection in perfect crystals leads one to expect an inverse square law of asymptotic decay at large distances from the peak of this monochromator window curve, even when the two-crystal spectrometer is used. As a result of this unavoidable experimental impurity the sharpness of definition of the continuous spectrum threshold is blurred because the observed intensity curve is the fold of the true spectrum into the window curve of the monochromator. It has been shown in an earlier paper[7] that if $F(z)$ is the observed intensity curve, where z stands for a variable proportional to the voltage if the curve is an isochromat, and $f(z)$ is the curve expressing the ideal shape of the continuous x-ray spectrum, that

$$F(z) = \int_{x=-\infty}^{x=z} g(x)f(z-x)dx. \qquad (18)$$

Herein we choose $z=0$ to be the quantum limit of the ideal spectrum so that $f(z)=0$ for $z \leqslant 0$. Here the monochromator window curve is the function $g(x)$ and the upper limit of the integral is $x=z$, since the ideal spectrum vanishes there, i.e., $f(z-x)=0$ for $x \geqslant z$.

The continuous x-ray spectrum from a thick target descends to meet the background at the quantum threshold in a more-or-less linear way with however certain localized breaks in slope or "knees" so that the curve becomes increasingly steep as the threshold is approached. Quite close to the threshold (within 10 or 20 volts) certain irregularities first reported by Ohlin[8] appear in the continuous spectrum which are believed to be related to the banded structure of (1) the incompletely filled energy levels of structure electrons in the solid target material, and (2) the losses sustained by the bombarding electrons due to energy communicated by them to structure electrons.[9]

An earlier method of locating the true threshold from the observed intensity curve was to project a tangent to that curve, from some point on it just above the threshold region where a stable slope seemed to have been attained, downward to the background level, taking the intersection of this tangent therewith as the true threshold point. If the window curve had wings whose asymptotic approach to the background was faster than the inverse square law this method might be made reliable, but it is not so as the case stands. Even a strictly linear spectrum without irregularities or breaks in slope, when folded into such a window curve with inverse square "tails," will give a curve whose slope increases logarithmically without limit as we go up from the threshold so that there is no definite correct point from which to draw the tangent. Window curves of the
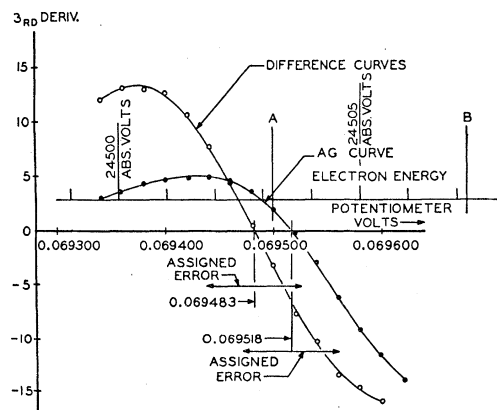

FIG. 5. The third derivative of the isochromat of Fig. 4. The mean crossover or zero point of the two curves was used to locate position A in Fig. 4. The assigned error in this position, which corresponds to the uncertainty indicated with the arrows in Fig. 4, was based on the spread in results obtained when the curve of Fig. 4 was smoothed through the observed points by different people.

[7] Panofsky, Green, and DuMond, Phys. Rev. 62, 215 (1942). See Sec. II.

[8] P. Ohlin, Arkiv Mat. Astron. Fysik 29A, No. 3 (1942); 29B, No. 4 (1942); 31A, No. 9 (1944); 33A, No. 23 (1946).
[9] B. R. A. Nijboer, Physica 12, 461 (1946).

type here described have infinite second moments, and even their first moments are logarithmically divergent. It is this circumstance which makes the difficulty. Consequently the following alternative method has been adopted.

If we differentiate Eq. (18) twice and assume that the ideal spectrum can be approximated by a series of straight-line segments with abrupt breaks in slope between them, i.e., let

$$f'(x) = a_i, \quad x_{i-1} < x < x_i, \quad i = 1, 2 \cdots \infty, \quad (19)$$

then it has been shown[7] that

$$F''(z) = g(z)f'(0) + \sum_{i=1}^{\infty} g(z-x_i)(a_{i+1}-a_i). \quad (20)$$

This means that the second derivative, $F''(z)$, of the observed intensity curve will consist of a series of images of the window curve, each centered at one of the breaks in slope of the ideal spectrum and each proportional in height to the magnitude, $(a_{i+1}-a_i)$, of the discontinuity in slope with which it is associated. The leading term $g(z)f'(0)$ is no exception to the rule since in deriving (20) the quantum threshold itself is assumed to be a second order discontinuity at $z=0$, i.e., a break in slope from zero slope to slope $f'(0)$.

In the case of all the determinations listed in Table X the method used for locating the true threshold position was to take it at the first point of maximum bending, i.e., at the maximum value of $F''(z)$. In the FHD determination this was done by finding the zero point of the third derivative. In some of the other curves taken by BS the bending was so sharp that the point of maximum bending could be estimated by inspection of the curve.

Now the point of maximum bending will fail to give the correct threshold position if there are adjacent
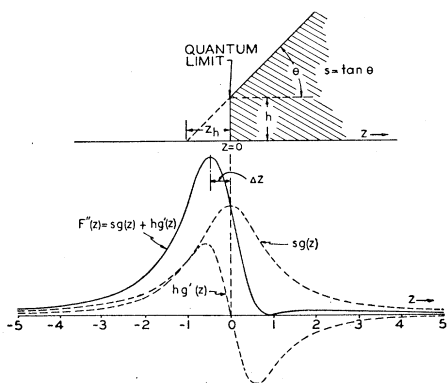

FIG. 6. Postulated precipice (first-order discontinuity) whose presence at the foot of the continuous x-ray spectrum from a thick target may account for the systematic trend (with increasing applied voltage) of the discrepancy between the observed points of maximum bending and the positions computed from the least-squares adjusted value (DC 53) of the voltage-wavelength conversion factor. The isochromat, $F(z)$, would be the fold of the spectrometer window-curve $g(z)$ into this structure and the second derivative F'' would then consist, as shown, of the sum of two components $g(z)$ and $hg'(z)$.
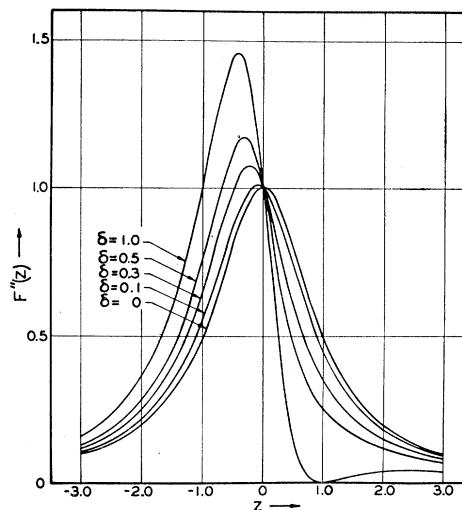

FIG. 7. Calculated curves of F'', the second derivative of the isochromat assuming a witch-like g-curve for the spectrometer window profile if the true spectrum has the postulated precipice of Fig. 6. The abscissae, z, are plotted in units of the window half-width, a. The numerical value, δ, attached to each curve is the ratio of the precipice overshoot z_h to the window half-width, a. The origin, $z=0$, is the quantum limit position and the shift of the maximum point away from this position with increasing δ is evident.

strong breaks in slope in the true spectrum which lie too close to the threshold break. This is because then the corresponding images of the window curve will lie so close together as to be only partially resolved or perhaps even totally unresolved. Such proximity of adjacent g-curves may produce a shifting of the peak corresponding to the quantum limit of the spectrum. We have made an investigation to see if any of the known Ohlin structures could have such an effect, but on no reasonable assumptions regarding their shape have we been able to conclude that they do so.

There remains the possibility that the assumption of a mere second-order discontinuity in the ideal spectrum at the quantum limit is too simple. We believe that the systematic trend indicated by the shifts of Table XI and Figs. 2 and 3 might be explained however if the ideal quantum limit consisted of a superposition of a first- and second-order discontinuity as shown in the upper diagram, Fig. 6. The first-order discontinuity or step function considered by itself may be seen to be the limiting case of two equal breaks in slope of opposite sign which have approached infinitely close to each other and have become infinitely large. Referring to Fig. 6, if h is the height of the precipice, $s = \tan\theta$ the slope above it, and $z_h = h/s$ is the overshoot as shown, then it is easy to show that

$$F''(z) = sg(z) + hg'(z) = sg(z) + sz_hg'(z). \quad (21)$$

Thus it should be clear that, whereas the second-order discontinuity generates a g-curve, the first-order discontinuity generates a curve which is the first derivative of the g-curve. The superposition of these two
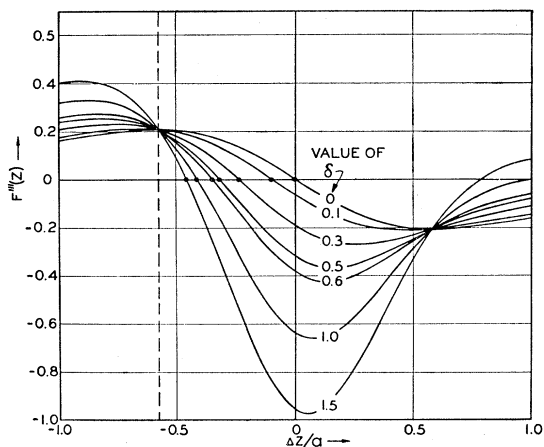
FIG. 8. Calculated curves of F''', the third derivative of the isochromat assuming a witch-like g-curve and a true spectrum with a precipice as well as a second-order discontinuity at the quantum limit. The parameter δ attached to each curve is the ratio of the overshoot, z_h, to the window half-width, a. The shift with increasing δ in the crossover or zero point of these curves away from the quantum limit at $z=0$ is clearly evident. These curves are to be compared with the curve of Fig. 5. The symmetry of the upper and lower portions of the latter curve indicate that a value of δ can hardly be ascribed to it much larger than 0.5.

curves, the primitive and its first derivative, may indeed result in a peak in the $F''(z)$ which is considerably shifted from the true quantum limit in just the direction which the observations show. It remains to investigate whether this explanation is quantitatively plausible as regards the magnitude of the shift. To test this we have assumed the window or g curve to be a "witch" of the form:

$$g(x) = A(1+x^2/a^2)^{-1}. \qquad (22)$$

This is the simplest curve which has the appropriate inverse square behavior in its approaches. It may fail to represent the true window curve somewhat by having its points of inflection occur too near the peak (at $x=a/\sqrt{3}$ in fact). Substitution of (22) into (21) gives us the curves shown in Fig. 7 in which the shifts of the peak of the F'' curve are clearly evident. One more differentiation gives us the F''' curves of Fig. 8, the shifts of whose zero points can be seen.

Let Δz represent the shift in the position of the maximum of the $F''(z)$ away from the true quantum limit, shifts to the left in Fig. 4 being counted as positive for convenience. Let a be the half-width at half-maximum height of the g-curve [witch, Eq. (22)], and z_h the overshoot as defined in Fig. 6. We show in Fig. 9 a plot of $\Delta z/z_h$ as a function of a/z_h for the witch. Points on this curve corresponding to different values of $\Delta z/a$ are also shown. The largest value of $\Delta z/a$, the slope of the curve of Fig. 9 at the origin, is $\Delta z/a = 1/\sqrt{3}$, and we see that in this region $\Delta z/z_h$ behaves almost linearly with a/z_h. According to Fig. 9 then, when the window half-width is much larger than the overshoot, the shift in the point of maximum bending away from the true quantum threshold is of the order of the overshoot and

$\Delta z/z_h$ cannot exceed unity. When the window half-width is of the order of or smaller than the overshoot, the shift is proportional to the window half-width and for a witch-shaped window the ratio $\Delta z/a$ cannot exceed $3^{-\frac{1}{2}}$.

Now if we assume that the overshoot, z_h, expressed in volts is independent of the voltage at which the experiment is performed and that the shift Δz is proportional to window half-width, a reference to the experimental data of Fig. 3 shows from the slope of the line that $\Delta z/a$ must be of the order of 0.6. Not only is this ratio uncomfortably large but, much worse, this hypothesis requires us to suppose that at the small window half-widths below 0.5 volt, such as that of BJW at 6 kv, the overshoot is so much larger than the window half-width that the presence of the precipice should be manifest in the experimental intensity curve. Nothing of this sort however appears there. We must therefore abandon this assumption.

Thus, if we are to explain the shift it appears necessary to make the hypothesis that the overshoot, Δz, varies with the voltage on the x-ray tube, becoming smaller at lower voltage, and that the window half-width, a, is large compared to the overshoot z_h so that we are working in the upper right-hand region of the curve of Fig. 9 where $\Delta z \cong z_h$.

It may not be implausible that the magnitude of the overshoot of this conjectured precipice should vary with applied voltage. Other features of the isochromat curve, such as the apparent distance of the Ohlin peaks from the first point of maximum bending seem to vary considerably with voltage. If the overshoot, z_h, and therefore the shift Δz were known to be approximately
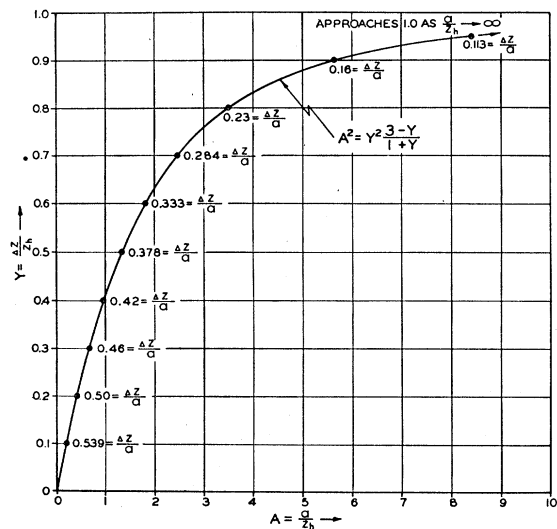

FIG. 9. The ordinates show the ratio of shift, Δz, to overshoot, z_h. The shift, Δz, means the amount by which the point of maximum bending of the isochromat is shifted away from the true quantum limit assuming a witch-like window curve and a true spectral profile incorporating both first- and second-order discontinuities at the quantum limit after the manner of Fig. 6.

proportional to the applied voltage then an extrapolation of the straight line of Fig. 2 to zero voltage might be expected to give a better value of $hc^2/(e\lambda_g/\lambda_s)$ than any of the observations. No comprehensive theory of the radiative interaction between high-voltage bombarding electrons and a real crystal lattice taking into account modern knowledge of the solid state has yet been attempted however and help from such a theory is probably needed before further progress can be made.

From the experimental side there is little hope of improving the spectral resolving power attainable with crystal diffraction much beyond what has been so far attained.

Note added August 10, 1955.—We are indebted to Professor John Tukey of Princeton University for certain privately communicated comments received after this paper had been accepted by the editors. Professor Tukey feels that it is wrong in principle to select the equation set (1111123) merely on the grounds that its $\chi^2(=3.25)$ falls very much closer than that of any of the other 3-degree-of-freedom sets to the expected value $\chi^2=3$. He much prefers the method of increments to χ^2 because it is a more conclusive method than the one we have used for the purpose of pinning suspicion of systematic error on specific equations. He therefore urges us still to make a complete exhaustive analysis involving determinations of χ^2 for equation sets containing *more than one equation of each kind.*

This would involve the additional evaluation of χ^2 for 4 times as many equation sets as we have already done, if only one equation were added to a single kind in each set, or 19 times as many if all possible combinations were explored! Our original restriction to sets with only one equation of each kind (selection rule, *a*) was to economize on the heavy expense for programming and for computer time. Neither funds nor other facilities are at present available to the authors of this paper to carry out Professor Tukey's suggestions.

We admit the cogency of Professor Tukey's contention, *if the problem had to be solved by the variance analysis alone* without support from physical considerations. However, we do not claim that the value, $\chi^2=3.25$, by itself consitutes a *compelling reason* for the choice of the set (1111123). Rather we regard it merely as a *clue* pointing out which equations to suspect in order that we may examine these more closely from the point of view of physics. In experimental physics most error estimates are at best very rough, and there is therefore wide room for honest differences of opinion as to how much money and effort it is wise to spend on the analysis of data whose weights must necessarily reflect this roughness. We understand Professor Tukey's eagerness as a mathematical statistician to see this variance analysis pursued exhaustively and regret that it is beyond our present means to do so. We believe however that even in its present fragmentary state it has served very usefully.

In discussing our choice of the set (1111123), Professor Tukey makes an important and valuable point. He notices that the next larger χ^2 (=7.71) among the 3 d.f. sets, corresponding to the set (1111122) is "still quite bearable." (According to Table I the chance of χ^2 exceeding 7.71 is about 5%.) If it is a permissible set at all, since this set uses Eq. (6$_2$) of weight 0.06 in place of equation 6$_3$ of weight only 0.015, it should be a stronger set, Professor Tukey argues. If both equation sets are acceptable, we presumably should combine them using due weights, he quite logically concludes.

When Professor Tukey's remarks were made, he had not been informed as yet about the voltage-dependent systematic trends (Table XI and Figs. 2 and 3) which appear when the individual measurements constituting the data of (6$_2$) and (6$_3$) are more closely examined. In the light of these trends and our surmise as to their origin we believe that a still better procedure than taking a

TABLE XII. Auxiliary constants.

Rydberg wave number for infinite mass*
$$R_\infty = 109737.309 \pm 0.012 \text{ cm}^{-1}$$
Rydberg wave numbers for the light nuclei
$$R_H = 109677.576 \pm 0.012 \text{ cm}^{-1}$$
$$R_D = 109707.419 \pm 0.012 \text{ cm}^{-1}$$
$$R_{\text{He}^3} = 109717.345 \pm 0.012 \text{ cm}^{-1}$$
$$R_{\text{He}^4} = 109722.267 \pm 0.012 \text{ cm}^{-1}$$
Velocity of light
$$c = 299793.0 \pm 0.3 \text{ km sec}^{-1}$$
Atomic mass of neutron (physical scale)
$$n = 1.008982 \pm 0.000003$$
Atomic mass of hydrogen (physical scale)
$$H = 1.008142 \pm 0.000003$$
Atomic mass ratio of hydrogen to proton*
$H/M_p = 1.00054461$ (Computed using atomic mass of electron,
$$Nm = 0.00054875)$$
Atomic mass of the proton* (physical scale)
$$M_p = 1.007593 \pm 0.000003$$
Atomic mass of deuterium* (physical scale)
$$D = 2.014735 \pm 0.000006$$
Atomic mass ratio of deuterium to deuteron*
$D/M_d = 1.00027244$ (Computed using atomic mass of electron,
$$Nm = 0.00054875) \text{ (physical scale)}$$
Ratio of electron magnetic moment to proton magnetic momenf of Koenig, Prodell, and Kusch[a] without diamagnetic correction*
$$[M_p/(Nm\mu')](1+\alpha/2\pi-2.973\alpha^2/\pi^2) = 658.2288 \pm 0.0004$$
Correction factor μ_e/μ_0 for anomalous magnetic moment ot electron*
$$\mu_e/\mu_0 = (1+\alpha/2\pi-2.973\alpha^2/\pi^2) = 1.0011453$$
(Computed using the value $1/\alpha = 137.04$)
Gas constant per mole (physical scale)
$$R_0 = (8.31696 \pm 0.00034) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1}$$
Standard volume of a perfect gas (physical scale)
$$V_0 = 22420.7 \pm 0.6 \text{ cm}^3 \text{ atmos mole}^{-1}$$

[a] Koenig, Prodell, and Kusch, Phys. Rev. **88**, 191 (1952).

weighted average of the results, (6$_2$) and (6$_3$), is to select from both of them *those individual determinations performed at the lowest voltages.* Nine of these, 2 from (6$_2$) and 7 from (6$_3$), form a quite homogeneous cluster in the voltage range 6112 to 10168. No determinations have been made at voltages below this range. The weighted mean results of this cluster is

$$hc^2/(e\lambda_g/\lambda_s) = 12370.8 \pm 0.2 \text{ kilovolt } x\text{-units,}$$

wherein the standard deviation, ± 0.2 is merely an index of the disagreement among the results of the 9 different measurements and does not reflect any allowance for the now-very-likely systematic error of the group mean (because of the use of the criterion of maximum bending). From the slope of the straight line in Fig. 2 this systematic error *could* well be of the order of a volt at the group-average voltage of 8000 volts. This corresponds to a shift of 1.5 kilovolt x-units in $hc^2/(e\lambda_g/\lambda_s)$. Thus the numerical value obtained as the mean from the selection of the individual data of Eqs. (6$_2$) and (6$_3$) does not differ significantly either as to value or probable weight from the one we have actually adopted using the results of Eq. (6$_3$) namely

$$hc^2/(e\lambda_g/\lambda_s) = 12370.77 \pm 1.03 \text{ kilovolt } x\text{-units.}$$

TABLE XIII. Least-squares adjusted output values. The quantity following each $\pm$ sign is the standard error. In the present adjustment, unlike that of DC 53, there is no significant difference between the scales of error by internal and by external consistency. Attention is called to the fact that the quantities in this table are *observationally correlated* so that in the computation of the error measures of derived values dependent on two or more of the values in this table the method explained in DC 53, Secs. 4 and 10 must be used. Table X of this article gives the elements of the error matrix to be used in such computations.

Avogadro's constant (physical scale)
$$N = (6.02486 \pm 0.00016) \times 10^{23} \ (\text{g mole})^{-1}$$

Loschmidt's constant (physical scale)
$$L_0 = N/V_0 = (2.68719 \pm 0.00010) \times 10^{19} \ \text{cm}^{-3}$$

Electronic charge
$$e = (4.80286 \pm 0.00009) \times 10^{-10} \ \text{esu}$$
$$e' = e/c = (1.60206 \pm 0.00003) \times 10^{-20} \ \text{emu}$$

Electron rest mass
$$m = (9.1083 \pm 0.0003) \times 10^{-28} \ \text{g}$$

Proton rest mass
$$m_p = M_p/N = (1.67239 \pm 0.00004) \times 10^{-24} \ \text{g}$$

Neutron rest mass
$$m_n = n/N = (1.67470 \pm 0.00004) \times 10^{-24} \ \text{g}$$

Planck's constant
$$h = (6.62517 \pm 0.00023) \times 10^{-27} \ \text{erg sec}$$
$$\hbar = h/2\pi = (1.05443 \pm 0.00004) \times 10^{-27} \ \text{erg sec}$$

Conversion factor from Siegbahn x-units to milliangstroms
$$\lambda_g/\lambda_s = 1.002039 \pm 0.000014$$

Faraday constant (physical scale)
$$F = Ne = (2.89366 \pm 0.00003) \times 10^{14} \ \text{esu} \ (\text{g mole})^{-1}$$
$$F' = Ne/c = (9652.19 \pm 0.11) \ \text{emu} \ (\text{g mole})^{-1}$$

Charge-to-mass ratio of the electron
$$e/m = (5.27305 \pm 0.00007) \times 10^{17} \ \text{esu gm}^{-1}$$
$$e'/m = e/(mc) = (1.75890 \pm 0.00002) \times 10^{7} \ \text{emu gm}^{-1}$$

Ratio h/e
$$h/e = (1.37942 \pm 0.00002) \times 10^{-17} \ \text{erg sec (esu)}^{-1}$$

Fine structure constant
$$\alpha = e^2/(\hbar c) = (7.29729 \pm 0.00003) \times 10^{-3}$$
$$1/\alpha = 137.0373 \pm 0.0006$$
$$\alpha/2\pi = (1.161398 \pm 0.000005) \times 10^{-3}$$
$$\alpha^2 = (5.32504 \pm 0.00005) \times 10^{-5}$$
$$1 - (1-\alpha^2)^{\frac{1}{2}} = (0.266252 \pm 0.000002) \times 10^{-4}$$

Atomic mass of the electron (physical scale)
$$Nm = (5.48763 \pm 0.00006) \times 10^{-4}$$

Ratio of mass of hydrogen to mass of proton[a]
$$H/M_p = \left[1 - \frac{Nm}{H}(1 - \tfrac{1}{2}\alpha^2)\right]^{-1}$$
$$= 1.000544613 \pm 0.000000006$$

Atomic mass of proton (physical scale)
$$M_p = H - Nm = 1.007593 \pm 0.000003$$

Ratio proton mass to electron mass
$$M_p/(Nm) = 1836.12 \pm 0.02$$

Reduced mass of electron in hydrogen atom
$$\mu = mM_p/H = (9.1034 \pm 0.0003) \times 10^{-28} \ \text{g}$$

Schrödinger constant for a fixed nucleus
$$2m/\hbar^2 = (1.63836 \pm 0.00007) \times 10^{27} \ \text{erg}^{-1} \ \text{cm}^{-2}$$

Schrödinger constant for the hydrogen atom
$$2\mu/\hbar^2 = (1.63748 \pm 0.00007) \times 10^{27} \ \text{erg}^{-1} \ \text{cm}^{-2}$$

First Bohr radius
$$a_0 = \hbar^2/(me^2) = \alpha/(4\pi R_\infty)$$
$$= (5.29172 \pm 0.00002) \times 10^{-9} \ \text{cm}$$

Radius of electron orbit in normal H^1, referred to center of mass
$$a_0' = a_0(1-\alpha^2)^{\frac{1}{2}} = (5.29158 \pm 0.00002) \times 10^{-9} \ \text{cm}$$

Separation of proton and electron in normal H^1
$$a_0'' = a_0' R_\infty/R_H = (5.29446 \pm 0.00002) \times 10^{-9} \ \text{cm}$$

Compton wavelength of the electron
$$\lambda_{ce} = h/(mc) = \alpha^2/(2R_\infty) = (24.2626 \pm 0.0002) \times 10^{-11} \ \text{cm}$$
$$\lambdabar_{ce} = \lambda_{ce}/(2\pi) = (3.86151 \pm 0.00004) \times 10^{-11} \ \text{cm}$$

Compton wavelength of the proton
$$\lambda_{cp} = h/(m_p c) = (13.2141 \pm 0.0002) \times 10^{-14} \ \text{cm}$$
$$\lambdabar_{cp} = \lambda_{cp}/(2\pi) = (2.10308 \pm 0.00003) \times 10^{-14} \ \text{cm}$$

Compton wavelength of the neutron
$$\lambda_{cn} = h/(m_n c) = (13.1959 \pm 0.0002) \times 10^{-14} \ \text{cm}$$
$$\lambdabar_{cn} = \lambda_{cn}/(2\pi) = (2.10019 \pm 0.00003) \times 10^{-14} \ \text{cm}$$

Classical electron radius
$$r_0 = e^2/(mc^2) = \alpha^3/(4\pi R_\infty)$$
$$= (2.81785 \pm 0.00004) \times 10^{-13} \ \text{cm}$$
$$r_0^2 = (7.94030 \pm 0.00021) \times 10^{-26} \ \text{cm}$$

Thomson cross section
$$(8/3)\pi r_0^2 = (6.65205 \pm 0.00018) \times 10^{-25} \ \text{cm}^2$$

Fine structure doublet separation in hydrogen
$$\Delta E_H = (1/16)R_H\alpha^2[1 + \alpha/\pi + (5/8 - 5.946/\pi^2)\alpha^2]$$
$$= 0.365871 \pm 0.000003 \ \text{cm}^{-1}$$
$$= 10968.56 \pm 0.10 \ \text{Mc sec}^{-1}$$

Fine structure separation in deuterium
$$\Delta E_D = \Delta E_H R_D/R_H = 0.365970 \pm 0.000003 \ \text{cm}^{-1}$$
$$= 10971.54 \pm 0.10 \ \text{Mc sec}^{-1}$$

Zeeman displacement per gauss
$$(e/mc)/(4\pi c) = (4.66885 \pm 0.00006) \times 10^{-5} \ \text{cm}^{-1} \ \text{gauss}^{-1}$$

Boltzmann's constant
$$k = R_0/N = (1.38044 \pm 0.00007) \times 10^{-16} \ \text{erg deg}^{-1}$$
$$k = (8.6167 \pm 0.0004) \times 10^{-5} \ \text{ev deg}^{-1}$$
$$1/k = 11605.4 \pm 0.5 \ \text{deg ev}^{-1}$$

First radiation constant
$$c_1 = 8\pi hc = (4.9918 \pm 0.0002) \times 10^{-15} \ \text{erg cm}$$

Second radiation constant
$$c_2 = hc/k = 1.43880 \pm 0.00007 \ \text{cm deg}$$

Atomic specific heat constant
$$c_2/c = (4.79931 \pm 0.00023) \times 10^{-11} \ \text{sec deg}$$

Wien displacement law constant[b]
$$\lambda_{\max}T = c_2/(4.96511423) = 0.289782 \pm 0.000013 \ \text{cm deg}$$

Stefan-Boltzmann constant
$$\sigma = (\pi^2/60)(k^4/\hbar^3 c^2) = (0.56687 \pm 0.00010)$$
$$\times 10^{-4} \ \text{erg cm}^{-2} \ \text{deg}^{-4} \ \text{sec}^{-1}$$

[a] The binding energy of the electron in the hydrogen atom has been included in the quantity. The mass of the electron when found in the hydrogen atom is not m, but more correctly $m(1 - \tfrac{1}{2}\alpha^2 + \cdots)$.
[b] The numerical constant 4.96511423 is the root of the transcendental equation, $x = 5(1 - e^{-x})$.

TABLE XIII.—*Continued.*

Sackur-Tetrode constant (physical scale of at. wt.)

$$(S_0/R_0)_{Ph} = 5/2 + \ln\{(2\pi R_0)^{\frac{3}{2}} h^{-3} N^{-4}\}$$
$$= -5.57324 \pm 0.00007$$
$$(S_0)_{Ph} = -(46.3524 \pm 0.0020) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1}$$

Sackur-Tetrode constant (chemical scale of at. wt.)

$$(S_0/R_0)_{Ch} = -5.57256 \pm 0.00007$$
$$(S_0)_{Ch} = -(46.3467 \pm 0.0020) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1}$$

Bohr magneton

$$\mu_0 = he/(4\pi mc) = \tfrac{1}{2}e\lambda_{ce}$$
$$= (0.92731 \pm 0.00002) \times 10^{-20} \text{ erg gauss}^{-1}$$

Anomalous electron moment correction

$$[1 + \alpha/(2\pi) - 2.973\alpha^2/\pi^2] = \mu_e/\mu_0 = 1.001145358 \pm 0.000000005$$

(Computed using adjusted value $\alpha = (7.29729 \pm 0.00003) \times 10^{-13}$)

Magnetic moment of the electron

$$\mu_e = (0.92837 \pm 0.00002) \times 10^{-20} \text{ erg gauss}^{-1}$$

Nuclear magneton

$$\mu_n = he/(4\pi m_p c) = \mu_0 Nm/H^+$$
$$= (0.505038 \pm 0.000018) \times 10^{-23} \text{ erg gauss}^{-1}$$

Proton moment

$$\mu = 2.79275 \pm 0.00003 \text{ nuclear magnetons}$$
$$= (1.41044 \pm 0.00004) \times 10^{-23} \text{ erg gauss}^{-1}$$

Gyromagnetic ratio of the proton in hydrogen, uncorrected for diamagnetism

$$\gamma' = (2.67523 \pm 0.00004) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1}$$

Gyromagnetic ratio of the proton (corrected)

$$\gamma = (2.67530 \pm 0.00004) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1}$$

Multiplier of (Curie constant)$^{\frac{1}{2}}$ to give magnetic moment per molecule

$$(3k/N)^{\frac{1}{2}} = (2.62178 \pm 0.00010) \times 10^{-20} \text{ (erg mole deg}^{-1})^{\frac{1}{2}}$$

Mass-Energy conversion factors

$$1g = (5.61000 \pm 0.00011) \times 10^{26} \text{ Mev}$$
$$1 \text{ electron mass} = 0.510976 \pm 0.000007 \text{ Mev}$$
$$1 \text{ atomic mass unit} = 931.141 \pm 0.010 \text{ Mev}$$
$$1 \text{ proton mass} = 938.211 \pm 0.010 \text{ Mev}$$
$$1 \text{ neutron mass} = 939.505 \pm 0.010 \text{ Mev}$$

Quantum energy conversion factors

$$1 \text{ ev} = (1.60206 \pm 0.00003) \times 10^{-12} \text{ erg}$$
$$E/\bar{\nu} = hc = (1.98618 \pm 0.00007) \times 10^{-16} \text{ erg cm}$$
$$E\lambda_g = (12397.67 \pm 0.22) \times 10^{-8} \text{ ev cm}$$
$$E\lambda_s = 12372.44 \pm 0.16 \text{ kilovolt } x\text{-units}$$
$$E/\nu = (6.62517 \pm 0.00023) \times 10^{-27} \text{ erg sec}$$
$$E/\nu = (4.13541 \pm 0.00007) \times 10^{-15} \text{ ev sec}$$
$$\bar{\nu}/E = (5.03479 \pm 0.00017) \times 10^{15} \text{ cm}^{-1} \text{ erg}^{-1}$$
$$\bar{\nu}/E = 8066.03 \pm 0.14 \text{ cm}^{-1} \text{ ev}^{-1}$$
$$\nu/E = (1.50940 \pm 0.00005) \times 10^{26} \text{ sec}^{-1} \text{ erg}^{-1}$$
$$\nu/E = (2.41814 \pm 0.00004) \times 10^{14} \text{ sec}^{-1} \text{ ev}^{-1}$$

de Broglie wavelengths, λ_D, of elementary particles[c]

Electrons

$$\lambda_{De} = (7.27377 \pm 0.00006) \text{ cm}^2 \text{ sec}^{-1}/\text{v}$$
$$= (1.552257 \pm 0.000016) \times 10^{-13} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (1.226378 \pm 0.000010) \times 10^{-7} \text{ cm (ev)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Protons

$$\lambda_{Dp} = (3.96149 \pm 0.00005) \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}/\text{v}$$
$$= (3.62253 \pm 0.00008) \times 10^{-15} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (2.86202 \pm 0.00004) \times 10^{-9} \text{ cm (ev)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Neutrons

$$\lambda_{Dn} = (3.95603 \pm 0.00005) \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}/\text{v}$$
$$= (3.62004 \pm 0.00008) \times 10^{-15} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (2.86005 \pm 0.00004) \times 10^{-9} \text{ cm (ev)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Energy of 2200 m/sec neutron

$$E_{2200} = 0.0252973 \pm 0.0000003 \text{ ev}$$

Velocity of 1/40 ev neutron

$$v_{0.025} = 2187.036 \pm 0.012 \text{ m/sec}$$

The Rydberg and related derived constants

$$R_\infty = 109737.309 \pm 0.012 \text{ cm}^{-1}$$
$$R_\infty c = (3.289848 \pm 0.000003) \times 10^{15} \text{ sec}^{-1}$$
$$R_\infty hc = (2.17958 \pm 0.00007) \times 10^{-11} \text{ erg}$$
$$R_\infty hc^2 e^{-1} \times 10^{-8} = 13.60488 \pm 0.00022 \text{ ev}$$

Hydrogen ionization potential

$$I_0 = R_H(hc^2/e)(1 + \alpha^2/4 + \cdots) \times 10^{-8}$$
$$= 13.59765 \pm 0.00022 \text{ ev}$$

[c] These formulas apply only to nonrelativistic velocities. If the velocity of the particle is not negligible compared to the velocity of light, c, or the energy not negligible compared to the rest mass energy, we must use $\lambda_D = \lambda_c[\epsilon(\epsilon+2)]^{-\frac{1}{2}}$, where λ_c is the appropriate Compton wavelength for the particle in question and ϵ is the kinetic energy measured in units of the particle rest-mass.

No significant modification whatever in any of our present output values would therefore have resulted.

VII. CALCULATION OF THE ATOMIC CONSTANTS AND CONVERSION FACTORS AS OF 1955

In order to calculate a useful table of atomic constants and conversion factors, from the adjusted values of the unknowns, α, e, N, and λ_g/λ_s, and their error elements, as given in Tables IX and X, it is necessary to combine these with certain auxiliary constants whose numerical values are in most cases known much more accurately than are the output values of the four unknowns. The less accurately known auxiliary constants are quantities whose methods of measurement render them in a practical sense statistically independent of the above four unknowns. Table XII lists these auxiliary constants most of which are identical with those used in DC 53. Two of them however merit brief discussion.

Velocity of Light

We have adopted the value and its standard error given by K. D. Froome[10] as the result of a set of ten measurements with a symmetrical free-space microwave interferometer with four electromagnetic horns operating at 24 005 Mc/sec. Because of diffraction, the velocity thus obtained was higher than the true free-space value by an amount dependent on the size of the horns and the spacing between them. The experiment was a preliminary one in preparation for a more accurate definitive experiment to be performed at 72 000 Mc/sec.

[10] K. D. Froome, Proc. Roy. Soc. (London) **A223**, 195–215 (1954).

Its purpose was primarily concerned with the use of the instrument under conditions of large diffraction correction (up to the equivalent of 100 km/sec), so that the accuracy obtainable in eliminating this effect could be assessed. Although even better accuracy can be anticipated for the final definitive experiment, it was possible in even these preliminary measurements to correct very satisfactorily for diffraction effects with highly consistent results for the different types of wavefront. The standard error of ±0.3 km/sec is stated by Froome to be the estimated error of a single observation, although the value obtained for the velocity depended on ten measurements, a number considerably in excess of that required to make the corrections for the diffraction effects. Hence this standard error of only one part per million is probably somewhat overestimated. The value obtained by Froome is in excellent agreement with the values obtained over long light paths with visible light waves by Bergstrand[11] in Norway and by Mackenzie[12] in Scotland. Both of these observers used Bergstrand's "Geodimeter," a method employing Kerr cell-modulated light beams. The relative uncertainty in the velocity of light, c, is probably now so small compared to the uncertainties in the output values of the present least-squares adjustment that it appears very unlikely that further improvements in our knowledge of it will make any significant change in those output values.

R_0, the Gas Constant per Mole (Physical Scale)

This is the least accurately known of the auxiliary constants (±41 ppm). Its numerical value is changed from the value given in DC 53 by reason of the recent change[13] in the definition of the Kelvin scale of temperature. The Tenth General Conference on Weights and Measures which met in Paris and Sevres during October, 1954 decided: "to define the thermodynamic scale of temperature by means of the triple point of water as fixed fundamental point, by assigning to it the temperature 273.16°K, exactly." This yields a new slightly different thermodynamic scale of temperature such

that the best value of the ice point is 273.15°K (instead of 273.16°±0.01°K as formerly).

All the other auxiliary fixed constants used in the present adjustment are unmodified, as to values or sources of the data, from those in DC 53 to which the reader should refer for such information.

The seven auxiliary constants in Table XII, to each of which a star is affixed, are the ones used in setting up the basic observational equations of Table II above. The remaining eight either enter the computations only for the purpose of computing the derived values of certain constants and conversion factors in Table XIII, *after* the least-squares adjusted values of the unknowns have been obtained, or are given simply for their intrinsic utility.

Throughout these tables, unless explicitly stated to the contrary, the physical scale of atomic weights is used because its definition is less ambiguous than that of the chemical scale. The chemical scale could be rendered not ambiguous by specifying a standard abundance ratio for the oxygen isotopes but no such action has, to our knowledge, been officially taken. R. T. Birge[14] has given the conversion factor $r = 1.000272$ ±0.000005 as the ratio of physical to chemical scales based on the assumed abundance ratio $O^{16}:O^{18}:O^{17}$ $= (506\pm10):1:(0.204\pm0.008)$, and this we have adopted in the present calculations. Alfred O. Nier[15] has discussed the variations in isotopic abundance of oxygen from various natural sources and the various resulting values of r which range from $r = 1.000268$ to $r = 1.000278$.

VIII. ACKNOWLEDGMENTS

[11] Eric Bergstrand, Arkiv Fysik 2, 119 (1950); 3, 479 (1951).
[12] I. C. C. Mackenzie, "The Geodimeter Measurement of the Ridgeway and Caithness Bases, 1953." Her Majesty's Stationary Office, 1954.
[13] E. C. Crittenden, Science 120, 1007 (1954).

[14] R. T. Birge, Repts. Progr. in Phys. VIII, 90 (1942).
[15] A. O. Nier, Phys. Rev. 77, 792 (1950).