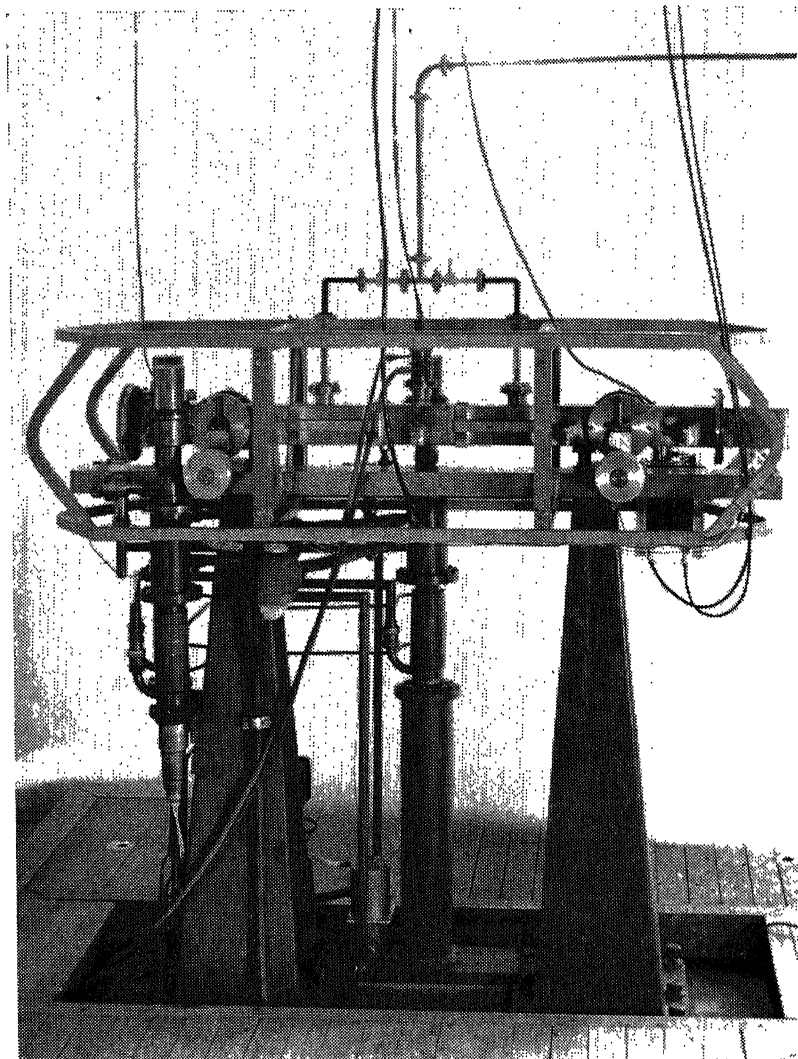

**INTERSCIENCE MONOGRAPHS
IN PHYSICS AND ASTRONOMY**

*Edited by R. E. MARSHAK
University of Rochester*

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The caesium clock of L. Essen at the National Physical Laboratory, Teddington, England; probably the world's most precise instrument.

THE FUNDAMENTAL CONSTANTS OF PHYSICS

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INTERSCIENCE PUBLISHERS, INC., NEW YORK
Interscience Publishers Ltd., London 1957



IIA Lib.

TO
PROFESSOR RAYMOND T. BIRGE

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Library of Congress Catalog Card Number 57-13013

INTERSCIENCE PUBLISHERS, INC., 250 Fifth Avenue, New York 1, N. Y.

For Great Britain and Northern Ireland:

INTERSCIENCE PUBLISHERS LTD., 88/90 Chancery Lane, London W. C. 2

PRINTED IN THE UNITED STATES OF AMERICA

Preface

Enormous strides have been made in the first half of the twentieth century toward the unification of many branches of physics and chemistry, once regarded as quite unrelated and distinct, into one body of well-organized knowledge. This unification is probably nowhere better reflected than in the history of the progress made toward improving the precision and consistency of our knowledge regarding the values of the fundamental physical constants and conversion factors. The number and the precision of the established theoretical relationships connecting these constants have also increased phenomenally. In fact a history of progress on the constants during the first half of the twentieth century is not very different from a history of physics itself during that period.

This book has been written with two primary objectives: (*a*) to give a complete survey of the present status of our knowledge of the fundamental constants and conversion factors of the physical sciences and to describe the modern precision experiments from which that knowledge is at present directly drawn, and (*b*) to present an account of the evolution of our knowledge of this subject through various degrees of experimental precision and theoretical sophistication in sufficient detail to permit the reader to appreciate the breadth and firmness of the entire experimental foundation. A substantial fraction of the world-wide research effort of physicists and chemists during the last half century has in fact been required to build that foundation. Most of the earlier and less precise experiments must of course be reviewed rather briefly. Care, however, has been taken to provide ample reference to the original sources so that the reader can look up omitted details for himself. The book has been written both for physics students at the graduate level and for professional physicists. No mathematical preparation beyond that required for graduate work in physics is presupposed.

The analysis of the data on the values of the atomic constants has relied heavily on the theory of least squares. Many physicists feel

quite unfriendly to the application of this branch of statistical theory to physical data. The famous Dutch physicist, H. A. Kramers, once said, "The theory of errors and least squares is like love—one cross word can spoil it all!" Nevertheless, we see no escape from it which is not subject to even worse objections. Actually most of the mistrust of least squares and error statistics, if carefully examined, is in reality mistrust of the data to which these doctrines are applied rather than mistrust of the doctrines themselves. Two examples will illustrate this:

It is related that a certain statistician sent 10,000 questionnaires to a randomly selected list of American citizens, requesting of each one their best estimate of the height of the Queen of Siam. Each report was also to be accompanied with the estimated standard deviation of the data furnished. Many of the answers attached error measures to the individual estimates as large as ± 50 per cent, but the statistician conscientiously took a weighted average of these data using, in accord with the accepted principles of error statistics, weights made inversely proportional to the square of the associated error estimate of each datum. Because of the very large number of independent estimates he came out with a height good to ± 0.5 per cent! There was only one trouble with the whole procedure—Siam didn't have a queen.

The second example concerns a certain retired sea captain who made his home in a secluded spot on the island of Zanzibar. As a sentimental reminder of his seafaring career he still had his ship's chronometer and religiously kept it wound and in good operating condition. Every day exactly at noon, as indicated on his chronometer, he observed the ritual of firing off a volley from a small cannon. On one rare occasion he received a visit from an old friend who inquired how the captain verified the correctness of his chronometer. "Oh," he replied, "there is a horologist over there in the town of Zanzibar where I go whenever I lay in supplies. He has very reliable time and as I have fairly frequent occasion to go that way I almost always walk past his window and check my time against his." After his visit was over the visitor dropped into the horologist's shop and inquired how the horologist checked his time. "Oh," replied he, "there's an old sea captain over on the other end of the island who, I am told, is quite a fanatic about accurate time and who shoots off a gun every day exactly at noon, so I always check my time and correct it by his."

We are indebted for this last story to Professor George Harrison of the Massachusetts Institute of Technology. Beyond the obvious

moral contained in both stories that no amount of statistics or replicated observations will yield reliable results from unreliable data, we believe the second yarn has a further value in that it may conceivably add a new word to our terminology, namely, "the Zanzibar." To commit a "Zanzibar" should henceforth convey a clear meaning to the reader of this book. It is a kind of error which he may be sure we have earnestly sought to avoid.

In an analysis of data, which may be based on least squares or any other analytic criterion, it is of utmost importance to assign weight to each datum in a consistent and equitable manner. The error measure associated with the result of an experiment is therefore just as important as the result itself. Furthermore the basis for the quotation of error measures must be uniform throughout. There are of course several such measures; e.g., probable error, "confidence limits" of error, standard error, mean absolute error. Because the root-mean-square, or standard error has a simple law of propagation which is not shared by other error measures except for the Gaussian, or normal, distribution, we have adopted it throughout this book. The meson data of Chapter 4 are an exception to this rule. Particularly with regard to meson lifetimes the literature is not clear whether probable errors or standard deviations are quoted, and the experimental data do not justify considering the assigned error measures as more than qualitative indications of accuracy. The choice that we shall use the standard error is, in some part, distinct from the question of how the accuracy of a measurement is to be determined. Standard errors either can be estimated from an analysis of the experimental situation and knowledge of how each component contributes to the uncertainty of the resultant measurement, or can be determined empirically by repeating the experiment several times and observing the distribution of the results. This latter method can, however, only detect the random errors of the experiment but cannot identify systematic errors. In practice both methods are combined, and the final assigned error is often strongly influenced by the experimenter's considered opinion of the results. If the experimenter is honest and unbiased there is no objection to this. In general each experiment must be finally reviewed by the analyst, who adds his considered opinion in an effort to place all the experiments on a more nearly uniform basis.

Whereas the precision of most of the experiments considered in this book is measured in parts per hundred thousand or parts per million,

the subject of the masses and lifetimes of mesons (Chapter 4) is hardly out of the early survey stage. The modern concepts of mesons and the recognition of the true complexity of the mass spectrum of fundamental particles is less than ten years old. The discussion of meson masses is therefore a subject unto itself. The errors involved are a factor of one thousand times larger than those associated with the "classical" atomic constants, and in many of the experiments there are certainly unidentified systematic errors. The situation is much less certain and much more fluid than the remainder of the book and is subject to alteration and modification much more rapidly. The field is at present so active that a new analysis would be required with each new issue of the *Physical Review*! The data are presented here as a tabulation of current results and as a possible source of material for future more detailed analysis. The table of Least-Squares Adjusted Values (Table 8-7) therefore omits all reference to mesons and hyperons in order to avoid giving an unwarranted aura of finality to the data. The data presented in Chapter 4 are summarized in Table 4-17.

Some readers accustomed to the MKS system of units may be disappointed to discover that our table of output values is not expressed in these units. All the disciplines of physics and chemistry meet and are represented in the fundamental constants and the truth is that the MKS has not been generally adopted in all these domains. One hesitates to express the normal mole volume of an ideal gas in cubic meters per kilogram molecule. Kilogram-molecule units for the gas constant, Avogadro's number, or the Faraday constant would seem equally unfamiliar and likely to be misunderstood. The MKS system is primarily an engineering system which may soon completely replace the FPS (or English) system. Its primary utility lies in the field of electrical engineering and classical electromagnetic theory. We have retained the cgs units because of their wide use in all fields of physics and chemistry. Those who prefer other systems of units may easily convert.

We wish to express our gratitude to the numerous research workers in many parts of the world (far too large a number to list here) who have been so kind as to keep us informed of their newly obtained results at the earliest possible moment. We are much indebted to Professor John Tukey of Princeton for much valuable advice and discussion on the topics of error statistics and least squares. We owe a great debt to Raymond T. Birge, whose pioneer work in this field of en-

deavor laid the foundation on which we have subsequently built. He was one of the first men to perceive the need for making from time to time broad general surveys and assessments of the state of our knowledge of the physical constants. His first paper of this kind published in 1929 set a noteworthy example of painstaking, careful research, based on a great many sources of information and carried out over a very broad range of research fields in physics and chemistry. The task was a severe one not only because of its sheer size but because there were huge discrepancies between sources of information and an enormous amount of patient effort was required to distinguish truth from error and to ferret out mistakes and oversights in this chaos. His kindly and constructive criticism and encouragement have been of inestimable value over a long period of years. It therefore is a pleasure to be able to express our homage and gratitude by dedicating this book to Professor Raymond T. Birge.

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August, 1957

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Contents

1. Introduction	1
1.1 Outline and Objectives.....	1
1.2 Physical Constants as Units.....	2
2. Arbitrarily Defined Physical Units and Standards	4
2.1 Length, Mass, and Volume.....	4
2.2 Time.....	5
2.3 Temperature.....	7
2.4 Electrical Units.....	9
2.5 Standard Atmosphere.....	11
3. Classical Measured Constants and Units	14
3.1 Newtonian Universal Constant of Gravitation, G	14
3.2 Acceleration of Gravity.....	17
3.3 Normal Mole Volume of an Ideal Gas; Gas Constant.....	18
3.4 Gas Constant.....	19
3.5 The Joule Equivalent.....	20
3.6 Electrochemical Determinations of the Faraday.....	21
4. Masses of Atoms and Mesons	29
4.1 Masses of Certain Light Atoms by Nuclear Reaction Energies.....	29
4.2 Masses and Properties of Light Mesons.....	32
4.3 Masses and Properties of K Mesons.....	62
4.4 Masses and Properties of Hyperons.....	78
5. History of the Atomic Constants	103
5.1 The Velocity of Light.....	105
5.2 Millikan's Oil-Drop Experiment.....	112
5.3 Harrington's Determination of the Viscosity of Air.....	115
5.4 Relationship of the Constant, e , to Other Atomic Constants.....	116
5.5 Ruled Grating Measurements of X-ray Wavelengths.....	118
5.6 Siegbahn's Scale of Wavelength; The X-Unit.....	121
5.7 Avogadro's Number by the XRCD Method and the Electronic Charge.....	126
5.8 The Chemical and Physical Scales of Atomic Weights.....	129
5.9 Experiments Bearing on e/m	130
5.10 J. A. Bearden's Measurement of the Refractive Index of X-rays in Diamond.....	142

5.11	Experiments Bearing on the Ratio, h/e	143
5.12	Other Experiments Bearing on Planck's Constant, h	154
5.13	Need for Critical Evaluations of Data on the Atomic Constants.....	158
5.14	Birge's Methods of Evaluating the Data on the Atomic Constants.....	159
5.15	Resolution of Discrepancies.....	160
	Addendum.....	178
6.	Postwar High-Precision Measurements.....	183
6.1	Development of New Techniques Yielding Increased Accuracy.....	183
6.2	The Velocity of Electromagnetic Radiation.....	183
6.3	Gyromagnetic Ratio of the Proton.....	188
6.4	Ratio of the Cyclotron Frequency of the Proton to Its Magnetic Resonance Frequency.....	189
6.5	The Fine Structure Separation in Deuterium.....	194
6.6	Ratio of Electron Magnetic Moment to Proton Magnetic Moment.....	197
6.7	The Hyperfine Structure Shift in Hydrogen.....	204
6.8	Precision Determinations of the Quantum Limit of the Continuous X-ray Spectrum.....	207
7.	The Method of Least Squares.....	222
7.1	The Basic Theory of Least-Squares Adjustment.....	222
7.2	Calculation of Standard Errors and Correlation Coefficients..	227
7.3	The Generalized Theory for Non-Gaussian Error Distributions.....	237
7.4	Specific Case of an Adjustment in Four Unknowns.....	240
7.5	The Standard Errors of the Residues of a Least-Squares Adjustment.....	244
8.	Least-Squares Adjustment of the Atomic Constants.....	247
8.1	Selection of Data for a Least-Squares Analysis.....	247
8.2	Preliminary Least-Squares Analysis.....	254
8.3	Analysis of the Preliminary Least-Squares Adjustment.....	258
8.4	Selection of "Best" Current Values.....	262
8.5	Output Values. Recommended (1955) Least-Squares Adjustment.....	265
	Author Index.....	272
	Subject Index.....	284

Introduction

1.1 OUTLINE AND OBJECTIVES

Our knowledge of the constants of physics has been greatly improved in the 25 years between 1930 and 1955, partly by reason of the development of new methods of measurement and the perfecting of new physical techniques and partly by the important advances in our understanding of the physical world achieved through research. Microwave resonance methods and atomic beam techniques are examples of important technical improvements which have contributed much since 1940. Our understanding of atomic and nuclear physics by reason of the development of the quantum theory through successive stages of refinement has greatly clarified relationships having to do with the interaction of electrons and radiation. Much stimulus for improvement has come during this period from critical studies of the physical constants undertaken by various authors who at various times have reviewed the consistency of the many experimental results in an effort to establish the most reliable values. The first of these reviews was a remarkable paper (1) by Raymond T. Birge in 1929 which opened this era of critical examination and improvement.

The accuracy of our knowledge of such constants as Avogadro's number, the electronic charge, Planck's constant, the velocity of light, or the fine structure constant of Sommerfeld has been greatly improved by new techniques which bear little relationship to the earlier and perhaps intuitively more direct measurements such as Millikan's oil-drop experiment or the studies of Brownian motion. Such earlier methods had great value for the progress of science and still possess historical importance for their role in the discovery and logical development of the concepts of atomic physics. They will be reviewed here because we cannot have faith in what we now know unless we see the path by which that knowledge was won.

But the earlier pioneer methods are now so greatly surpassed in accuracy by the more modern though frequently less direct methods that, although the earlier results are not inconsistent with the later ones, these alone are significant today in determining the numerical values of the physical constants.

Because of this situation this tract will concern itself with three objectives: (1) a brief introductory outline of the system of physical units and the standards set up to maintain them; (2) a sketch of the history of the progress of our knowledge of the general physical constants with special emphasis on the atomic constants, giving brief descriptions of both the earlier methods employed and the more modern methods now in use for their evaluation; (3) a detailed study as of 1955 of the status of our knowledge of the physical constants and a least-squares evaluation to obtain the best compromise values consistent with the entire body of present knowledge. These final output results are tabulated at the end of this text.

1.2 PHYSICAL CONSTANTS AS UNITS

When the science of physics was in its infancy arbitrary units were chosen, such as the kilogram, the meter, and the second; and standards were set up to maintain them. Although the motivation was commercial as well as purely scientific, no science of physical measurement could have been developed without this step. One of the important fruits of physical research has been the discovery that Nature herself has fundamental units such as the charge on the electron, the rest mass of the electron, Planck's constant of action, the speed of light.

In this connection it may be well to restate a postulate which R. C. Tolman clearly recognized but which is frequently overlooked or tacitly assumed. We shall call this the "postulate of the reproducibility of proper quantities." By this is meant that when a quantitative property of some fundamental system, such as the mass of a particular atom or one of its characteristic wavelengths, is observed in a Lorentz frame in which that system is at rest (called the "proper frame" of the system), we postulate that the same result will always be obtained. Nothing in our framework of well-established physical observations seems at variance with this postulate, and we shall therefore make it.

The thought lies close at hand that since Nature supplies us with

reliable and invariable units it might be well to abandon the earlier and more arbitrary artificial units completely. The convenience, the accessibility, and in many cases the superior precision of the arbitrary units make their complete abandonment extremely improbable in the foreseeable future. No one will care to check the accuracy of an ammeter by counting the number of electrons which flow in unit time through its windings. In spite of the very satisfactory accuracy which has recently been attained in measuring many of the natural constants, the artificial arbitrary standards of the cgs system are still superior in accuracy. The statement is true save perhaps for one exception—the meter bar, which, since the supplementary definition of the meter in terms of the wavelength of a certain line in the spectrum of cadmium in 1927, is no longer to be considered as a primary standard of length.

Even if such important practical considerations were ignored, we do not as yet know enough to select wisely the natural constants on which to base such a system. In the present state of our knowledge of physics there is in fact a great embarrassment of choice as regards natural constants that might be adopted as units of measurement. The mass of any one of a dozen or more “fundamental particles” might be chosen to replace the kilogram. As units of length any one of the famous hierarchy of four present themselves: The Rydberg wavelength, $R_\infty = 4\pi a_0/\alpha$; the Bohr radius, $a_0 = \hbar^2/(4\pi^2 m e^2)$; the Compton wavelength, $\hbar/(mc) = 2\pi\alpha a_0$; and the Lorentz radius of the electron, $r_0 = \alpha^2 a_0$. The speed of light could be combined with any one of these fundamental lengths to furnish a fundamental unit of time. Almost the only physical magnitudes about which there would be little doubt as to choice are the unit of electrical charge and the unit of velocity. For these the electronic charge and the velocity of light would certainly be indicated. Our present arbitrary standards, however, still afford a precision for defining velocity and charge many orders of magnitude superior to the accuracy with which the velocity of light and the electronic charge have been determined.

It is proper then to begin by outlining the base of our system of physical measurements in terms of its units, standards, and fundamental constants.

REFERENCE

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

Arbitrarily Defined Physical Units and Standards

2.1 LENGTH, MASS, AND VOLUME

In its original conception the meter was intended to be defined as one ten-millionth of the earth's quadrant on the meridian through Paris, and all units of volume were to be derived from it. It was planned that the unit of mass, the kilogram, should be identical to the mass of a cubic decimeter of water at its maximum density. The units of length and mass are, however, now defined independently of these conceptions.

The meter is defined as the distance between two engraved lines on a certain platinum-iridium bar, kept at the International Bureau of Weights and Measures at Sèvres near Paris, France, when the bar is supported in a definitely specified manner at the temperature of melting ice and at standard atmospheric pressure (760 millimeters of mercury). A supplementary definition of the meter in terms of the wavelength of a certain line in the spectrum of red cadmium light was adopted in 1927 by the Seventh General International Conference on Weights and Measures. The definition was based on the work (1) of Benoit, Fabry, and Perot in 1913 and is as follows:

$$1 \text{ meter} = 1,553,164.13 \text{ wavelengths} \quad (2-1)$$

The conditions of temperature, pressure, and humidity together with many specifications regarding the light source which emits the line must be fulfilled for the definition of equation (2-1) to hold accurately.

Several spectral lines emitted by various isotopically pure substances, Hg^{198} , Kr^{86} , Xe^{136} , or Cd^{114} have been studied and are recommended by different proponents as preferable to the cadmium red line of the present definition. However, as of 1955 no international action had yet been taken to replace that standard, since the best choice was not entirely clear (3).

The kilogram is independently defined as the mass of a definite platinum-iridium standard, the International Prototype Kilogram, also kept at the International Bureau of Weights and Measures. The liter is defined as the volume of a kilogram of water, at standard atmospheric pressure and at the temperature of its maximum density, approximately 4°C. On a level of sufficient precision this is an ambiguous definition, since it does not specify the isotopic constitution of the water. The meter is the fundamental cgs unit of length and area and of such volumes as are based on linear measurements. Note, however, that, since the liter is defined independently of the meter, a conversion factor relating the cubic decimeter to the liter must be established by physical measurement. Henning and Jaeger (2) have obtained a result which Guillaume (2a) has corrected upward 1 ppm in 1927. We adopt this value with somewhat increased standard error* because of the ambiguity of unspecified isotopic constitution.

$$1 \text{ liter} = 1000.028 \pm 0.004 \text{ cm}^3 \quad (2-2)$$

Thus the maximum density of water is

$$\delta_m = (1.000028)^{-1} = 0.999972 \pm 0.000004 \text{ kg} \cdot \text{dm}^{-3} \quad (2-3)$$

It was once customary to define 1 cc as liter/1000, whereas 1 cm³ is liter/1000.028, but because of the frequent confusion of cc with cm³, the Joint Committee for the Standardization of Scientific Glassware recommended in 1924 that the designation ml (for milliliter) be used in place of cc.

2.2 TIME

The second is the fundamental unit of time. To quote a recent report (3a) by E. C. Crittenden on the actions taken at the Tenth General Conference on Weights and Measures in Paris, October 1954, "the second will presumably be defined [by the standing International Committee without waiting for another conference] as the fraction, 1/31,556,925.975 of the tropical year 1900.0." Techniques now exist for controlling the frequencies of electrical oscillations by means of the natural frequencies of vibration of cer-

* Throughout this book we shall quote uncertainties in terms of the root-mean-square or "standard error." This, for reasons which we shall explain in Section 7.3, is preferred rather than the "probable error" or "mean absolute error."

tain molecules of which the ammonia molecule is one example. The three hydrogen atoms of the ammonia molecule form an equilateral triangle; the nitrogen atom is situated equidistant from the three hydrogen atoms but not in the same plane, so that the molecule has a tetrahedral structure. There are, however, two stable positions for the nitrogen atom, one on either side of the plane of the hydrogen atoms. Under suitable conditions the nitrogen atom may be made to oscillate back and forth between these two positions and the frequency of this oscillation may be very accurately measured and maintained.

A similar type of atomic clock makes use of the transitions in caesium between the hyperfine structure energy levels caused by the interaction between the electronic and nuclear spins. This hyperfine structure is the same phenomenon as that discussed in Section 6.7 in connection with the measurements of hyperfine structure splitting in hydrogen. The measured frequency of the central line of the hyperfine Zeeman pattern extrapolated to zero field is (3b)

$$\nu_0 = 9192631830 \pm 10 \text{ cycles sec}^{-1}$$

This represents an accuracy of one part in a thousand million and is by far the most accurate physical magnitude which has been measured.

A time standard based on this caesium resonance was suggested by H. Lyons (3c) and an early model was built at the United States National Bureau of Standards. A somewhat different type has been described by Zacharias, Yates, and Haun (3d). An improved resonance clock has recently been constructed at the National Physical Laboratory, Teddington, England, by Essen and Parry with which the above-quoted resonance frequency was determined. A photograph of this remarkable equipment appears as the frontispiece of this text.

These atomic clocks can furnish a more uniform standard of time than can be obtained from the rotation of the earth. The earth's rotation is known to have variations in rate of the order of 1 part in 10^8 by means of comparisons with sidereal time standards. The fact that the second is defined in terms of the tropical year *at the epoch 1900.0* indicates implicitly that the International Committee at the Tenth General Conference of 1954 was aware of the variability

of the year and that techniques exist whereby this variation can be measured. Hence the existence of time standards more accurate than the revolution of the earth in its orbit is implied. Without such standards it would be meaningless to refer the year to the epoch 1900.0 in preference to a current determination (i.e., epoch 1950.0 or 1956.0). There is another, and perhaps more compelling, reason for using atomic standards in place of astronomical ones. The unit of time can be determined by astronomical observation only after several years and hence we have our standards only in retrospect. The advantage of an atomic standard is that it enables frequency standardization to be effected in a few minutes, and the information can then be made available throughout the world almost instantaneously by utilizing the network of standard frequency transmission. At present the "Atomic Clocks" are used only to maintain a standard which is defined in terms of astronomical data; ultimately the unit of time will probably be defined directly in terms of the frequency of such atomic oscillations, but as yet (1955) no such action has been taken.

2.3 TEMPERATURE

The history of the measurement of temperature and the refinement of this concept from the early subjective stage based on sensations of hot and cold to the present definition of the absolute Kelvin or thermodynamic scale of temperature is outlined in many texts on thermodynamics. As an outgrowth of this history and the practical requirement of defining a number of convenient fixed points in different ranges of temperature for the purpose of calibrating thermometers we have two scales of temperature, namely, the International and the Kelvin, absolute, or thermodynamic scales. The reader should refer to the Smithsonian Physical Tables (4) or to the *Journal of Research of the National Bureau of Standards* (5) for the details of the definition of the 1948 International Temperature Scale. This is defined in terms of the platinum resistance thermometer and the electromotive force of a thermocouple over specified lower temperature ranges and in terms of Planck's black body law of radiation and certain fixed points at higher temperatures. The justification for such a scale is its convenience and reproducibility. The effort has been to define the International Temperature Scale in such a way as to make it as nearly as possible proportional

to Kelvin's absolute thermodynamic temperature scale. That temperature scale is the one which would result if the measurements could be made with a gas thermometer employing an ideal gas. It is the fundamentally significant physical scale and is independent of the properties of any particular substance. Kelvin himself urged that this absolute scale of temperature be defined by assigning a numerical value to the temperature of a single fixed point instead of the earlier method which defined two fixed points—the freezing and boiling points of water. With these earlier definitions the temperature of absolute zero is a matter of experimental determination, as in the centigrade or Fahrenheit scales. The Tenth General Conference on Weights and Measures in October 1954 decided (3a) “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° Kelvin exactly.” This yields a new thermodynamic scale of temperature numerically slightly different from the earlier one such that the best value of the ice point is $273.1500 \pm 0.0002^\circ$ K instead of $273.16^\circ \pm 0.01^\circ$ K as formerly. The reason for the choice of the triple point of water rather than the ice point is the fact that it is uniquely defined without need for specifying a pressure. The reason for the change in the numerical definition is asserted to be that it achieves a better coincidence between the thermodynamic and International scales. As a result of this change, however, the centigrade degree is no longer exactly equal to the Kelvin degree and we have 1° (Centigrade) = $0.999964 \pm 0.000036^\circ$ (Kelvin), and the boiling point of water is $100^\circ\text{C} = 373.1464 \pm 0.0036^\circ\text{K}$.

Studies of the absolute temperature of the ice point or the triple point of water have been made by Joule and Thomson (6) using their porous plug method, by Chappuis (7a), Berthelot (7b), Henning and Heuse (7c), and Roebuck (7d). R. T. Birge (see reference 1, Chapter 1) has summarized and critically examined these experiments in his 1929 review. More recently Roebuck and Murrill (8a), Beattie (8b), and Keesom and Tuyn (8c) have reviewed the entire situation including their own work on the temperature of the ice point. All such measurements involve the determination of empirical constants to describe the departure in the behavior of the working gas in a gas thermometer from that of an ideal gas in terms of which the thermodynamic scale is conceived.

2.4 ELECTRICAL UNITS

Up to January 1, 1948, two systems of electrical units, the "international" and "absolute" systems, coexisted for much the same practical reasons as the two temperature scales described in the preceding section.

The International Conference on Electrical Units and Standards of 1908 resolved that the magnitudes of the fundamental electrical units should be determined on the [absolute] electromagnetic system of measurement so as to be consistent with the physical cgs system of mechanical units. (In this absolute system an ampere is a unit of current such that given a circular coil of 1 cm radius a unit magnetic pole placed in its plane at the center would experience a force of 1 dyne for each radian of arc of the coil in which the current flows. Two magnetic poles each of unit strength separated by 1 cm exert on each other a force of 1 dyne. The absolute volt and ohm are defined so that the familiar formulas EI and RI^2 will yield the power in watts, i.e., 10^7 erg sec⁻¹.)

At the same time, however, this conference recommended—"as a system of units representing the above [absolute electromagnetic cgs units] and sufficiently near to them to be adopted for the purpose of electrical measurements"—the adoption of the International Ohm, Ampere, and Volt. The International Ohm was defined as the resistance of a column of mercury of specified physical dimensions. The International Ampere was defined in terms of the silver deposited per unit time on the cathode of the silver voltameter, in spite of the fact that it had been clearly shown that silver voltameters of various types might give consistently different results. The International Volt was defined such that 1 International Ampere flowing through 1 International Ohm would require 1 International Volt to maintain it. Under such circumstances 1 International Watt was by definition dissipated in the resistance. As might be anticipated, the International Watt did not turn out to be exactly equivalent to 10^7 erg sec⁻¹ of the cgs system.

The international system of units in its final form was maintained for 37 years, 1911 to 1948. Actually, in practice the International Units were maintained in the standardizing laboratories of various countries by means of banks of standard cells and banks of standard resistance coils which had been initially intercompared by the International Technical Committee and then carried by each dele-

gate back to the laboratories of the different countries. Only very infrequently indeed were the official definitions of the International Ohm and Ampere in terms of the mercury column and the electrolytic deposition of silver resorted to as a means of reestablishing the units. This was done only when suspicion arose of a drift in the mean value of the bank of resistors or of the bank of standard cells in a particular country. Thus in an operational sense the standards that were really maintained during this 37-year period were the ohm and the volt. With steady improvement in the precision of electrical measurements the advisability of return to the absolute cgs electromagnetic system of units became increasingly evident.

The history of this development and the eventual establishment of the electrical units in the absolute cgs system is well described in a circular of the U. S. National Bureau of Standards (9). The objective was chiefly accomplished in the United States and in England by the work of physicists at the National Bureau of Standards and at the British National Physical Laboratory. An important technical part of the problem involved the construction of coils of wire of very accurately established geometrical dimensions to be used either as self inductances, as mutual inductances, or as elements of precision current balances. During the period of coexistence of the two systems of units, conversion factors between the international and absolute units were frequently determined with ever-increasing precision. The techniques of establishment of the absolute units having finally advanced to a point where they compared favorably in precision with the reproducibility and constancy of the International Units (based on intercomparisons of standard cells and resistors), definite action was taken by the International Committee in October 1946 to abolish the International Units as of January 1, 1948, and to adopt the absolute system for the certification of all standard cells and resistors. In this action the following ratios were fixed as those governing the change:

$$1 \text{ mean international ohm} = 1.00049 \text{ absolute ohms} \quad (2-4)$$

$$1 \text{ mean international volt} = 1.00034 \text{ absolute volts} \quad (2-5)$$

Because of small drifts which had occurred with time, slight differences existed between the International Units as maintained in Washington and the Mean International Units referred to in equa-

tions (2-4) and (2-5). These differences were established by inter-comparisons at the International Bureau in Sèvres at or near the time of the change of units (January 1, 1948), and the ratio of the old units *as certified by the National Bureau of Standards* prior to January 1, 1948, to the absolute units used after that date are given in Table 2-1.

In interpreting the results of precision measurements involving the electrical units care must therefore be used to ascertain in what terms the standard cells and resistors were certified, since these may differ depending on where and when they were certified.

Table 2-1. Ratios of Washington International Electrical Units (as Certified Prior to 1948) to Absolute Electromagnetic Units

1 U.S. international ohm	= 1.000495 absolute ohms	(2-6)
1 U.S. international volt	= 1.000330 absolute volts	(2-7)
1 U.S. international ampere	= 0.999835 absolute ampere	(2-8)
1 U.S. international coulomb	= 0.999835 absolute coulomb	(2-9)
1 U.S. international henry	= 1.000495 absolute henries	(2-10)
1 U.S. international farad	= 0.999505 absolute farad	(2-11)
1 U.S. international watt	= 1.000165 absolute watts	(2-12)

2.5 STANDARD ATMOSPHERE

The Tenth General Conference on Weights and Measures in October 1954 ruled (3a) that the unit known as "normal atmospheric pressure" is to be accepted "for all purposes" as

$$1 \text{ atm} = 1,013,250 \text{ dynes cm}^{-2} \quad (2-13)$$

So defined this is a conventional constant, with no error. The earlier definition adopted in 1927 by the International Commission of Weights and Measures (10), "the pressure due to a column of mercury 760 mm high, having a mass of 13.5951 g cm⁻³ subject to a gravitational acceleration of 980.665 cm sec⁻² and equal to 1,013,250 dyne cm⁻²" is equivalent to that of (2-13) but is decidedly open to objection. As R. T. Birge points out (see reference 1, Chapter 1), no temperature is specified in the 1927 definition and the word "mercury" is technically superfluous. The definition is operationally open to even more severe criticism, since it specifies no simple method for reducing to standard atmospheres an actual barometer reading at an actual observed temperature. Since ρ , g ,

and h are specified in the definition, the atmosphere is uniquely defined as $(13.5951)(980.665)(76.0)$ dyne cm^{-2} or 1013250.144354 dyne cm^{-2} . Since the result of measurement is completely defined in the definition, the definition is not only operationally poor but operationally impossible—a measurement of the value of the atmosphere is meaningless. If the result is not the one quoted in the definition (or implied by it), it is wrong!

Geiger and Scheel's *Handbuch der Physik* (11) gave a definition of the normal atmosphere as

$$A_n = H_n \rho_n(\text{Hg}) \delta_m(\text{H}_2\text{O}) g_n = 1.01325_3 \times 10^6 \text{ dyne cm}^{-2} \quad (2-14)$$

in which

H_n = height of normal barometer = 76.000 cm.

ρ_n = normal specific gravity of Hg (at 0° C, A_n), referred to air-free water of maximum density.

$\delta_m(\text{H}_2\text{O})$ = maximum density of water.

g_n = normal gravity (as adopted by the Fifth General Conference 1913);

= $980.665 \text{ cm sec}^{-2}$.

R. T. Birge remarks (see reference 1, Chapter 1) that because it is operationally explicit the definition of equation (2-14) "seems preferable in spite of international agreement to the contrary." In his 1941 review (12) of the physical constants R. T. Birge, on the basis of later work on $\rho_n(\text{Hg})$ (equation (2-14)) arrived at a slightly lower value for A_n (defined according to his preference as in the equation (2-14) of $(1.013246 \pm 0.000004) \times 10^6$ dyne cm^{-2} . Small differences in ρ_n for natural mercury from different sources are not surprising since minute amounts of impurity may be present and variations in its isotopic constitution may also contribute a small amount of variation.

Birge's two values of A_n , as he prefers to define it, agree with the definition by international convention to within a few parts per million. The only physical constants in our Tables 8-6 and 8-7 dependent on the definition of the normal atmosphere are the gas constant, R_0 ; the Boltzmann constant, $k = R_0/N$; the four radiation and thermal constants dependent on R_0 or k ; the Sackur-Tetrode constant (dependent on $\ln R_0^{3/2}$); and the multiplier of the (curie constant) $^{\frac{1}{2}}$ to give magnetic moment per molecule, $(3k/N)^{\frac{1}{2}}$.

None of these constants are known at present with sufficient accuracy to warrant concern over the slight differences in the defined values of A_n .

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Classical Measured Constants and Units

3.1 NEWTONIAN UNIVERSAL CONSTANT OF GRAVITATION, G

This constant gives the gravitational attractive force, G , exerted between two unit masses separated by unit distance. If $M = (4/3)\pi R^3 D$ is the mass of the earth, R being its radius and D its mean density, then g , the acceleration of gravity at radius, R will be

$$g = GM/R^2 \quad (3-1)$$

Since both g and R can be determined, the determinations of G fall into two large classes: (1) Determinations of M with calculation of G from equation (3-1) or (2) direct determinations of G by measuring the gravitational force between two masses in the laboratory. The second method leads to the more accurate results.

Attempts to estimate M , the mass of the earth, have been of two kinds: (1) The mass of a mountain and the position of its center of gravity are determined from the density of its constituent rock and a survey of its shape. The deflection of a plumb line away from the vertical by reason of the attraction of the mountain is then determined. This was done, for example, by astronomical observations of the direction of the plumb line on two sides of the mountain in a determination in 1775 by Maskelyne, British Astronomer Royal on Mount Schiehallion in Perthshire. The estimated average density of the mountain was 2.5 g cm^{-3} , and the difference in direction of the two plumb lines was 12 sec of arc. From these results the earth's mean density was calculated to be 5.0 g cm^{-3} . This results in a value

$$G = 7.4 \times 10^{-8} \text{ dyne cm}^2 \text{ g}^{-2} \quad (3-2)$$

(2) In 1854 Airy made precise determinations of g , the acceleration of gravity, by means of a pendulum at the top and bottom of a

mine shaft. Let g_1 and g_2 be these two values. By this means he was able to compare D , the mean density of the earth, with d , the density of the surface constituents in the layer above his lower point of observation, and since d could be estimated from density determinations on samples of rock, D could be computed. If h is the depth below the surface at which g_2 is measured it can be shown that, to first approximation,

$$\frac{g_2 - g_1}{g_2} \cong \frac{h}{R} \left[2 - \frac{3d}{D} \right] \quad (3-3)$$

The value of d was found to be 2.5 g cm^{-3} and D , the mean density of the earth, was calculated to be 6.5 g cm^{-3} . This results in a value

$$G = 5.7 \times 10^{-8} \text{ dyne cm}^2 \text{ g}^{-2} \quad (3-4)$$

In view of the difficulties of estimating the mean density of a mountain or of an extended layer of the earth's crust from a few samples of rock it is not surprising that the above values are correct to only about 10 or 15 per cent.

Direct determinations of G by measuring the gravitational force attracting two masses in the laboratory have been made by two methods called static and dynamic.

1. In the static method the force of attraction of a stationary mass for a movable mass is measured either by the steady deflection of a torsion fiber or by the additional angular deflection of the beam of a chemical balance when a large mass is placed at a measured distance, close underneath a weight suspended from one arm of the balance. Many corrections in such experiments for the gravitational forces exerted by the stationary mass on other parts of the moving system are required, and very great care to eliminate air convection currents is necessary. Table 3-1 contains some results obtained in this way.

2. In the dynamic method, undoubtedly the most accurate of all, two masses in the shape of spheres situated at either end of a straight horizontal rod of light material are suspended by a torsion wire or fiber attached to the center of the rod. Two heavy stationary masses in the shape of spheres or cylinders with their centers of gravity in the same horizontal plane as that of the rod are arranged so that they can be placed in either of two positions: (a) with all four centers in line horizontally, and (b) with the horizontal line

joining the stationary masses, perpendicularly bisecting the line through the centers of the masses on the suspended rod. In position (a) the gravitational force supplies an additional restoring force to that of the suspension. In position (b) the gravitational forces reduce the restoring force. There will thus be a change in the period of free oscillation of the suspended system depending on the position of the stationary masses, which if determined yields a value of G , provided the masses and their complete geometry are accurately known. Corrections for the forces exerted on the oscillating bar are required. Probably the best determination not only by this

Table 3-1. Measurements of G , the Newtonian Universal Constant of Gravitation

Date and Experimenter	Method of Measurement	$G \times 10^8$ dyne cm ² g ⁻²
1798 H. Cavendish (1a)	Static torsion balance	6.754 \pm 0.041
1878 Cornu and Baille	Static torsion balance	6.618
1881 von Jolly	Chemical beam balance	6.465
1891 Poynting (1b)	Chemical beam balance	6.6984
1895 Boys (1c)	Static torsion balance	6.6576
1896 Braun	Dynamic torsion balance	6.658
1896 Eötvös	Static torsion balance	6.66
1898 Richarz and Krigar-Menzel	Chemical beam balance	6.684
1901 Burgess	Dynamic torsion balance	6.64
1930 Heyl (1d)	Dynamic torsion balance	6.670 \pm 0.005
1942 Heyl and Chrzanowski (1e)	Dynamic torsion balance	6.670 \pm 0.005

method but of all determinations made to date is that of Heyl and Chrzanowski at the U. S. National Bureau of Standards (1e) in which they obtained

$$G = (6.670 \pm 0.005) 10^{-8} \text{ dyne cm}^2 \text{ g}^{-2} \quad (3-5)$$

It is this value which, following R. T. Birge (see reference 12, Chapter 2), we adopt for recommendation.

Table 3-1 lists most of the precision determinations of G .

The constant G is a very exceptional universal constant in that no generally accepted theoretical formulas as yet relate it to any of the other constants or magnitudes of physics. A. Eddington has proposed a formula relating G to the total number of particles in the universe and to the ratio $e^2/(m_p + m_e)^2$, where e is the elec-

tronic charge and m_p and m_e are the masses of electron and proton. His formula also involved the exact whole numbers, 136 and 137, which played a prominent role throughout Eddington's theory. Eddington's ambitious attempt to construct a purely deductive theory "based on epistemological principles and not on physical hypotheses" by which he endeavored to *compute* the fundamental constants of nature without appeal to experimental observations can no longer be taken seriously. Eddington's relatively simple world picture assuming a closed universe with a finite constant number of elementary particles and including explicitly only the electron and the proton is certainly not in accord with our more recent observations.

3.2 ACCELERATION OF GRAVITY

The acceleration of gravity varies from point to point on the earth's surface because of (1) the centrifugal force accompanying the earth's rotation, (2) departures of the earth's figure from a perfect sphere, (3) local variations of density. The International Gravity Formula giving the dependence of the acceleration of gravity, g , at sea level on the latitude, ϕ , is given (2) as

$$g = 978.0495 \quad (3-6)$$

$$\cdot [1 + 0.0052892 \sin^2\phi - 0.0000073 \sin^2 2\phi] \text{ cm sec}^{-2}$$

The acceleration, g , falls off at the rate of $-0.0003086 \text{ cm sec}^{-2}$ per meter increase in altitude above sea level.

The standard value of gravity, or "normal gravity," g_n , adopted by the Fifth General Conference of 1913, was defined as (3)

$$g_n = 980.665 \text{ cm sec}^{-2} \quad (3-7)$$

It corresponds nearly to the value of g at latitude 45° and sea level.

Preliminary results of a precision redetermination of g at the International Bureau of Weights and Measures were reported at the Tenth General Conference (see reference 3, Chapter 2) on Weights and Measures, October, 1954. According to this new work it appears that the "Potsdam value" of gravity in use for the last 50 years may have been too large by 24 ppm. What revisions in the formula (3-6) may be required when definitive results of this new work are available are at present unpredictable.

3.3 NORMAL MOLE VOLUME OF AN IDEAL GAS; GAS CONSTANT

The normal mole volume of an ideal gas is the volume occupied by 1 g mole at 0°C under 1 atm pressure. R. T. Birge (see reference 1, Chapter 1) and later in more detail Birge and Jenkins (4) have given the theory connected with the determination of this constant.

For an ideal gas we have

$$pV = mR_0 T_0/M \quad (3-8)$$

where p = pressure, V = volume, m = mass in grams, M = gram molecular weight, T_0 = absolute temperature of the ice point (0°C), and R_0 = gas constant per mole. If $m/M = 1$ and $p = 1$, we get

$$V = V_0 = R_0 T_0 \quad (3-9)$$

where V_0 is the normal mole volume in the units chosen. We shall choose the conventional standard atmosphere of equation (2-13) as the unit of pressure. Some care is required in reading the research literature since it is customary for workers in the field of limiting gas densities to express their experimental results in terms of the 45° Atmosphere, based on a definition of the atmosphere using the value of g at 45° latitude in equation (2-14) rather than standard, $g_n = 980.665 \text{ cm sec}^{-2}$. ($g_{45} = 980.616 \text{ cm sec}^{-2}$.) It must also be recalled that there exist two scales of atomic weights, the chemical and the physical scales, as will be explained in Chapter 4. We shall use the physical scale of atomic weights in which the O^{16} isotope of oxygen has the atomic weight 16 exactly.

A real gas satisfies equation (3-8) only at zero pressure. From (3-8) and (3-9) we may write

$$(pV)_0 = mV_0/M \quad (3-10)$$

an equation holding for a real gas, where $(pV)_0$ is the limiting value of pV at zero pressure. Let us define the quantity, α , by

$$(pV)_0/(pV)_1 = 1 - \alpha \quad (3-11)$$

where $(pV)_1$ is the value of pV for 1 atm pressure. Let us also define three quantities, L , L_1 , and L_{lim} as follows:

$$L = m/(pV) \quad L_1 = m/(pV)_1 \quad L_{\text{lim}} = m/(pV)_0 \quad (3-12)$$

Since $m/V = \rho =$ the gas density, we have $L = \rho/p$ and $L = L_1 = \rho$ for $p = 1$. Thus L_1 is the actual density at 1 atm and $L_{1\text{lim}}$ is the density the gas would have at 1 atm, if it were an ideal gas. Both L and pV vary with p for a real gas and $L_{1\text{lim}}$ and $(pV)_0$ are the limiting values at $p = 0$ (obtained by extrapolation).

From equations (3-11) and (3-12)

$$L_1/L_{1\text{lim}} = (pV)_0/(pV)_1 = 1 - \alpha \quad (3-13)$$

From equations (3-10), (3-12), and (3-13)

$$V_0 = M/L_{1\text{lim}} = M(1 - \alpha)/L_1 \quad (3-14)$$

This equation is used to evaluate V_0 . The values of $(1 - \alpha)$ and L_1 may be obtained in the same or in separate investigations. Oxygen is always used as the gas to minimize the error in M . In a method due to Cragoe described by Birge (see reference 12, Chapter 2) the behavior of $pV/(pV)_1$ over a wide range of pressures (0 to 100 atm) is empirically fitted to a power law in the variable $(V_1/V - 1)$ by least squares, and this expression is extrapolated to zero pressure by putting $V = \infty$, from which Birge deduces

$$(pV)_0/(pV)_1 = 1 - \alpha = 1.0009535 \quad (3-15)$$

After a consideration of the work of several authorities, Baxter and Starkweather (1928) (5a), Batuecas (1935) (5b), Moles, Toral, and Escribano (1939) (5c), and Cragoe (1941) (5d), Birge (see reference 12, Chapter 2) arrived at the value

$$V_0 = 22414.6 \pm 0.9 \text{ cm}^3 \text{ atm mole}^{-1} \text{ (chem. scale)} \quad (3-16)$$

If one converts this to the physical scale of atomic weights using Birge's value of the conversion constant, $r = 1.000272$, one obtains

$$V_0 = 22420.7 \pm 0.9 \text{ cm}^3 \text{ atm mole}^{-1} \text{ (phys. scale)} \quad (3-17)$$

3.4 GAS CONSTANT

R_0 , the gas constant per mole follows directly from equation (3-9) and the value of T_0 , the ice point on the Kelvin scale. Using for the latter the most recent (1954) definition in which $T_0 = 273.15^\circ \text{K}$, we obtain

$$R_0 = V_0/T_0 = (8.31696 \pm 0.00034) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1} \text{ (phys. scale)} \quad (3-18)$$

3.5 THE JOULE EQUIVALENT

Two factors for converting magnitudes expressed in units of heat quantity (the cal_{15}°) to units of energy were distinguished by R. T. Birge in his 1941 review (see reference 12, Chapter 2), depending on whether the energy units were "international joules" or "absolute joules." The first, J'_{15} , which he gave as 4.1847 ± 0.0003 int-joule cal^{-1}_{15} , he called the "electrical joule equivalent," while the second, J_{15} , which he gave as 4.1855 ± 0.0004 abs-joule cal^{-1}_{15} , he called the "mechanical joule equivalent." The distinction was required because of the difference between the unit of energy, the int-joule on the International system of electrical units (Section 2.4) and the unit of energy on the cgs system, the abs-joule. Fortunately, the abolition of the international units in 1948 makes the distinction no longer necessary save that it must be borne in mind in analyzing determinations expressed in the earlier units. A new distinction, however, is pertinent as regards the units of heat quantity involved in this conversion factor. This comes about because of a recommendation by F. D. Rossini (6) to *define* a unit of heat quantity, the "thermochemical calorie" at the *exact* value:

$$1 \text{ thermochemical calorie} = 4.1840 \text{ absolute joules} \quad (3-19)$$

The thermochemical calorie is to be distinguished then from the older unit, the 15° calorie defined in terms of the heat capacity of water at 15°C .

Birge's 1941 evaluation of the Joule equivalent was based on three experimental sources, Jaeger and Steinwehr (1921) (7), Laby and Hercus (1927) (8), and Osborne, Stimson, and Ginnings (1939) (9). Laby and Hercus determined the "mechanical joule equivalent" directly without electrical energy measurements, whereas the other two investigations determined the thermal equivalent of a measured amount of electrical energy. No new work of this kind that has been done since 1941 is known to us, and we therefore adopt Birge's average value

$$J_{15} = 4.1854 \pm 0.0004 \text{ abs-joule } \text{cal}^{-1}_{15} \quad (3-20)$$

with a scarcely significant modification of one unit in the last place because of the change in the definition of the scale of absolute temperature effected at the 1954 Tenth General Conference (Section

2.3). The relation between Rossini's thermochemical calorie and $J_{15^\circ\text{C}}$ of equation (3-20) is then

$$\text{cal}_{15^\circ\text{C}} = 1.00034 \pm 0.00010 \text{ thermochemical calories} \quad (3-21)$$

3.6 ELECTROCHEMICAL DETERMINATIONS OF THE FARADAY

The Faraday, F , may be defined as that quantity of electricity whose flow is associated in electrolysis with an amount of aggregate chemical effect at each of the metallic-electrolytic boundaries in the electrical circuit equal in magnitude to a total of 1 g equiv, W , of the atoms or molecules entering into the reaction. If, as is frequently the case, several electrochemical reactions occur simultaneously at an electrode, Faraday's law will hold only if the total number of equivalents which have entered into reaction are used in the computation. If the product of one electrode in a cell is carried by diffusion or other means to the other electrode, the product may be wholly or in part restored to its original condition. Let us confine our attention for the moment to the simple case of a pure reaction at one electrode with which m grams of mass of a single reactant alone are involved as the sole product.

If a charge, Q , is associated in the electrolysis with m grams mass, then we shall have

$$F = Q/(m/W) = W/(m/Q) = W/E \quad (3-22)$$

Here m/W is the number of gram equivalents of the substance electrolyzed. The electrolytic experiment consists in measuring the mass, m , and the corresponding charge, Q . $m/Q = E$, is called the electrochemical equivalent, i.e., the mass associated in the electrolysis with unit charge. To obtain the Faraday, then, one must know not only the measured electrochemical equivalent, E , but also the gram equivalent, W , i.e., the quotient of the atomic or molecular weight by the valence. If the substance is univalent, the gram equivalent, W , is simply the atomic or molecular weight in grams. The number of atoms or molecules in a gram equivalent is N/v , where N is Avogadro's number and v is the valence. Each atom or molecule carries a charge, ve , where e is the electronic charge. Hence the total charge carried by 1 g equiv is $F = Ne$. It is this relationship between the Faraday and the two important atomic constants, N and e , which accounts for our interest in measuring F .

The value E is measured by means of an electrolytic cell, and the mass actually liberated or deposited per unit charge passing through the cell is unfortunately not in general exactly the true mass associated with the charge. This difficulty was clearly evident in 1910 from the work of the International Technical Committee in their efforts to establish a reliable procedure for reproducing the International Ampere with the silver voltameter (see reference 9, Chapter 2). In that device it is observed that "anode slime" is formed at the silver anode. To prevent this slime from getting to the cathode, where it might cause an error in the weight of the deposit, several arrangements have been used. In the Rayleigh form the anode is wrapped in filter paper. In the Richards form a porous procelain pot surrounds the anode to catch the slime while permitting the current to flow in the electrolyte in the pores. In the Kohlrausch form a glass cup catches the slime. In the Smith form a glass cylinder can be lowered at the completion of the run so as to fit tightly on the upper edge of the cup and prevent any spilling of material when the voltameter is disassembled. A siphon form was also tried in which the two electrodes were in separate vessels. The work of the committee showed clearly that voltameters of different types might give consistently different results. For instance the silver deposits in which filter paper was used were heavier by about 150 ppm. The 1910 committee was "of the opinion that the specifications for the silver voltameter should not be completed until further experiments shall be made." A great deal of work (10) was done at the U. S. National Bureau of Standards in response to this recommendation. A number of sources of error were tracked down and definite operating procedures for the silver voltameter were formulated, but the specifications were never officially adopted.

A study of this work on the silver voltameter clearly shows that the emphasis at that time was directed towards obtaining *reproducible* values of the electrochemical equivalent rather than a measurement of fundamental absolute significance for the purpose of determining the Faraday. This was natural since the objective at the time was to obtain specifications for a working procedure which would empirically define the ampere with as much reproducibility as possible. Three possible sources of error in the use of the silver voltameter for an absolute precision determination of the Faraday can be cited. (1) The measured gain in weight of the cathode may not be entirely due to deposited silver; there may be in the deposit

“inclusions” of other matter from the electrolyte. (2) Some of the deposited silver may redissolve in the electrolyte, or otherwise become detached, before weighing. (3) The deposited silver may not have quite the same isotopic constitution as that of “natural” silver on which the accepted value of the chemical atomic weight of that element (the value used in computing the Faraday) is based. When these voltameter experiments were performed isotopes had not yet been discovered, and the atomic weight of a naturally occurring element such as silver was thought to be an invariable quantity. It is now known that electrolysis may well introduce an appreciable change in isotopic constitution and thereby affect the mean atomic weight. Silver has two isotopes of almost equal abundance which differ in mass by about 2 per cent. This abundance ratio is the most favorable one for producing a systematic error through selective electrolytic separation. If in the cathode deposit the ratio of the light to the heavy isotope content is greater by 1 per cent than it is in the solution, the deposit will be 46 ppm lighter than if no such selective separation had occurred.

Iodine, on the other hand, occurs naturally in only one stable isotopic form, I^{127} , and it is possibly significant that the electrolytic Faraday determinations of G. W. Vinal and S. J. Bates made with the “iodine coulometer” (developed by E. W. Washburn and further perfected by one of his students, S. J. Bates) disagree with those of the silver voltameter by an amount considerably greater than the obvious experimental estimates of uncertainty would lead one to expect. Not only is this true but the iodine results are in much better accord with the consensus of the now considerably overdetermined remaining relevant data on the atomic constants than are the silver results. (See Section 8.3.) In view of the great advantages of the iodine coulometer over the silver voltameter it is most surprising that this method was not adopted in place of the electrolysis of silver for standardizing and reproducing the coulomb and the ampere by the International Technical Committee. These advantages, listed by S. J. Bates in his doctoral thesis, 1912 (11), were later fully substantiated by a study at the U. S. National Bureau of Standards done in 1914 by S. J. Bates and G. W. Vinal, entitled “Comparison of the Silver and the Iodine Coulometers and the Determination of the Value of the Faraday” (12). Bates in his thesis explains the working of the iodine coulometer as follows:

“An aqueous solution of potassium iodide to which iodine has

been added contains both iodide and tri-iodide ions. When a current of electricity is passed through such a solution the reaction



takes place in the direction from left to right at the cathode and in the reverse direction at the anode. Hence a cell in which the electrodes are surrounded by such a solution should contain the same total amount of 'free iodine' before and after the passage of an electric current. By separating the electrodes and the solutions surrounding them by a conducting solution of an iodide, the changes in the amounts of 'free iodine' at the two electrodes can be determined [by titration] and if the reaction is a perfectly clean-cut one, free from all disturbing side reactions, the results at the two electrodes should check each other. The iodine coulometer therefore contains within itself the proof of its own correctness, for if it can be shown that identical amounts of iodine are involved in the reactions at *both* electrodes under varying conditions of concentration and current density it will establish beyond question the fact that *the only reaction*, involving electricity, which occurs at the anode is that expressed by the equation (3-23). In this particular the iodine coulometer possesses an enormous advantage over the silver coulometer, for, as is well known, no such quantitative proof of the nature of the reaction is possible with the latter coulometer." Bates in his thesis compared the results of eight runs with two iodine coulometers in series and obtained an average deviation from the mean of each pair of results of only 20 ppm. He also compared the equality of the anode and cathode reactions in four runs and concluded, "The results show that, within the limit of error of the analysis the same amount of iodine is formed *from* iodide ions at the anode as is converted *into* iodide ions at the cathode."

He continues, "The iodine coulometer is, therefore, certainly free from any constant source of error amounting to more than 0.002 percent. The reproducibility of the reaction at the anode is all that could be desired and fulfills all of the requirements necessary for a trustworthy determination of the value of the Faraday within 0.005 percent."

In the Bureau of Standards comparison of the iodine and silver coulometers by Vinal and Bates the arithmetic mean deviation from the mean in six determinations of the ratio of iodine titrated to silver

deposited was 85 ppm, whereas for the same runs the ratio of iodine to quantity of electricity (as measured by standard cell and resistance) showed an arithmetic mean deviation from its mean value of 79 ppm. The ratio of silver deposited to quantity of electricity showed an arithmetic mean deviation from its mean value of 30 ppm. Thus the iodine coulometer was not quite as reproducible as the silver in these six runs. The two most approved forms of the silver coulometer, that of the porous cup and that of Smith, developed expressly to obtain high reproducibility, were used. However, the relative merits of the two coulometers for obtaining absolute accuracy in the determination of the Faraday must be clearly distinguished from their relative reproducibility. The Faraday values obtained by the two coulometers have recently been recalculated by G. W. Vinal (1949) and later (1951) corrected by J. A. Hipple for the new atomic mass of iodine with the following results:

Iodine Faraday = Ne'

$$= 9652.15 \pm 0.13 \text{ abs emu (g equiv)}^{-1} \text{ (phys. scale)} \quad (3-24)$$

Silver Faraday = Ne'

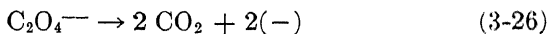
$$= 9651.29 \pm 0.19 \text{ abs emu (g equiv)}^{-1} \text{ (phys. scale)} \quad (3-25)$$

The difference between these two results, 0.86 ± 0.23 , is uncomfortably large in comparison to its expected standard error.

It was the effort to achieve better consistency in the entire picture of the determinations bearing on the atomic constants which first emphasized the above discrepancies and indicated that the iodine value was more likely to be the true one. As early as 1928 R. T. Birge (reference 1 Chapter 1) distinguished a systematic difference between what he called the "spectroscopic" and the "deflection" values of e/m , the charge-to-mass ratio for the electron. He at first thought that e/m might be different depending on whether the electron was "inside" an atom or "in free space." In reality his so-called spectroscopic measurements of e/m amounted to determinations of the ratio of the electronic and nuclear masses (by comparison of the Rydberg values for different light atoms), and a value of the Faraday constant had to be introduced to compute e/m from the spectroscopic data. This constant did not enter in deriving e/m from "deflection" measurements, however. Birge initially had preferred the silver value to the iodine value because of the great care

which had been expended to make the method highly reproducible and partly because it was then regarded as the basis for defining the international coulomb. It was first pointed out (in 1940) by one of the present authors that the apparent difference between the two sets of values of e/m might stem from a systematic error in the silver Faraday value—a suggestion which Birge (reference 12, Chapter 2) immediately accepted as plausible.

The most recent adjustment of the atomic constants still supports the view that the iodine value is more nearly correct than the silver value. The true source of the discrepancy is still obscure, however, in spite of two further investigations undertaken recently by A. F. Scott of Reed College, Portland, Oregon (13) and by D. N. Craig and J. I. Hoffman at the U. S. National Bureau of Standards (14) in an effort to clarify the matter. The first of these comprised a careful review of all methods to determine the amount of "inclusions" in the silver deposit of the silver coulometer and an attempt to estimate inclusions by means of radioactive tracers. The second was a redetermination of the Faraday with a coulometer employing the electrolytic oxidation of sodium oxalate in a supporting solution of sulfuric acid. The reaction



was carried out in a coulometer with a gold anode and a platinum cathode, the anode and cathode vessels being connected electrically through four siphons dipping into three beakers to isolate anode and cathode solutions. A weighed quantity of sodium oxalate was added to the anode vessel and, after the electrolytic oxidation, the residual oxalate was determined by titration with KMnO_4 . As Craig and Hoffman point out, the oxalate coulometer has the advantage that since a large fraction by weight of the measured substance, C_2O_4 , is oxygen, the errors resulting from uncertainties in atomic weight are minimized.

Seventeen determinations of the Faraday, twelve with a small and five with a large oxalate coulometer, were made with results ranging from about 9652.6 to 9651.1 absolute emu per gram equivalent on the physical scale of atomic weights. The mean of their oxalate values came out lower than the iodine Faraday. The difference,

$$0.8 \pm 0.32 \text{ abs emu (g equiv)}^{-1} \quad (3-27)$$

is still uncomfortably large relative to its expected standard deviation. The difference between the mean of the oxalate values and the silver values, on the other hand, is

$$0.06 \pm 0.36 \text{ abs emu (g equiv)}^{-1} \quad (3-28)$$

This very good agreement could indeed be considered as a verification of the silver value if no other information were available. Actually, however, a study of the sequence of results obtained in seventeen measurements by the oxalate method shows a decidedly marked trend downward when the results are arranged in the temporal order in which the measurements were performed. The first two measurements are in good accord with the weighted mean of the iodine values, whereas the mean of the last two measurements yields a value more than 1 absolute emu lower. This downward trend shows no suggestion of leveling off in the plot presented in Craig and Hoffman's paper (14). Such behavior strongly suggests an experiment "out of control." The reason is obscure but the suspicion is inescapable.

Craig and Hoffman conclude that the errors from the electrical measurements, and the determinations of mass of input oxalate and residual oxalate by titration are negligible, as are also errors from possible abnormal isotopic abundances of the carbon and oxygen isotopes. To establish this, mass spectroscopic studies were made of the carbon and oxygen used. Craig and Hoffman say that the uncertainties in the equivalent weight and purity of the sodium oxalate are their principal sources of error.

Further work on the iodine coulometer is reported to be in progress at the Rockefeller Institute for Medical Research, New York, New York, by D. A. MacInnes (15) using several improvements depending on newly developed modern techniques.

The high Faraday value obtained with the iodine coulometer has received support not only from indirect considerations of consistency with independent information from other physical measurements on the atomic constants but also from a direct measurement of the charge-to-mass ratio for protons. This was done at the U. S. National Bureau of Standards as the result of two admirable pieces of precision measurement involving the new proton resonance techniques which have revolutionized the stabilization and measurement of

magnetic fields. This will be described in Sections 6.3 and 6.4; we shall here only quote the result as

$$F = 9652.2 \pm 0.3 \text{ abs emu g}^{-1} \text{ (phys. scale)} \quad (3-29)$$

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Masses of Atoms and Mesons

4.1 MASSES OF CERTAIN LIGHT ATOMS BY NUCLEAR REACTION ENERGIES

The atomic masses of light nuclei on the physical scale of atomic masses have been obtained with great accuracy by the method of measuring the energy balance in nuclear reaction energies. The literature on this method has now become quite extensive (1). This method at the date of writing is probably more accurate for determining the relative masses of the lighter atoms than any mass spectrographic method and far more accurate than any of the older chemical methods. Consider a nuclear reaction



in which a bombarding particle, x , with measured kinetic energy, T_x reacts with a target nucleus, X (initially stationary). The final products of the reaction are a nucleus, Y , with measured kinetic energy, T_Y , of mass, M_Y , and a particle, y , with kinetic energy and mass, T_y and m_y . Since mass and energy are relativistically equivalent under the Einstein relation

$$(\text{Mass}) c^2 = \text{Energy} \quad (4-2)$$

the conservation of energy for the reaction (4-1) can be written

$$(T_x + m_x c^2) + (M_X c^2) = (T_Y + M_Y c^2) + (T_y + m_y c^2) \quad (4-3)$$

The net gain, in total kinetic energy associated with the product particles, relative to the total kinetic energy of the input or reactant particles is called the reaction energy balance or the Q of the reaction.

$$Q = T_Y + T_y - T_x = (M_X + m_x - M_Y - m_y) c^2 \quad (4-4)$$

If Q is positive the reaction is said to be exothermic or exoergic,

and the contrary reactions are called endothermic or endoergic. Clearly a study of such reactions with precision measurements of Q -values in terms of energy in electron volts affords a very sensitive method of determining mass differences between particles of nearly equal mass. The differences are relatively much smaller than the masses so that very moderate precision in the Q -value measurements is all that is needed to establish the masses with very high precision. More than one nuclear reaction may well be needed to yield enough simultaneous equations such as (4-4) to obtain the mass difference between a pair of particles as, for example, the neutron and the proton. However, a great number of nuclear reactions in the light elements have been precisely measured; so many in fact that the available information on nuclear Q -values

Table 4-1. Atomic Masses and Mass Ratios of Certain Light Atoms and Nucleons (Physical Scale).

Neutron	$n = 1.008982 \pm 0.000003$	(4-9)
Hydrogen Atom	$H = 1.008142 \pm 0.000003$	(4-10)
Deuterium Atom	$D = 2.014735 \pm 0.000006$	(4-11)
Atomic Mass of Proton	$M_p = H - Nm = 1.007593 \pm 0.000003$	(4-12)
Ratio, Hydrogen to Proton	$H/M_p = 1.00054461$	(4-13)
Atomic Mass of Deuteron	$M_d = D - Nm = 2.014186 \pm 0.000006$	(4-14)
Ratio, Deuterium to Deuteron	$D/M_d = 1.00027244$	(4-15)

affords a high degree of overdetermination for establishing mass differences of all the isotopes of all the light elements from the neutron through sulfur ($Z = 16$). Since this includes O^{16} , the isotope which by definition has atomic mass exactly 16 on the physical scale, the method affords an extremely precise set of atomic mass values good to a few parts in a million for all these light nuclei. This corresponds to determining the Q -values of the reactions with an accuracy of the order of 1 kv. Li, Whaling, Fowler, and Lauritsen in an important study in 1951 used the Q -values of 57 different nuclear reactions to establish a table of masses of 31 isotopes between $Z = 0$ (the neutron) and $Z = 9$ (fluorine). Van Patter and Whaling (2) in 1954 list separately all the Q -value determinations that have been made on no less than 474 nuclear reactions. About 600 independent Q determinations are tabulated by them. To the date of this writing no evidence has appeared significantly discordant with the mass values and their error measures as given by Li,

Whaling, Fowler, and Lauritsen, though some work claiming slightly smaller error measures has recently been published by Wapstra (3). The precision of the mass values given by Li, Whaling, Fowler, and Lauritsen is amply sufficient for the purpose we shall make of them in determining the general constants of physics. We therefore adopt the values given in Table 4-1, which are based on the work of these authors combined with Nm , the atomic mass of the electron, which is required in order to compute M_p and M_d , the atomic masses of the proton and the deuteron.

Atomic mass of electron, $Nm = 0.000549$ (physical scale) (4-5)

Information on the atomic mass of the electron is available from two independent sources (4).

1. The isotopic shift in the spectrum of hydrogen and deuterium caused by the effect known in German as the "mitbewegung des kerns" leads to an evaluation of the atomic mass of the electron. The wave number difference, $\tilde{\nu}_D - \tilde{\nu}_H$, between the $H\alpha$ and $D\alpha$ lines of the Balmer series is easily shown to be related to the atomic mass, Nm , of the electron* and to the atomic masses, H and D , of the hydrogen and deuterium atoms by the formula

$$Nm = \frac{DH(\tilde{\nu}_D - \tilde{\nu}_H)}{D\tilde{\nu}_D - H\tilde{\nu}_H} = \frac{DH\Delta}{(D - H)\tilde{\nu}_D + H\Delta} = \frac{DH\Delta}{(D - H)\tilde{\nu}_H + D\Delta} \quad (4-6)$$

where $\Delta = \tilde{\nu}_D - \tilde{\nu}_H$.

If we can neglect $H\Delta \ll (D - H)\tilde{\nu}_D$; $1 \ll 3700$, we have

$$Nm = \frac{DH}{D - H} \cdot \frac{\Delta}{\tilde{\nu}_D}$$

Using the Li, Whaling, Fowler, and Lauritsen values for H and D , a least-squares evaluation (4) of the data obtained by three independent sources, Shane and Spedding (5), C. F. Robinson (6), and R. C. Williams (7), leads to the atomic mass for the electron

$$(Nm)_{\text{spect}} = (5.4895 \pm 0.0008) \times 10^{-4} \quad (4-7)$$

* We reserve the letter, m , to designate the absolute mass of the electron in grams; Nm is the atomic mass of the electron on the physical scale of atomic masses.

2. The atomic mass of the electron may also be determined from a comparison of the "cyclotron frequency of the electron" with the "cyclotron frequency of the proton." Comparison of the results of Gardner and Purcell on the cyclotron frequency of the electron with those of Hipple, Sommer, and Thomas measuring the cyclotron frequency of the proton in magnetic fields standardized in both cases by the method of proton resonance leads to the mass ratio of electron to proton, $m/M_p = 5.44640 \times 10^{-4}$, and using 1.007593 for the atomic mass of the proton we find

$$(Nm)_{\text{Microwave}} = (5.48775 \pm 0.00013) \times 10^{-4} \quad (4-8)$$

which is smaller than $(Nm)_{\text{Spect}}$ by 0.0018 ± 0.0008 . We need not be concerned with this discrepancy here, however, because for our present purpose of calculating M_p and M_a only the first three digits need be known accurately, as given in equation (4-5). We shall return in Chapter 6 to a fuller description of such microwave and cyclotron resonance experiments.

4.2 MASSES AND PROPERTIES OF LIGHT MESONS

Since the prediction of mesons by Yukawa (8) and the discovery of the mesotron in cosmic rays in 1933-1936 (9), there has been a gigantic growth in the field of elementary particles. Not only does the number of well-established unstable particles grow at an alarming rate, but also the number of basically new and more powerful techniques for their production and study increases without apparent limit. The available fluxes and energy ranges of these particles increase steadily. In fact, the sheer concentration of physicists concerning themselves with these problems guarantees that the new developments and the basic understanding of the elementary-particle processes will be such that at any time it is hopeless to try to summarize a very large part of the information. Merely the delay in publication renders even a last-minute account obsolete by the time it reaches the readers. On the other hand, there is a limited number of what might be called the static properties of the particles—their masses, mean lives, and modes of the decay processes, spins, parities,* and charges, and perhaps their reactions when they

* The recent evidence on parity nonconservation in weak interactions is discussed in Sections 4.3a and 4.3g. The detailed consequences, both theoretical and experimental, of this evidence cannot be completely evaluated at this time. Although most of the effects in strong interactions must be negligible, the polarization effects may have been overlooked where the decay processes are involved.

come to rest. However, the production processes and their interactions will present a changing picture for a long time to come as higher energies and higher fluxes become available through technical advances. For this reason the reader is urged to consult the comprehensive study by Bethe and de Hoffmann of mesons and fields (10), as well as the excellent reviews on interactions of pions by Henley, Ruderman, and Steinberger (11) and by Gell-Mann and Watson (12).

There are several properties of particles that can be exploited to measure their masses. In general one selects a pair of easily measurable quantities that have different functional dependences on mass and velocity and that can be measured simultaneously—a technique that is crudely analogous to electric and magnetic analysis of particles in mass spectroscopy. Examples of what might be selected are: (1) The velocity as measured by time of flight or by the angle of its characteristic Čerenkov radiation. (2) The energy loss, which is very closely a function of the charge and velocity only. In a nuclear-emulsion track, the number of developed grains per unit length, the gap count, and the relative opacity of the track, each can be empirically related to the energy loss. Similarly, the drop count or density or the width of a cloud-chamber track, and the bubble density in a bubble-chamber track, are useful measures of ionization loss. (3) The total range, which will be shown to be proportional to the mass times a function of velocity and charge. (4) The curvature or angle of deflection in a magnetic field, as specified by the momentum and charge of a particle. (5) The multiple-scattering angle as observed in nuclear emulsion, which depends on the quantity Z/pv , where the charge is equal to Ze .

These general properties—which are, apart from velocity, all basically electromagnetic interactions—have been combined in all the possible combinations to identify various mesons, and a few combinations have proved remarkably precise.

The conservation of charge in all reactions assures that the specific charge on the meson will be an exact multiple of the electronic charge. This equality will be assumed throughout the discussion.

In addition, the kinematics of the reactions that mesons undergo furnish mass data. Recently, the mesic x-ray studies have developed to the point where precise limits on the masses have been found. These data will be reviewed.

A more or less arbitrary division is made between those rough,

early measurements that served chiefly to identify a new particle, and later, more precise mass measurements that may be regarded as of quantitative value. Many of the earlier mass determinations of the light mesons will, of course, be arbitrarily excluded; when possible some hint of the cause of any discrepancy will be made; for the most part, however, we shall concentrate on those measurements with comparable errors.

a. Pion Mass—Momentum and Range

The best values of the π - and μ -meson masses are obtained by a method stemming basically from the earliest cosmic-ray measurements, made with the cloud chamber by Brode and his collaborators (13). The simultaneous measurements of the momentum by curvature in a magnetic field and of the range in a known material are sufficient to fix the mass. With a controllable source of pions and their observation in nuclear emulsions, Gardner and Lattes (14) were able to do substantially the same experiment by defining the trajectories in the cyclotron field to fix the momentum of the pions and determine the range in nuclear emulsion. The range can be calculated from the energy-loss theory (15) and the composition of the emulsion. To the accuracy obtainable by this experiment, it is necessary to extend the emulsion proton range-energy measurements (actually range-velocity measurements) to match the velocities of the pions. This was done by Bradner *et al.* (16) in a separate experiment, and the early published pion mass (17) included the errors due to uncertainties in both experiments:

$$\begin{aligned}M_{\pi} &= (276 \pm 6) m \\M_{\mu} &= (210 \pm 4) m\end{aligned}\tag{4-16}$$

In the following, we will refer to meson masses in electron-mass units m .

In 1949, a group headed by Eugene Gardner began an experiment to reduce the large errors by an ingenious successive approximation that would eliminate the specific dependence upon the range-energy relations. This idea, chiefly due to W. H. Barkas, is as follows: One uses for range-calibrating particles protons with a velocity equal to that of the pions. These enter the emulsions in the same bombardment as the pions (see Figure 4-1). To a very

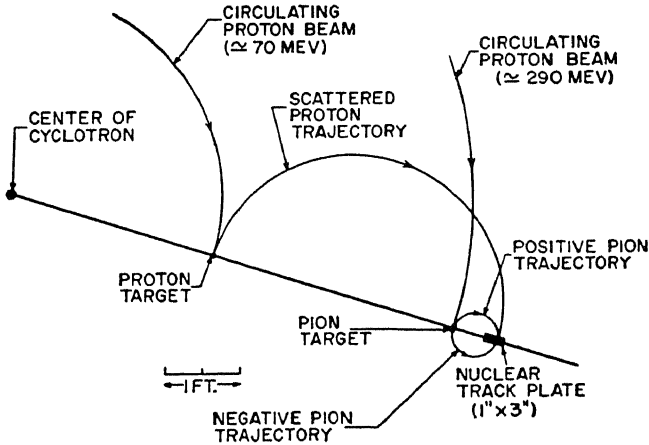


Figure 4-1. Plan view of the mass ratio experiment, from the work of Barka *et al.* (21). Either the proton target or the pion target is bombarded in two exposures made on the same nuclear plate.

good approximation the energy loss in condensed materials is a function only of the velocity of the particle. For a particle of velocity $v = \beta c$, and with charge Ze ,

$$dE/dx = -Z^2f(\beta) \tag{4-17}$$

where the energy $E = T + Mc^2 = \gamma Mc^2$, and $\gamma = (1 - \beta^2)^{-\frac{1}{2}}$. By integrating the energy-loss relation to find the range R for the particle that has an initial energy E , one has

$$R = \int_{Mc^2}^E \frac{dE}{Z^2f(\beta)} = \frac{Mc^2}{Z^2} \int_0^{\beta} \frac{\gamma^3 \beta d\beta}{f(\beta)} = \frac{M}{Z^2} G(\beta) \tag{4-18}$$

It follows that the quantity R/M is also a function of velocity only, so that for unit charges, if $P_\pi/P_p = M_\pi/M_p$,

$$\frac{R_p}{M_p} = G(\beta_p) = g\left(\frac{P_p}{M_p}\right) = g\left(\frac{P_\pi}{M_\pi}\right) = \frac{R_\pi}{M_\pi} \tag{4-19}$$

It therefore follows that if one chooses the momentum ratio in proportion to the estimated mass ratio, one obtains successively better estimates from the ratio of the ranges. The convergence to a sta-

tionary ratio in practice is rapid since there is an approximate power law

$$g(P/M) = \text{constant} \times (P/M)^q \quad (4-20)$$

where $q = 3.44 \pm 0.03$ in the interval used in this measurement.

By going one step further, one can solve for the mass ratio for a particular pair of particles i and j as follows:

$$\frac{M_{\pi_j}}{M_{p_i}} = \left[\frac{R_{p_i}}{R_{\pi_j}} \left(\frac{P_{\pi_j}}{P_{p_i}} \right)^q \right]^{1/(q-1)} \quad (4-21)$$

Fluctuations and straggling in the ranges will produce a distribution of inferred masses. The theory of the range straggling was developed by Bohr and others (18). Barkas *et al.* (19) have applied the theory to nuclear-emulsion range measurement, and the measured moments of the distribution are in good agreement with the theory. In this way, by basing the inferred mass upon the entire distribution, the observation of only a relatively small number of events can lead to a precise mean value for expression (4-21).

The dependence of equation (4-21) on q must disappear as one approaches the correct ratio of the momenta. The orbits are defined by measuring accurately the coordinates and the angle of entry of the pions and protons entering the emulsions. If the shape of the cyclotron field is known, these coordinates fix the momenta of the particles. The absolute field intensity does not enter since it cancels out in the ratio of the momenta.

Barkas, Smith, and Birnbaum investigated the detailed theory of the measurement and carried the work to completion several years after Gardner's death. Barkas, Smith, and Gardner (20) published a preliminary result

$$\begin{aligned} M_{\pi^+} &= (277.4 \pm 1.1) m \\ M_{\pi^-} &= (276.1 \pm 1.3) m \end{aligned} \quad (4-22)$$

In the reduction of the data, an appreciable spread in the distributions appeared that was traced to secondary pion sources; when these sources were shielded out or eliminated, analysis of 368 positive pions and 60 protons gave (21)

$$M_{\pi^+} = (273.3 \pm 0.2) m \text{ [PE]} \quad (4-23)$$

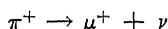
The final publication gives an excellent fit for the straggling dis-

tribution: for example, for the pions the range straggling amounts to a measured standard deviation (3.7 ± 0.4) per cent, and the calculated value is 3.7 per cent; the protons have a measured straggling standard deviation of (1.5 ± 0.3) per cent and a calculated standard deviation of 1.42 per cent. The standard deviation in equation (4-23) is based on the standard deviations of the distributions, and is equal to

$$\frac{1}{(q-1)} \left[\frac{(3.7)^2}{368} + \frac{(1.5)^2}{60} \right]^{\frac{1}{2}} \quad (4-24)$$

where $q = 3.44$ is the exponent of equation (4-20).

As an additional check on the range straggling, the range distribution of positive muons produced from the decay at rest of positive pions was also observed in the same plates: the decay reaction is



$$T_\mu = (4.123 \pm 0.016) \text{ Mev} \quad (4-25)$$

The standard deviation of this distribution is observed to be (4.6 ± 0.4) per cent, and calculated to be 4.3 per cent. The muon kinetic energy will be important in the section on muon masses.

To obtain a mass for the negative pion, one has two choices using the technique described by equations (4-19) and (4-21): the ratio of M_{π^-} to the proton mass, or the ratio of π^+ to π^- from the same target. The first method, based on 147 negative pions (21), gives the more accurate value for the π^- mass:

$$M_{\pi^-} = (272.8 \pm 0.3) m [\text{PIE}] \quad (4-26)$$

A small correction must be applied to equation (4-21) in the evaluation of the π^- mass to account for the difference in energy losses by positive and negative particles; this has been included in the result given in equation (4-26).

The masses of the π^- and π^+ are thus equal within the statistical errors.

The direct ratio obtained using positive and negative pions by the second method is

$$M_{\pi^+}/M_{\pi^-} = 1.0021 \pm 0.0018 [\text{PIE}] \quad (4-27)$$

This ratio should be insensitive to systematic errors.

b. π^- -Capture γ -Ray Spectrum

The study of the capture γ -ray energy spectrum produced when negative pions are absorbed at rest in hydrogen permits a precise mass measurement. The reaction studied is



One measures only one quantity, E_γ , which is related to the pion mass as follows:

$$E_\gamma = M_\pi c^2 - \frac{E_\gamma^2}{2M_n c^2} - \Delta(n, p)c^2 - \frac{\alpha^2 M_\pi c^2}{2} + \dots \quad (4-29)$$

On the right, the second term is essentially the recoil energy of the neutron; the third term represents the neutron-proton mass difference, which is known with high accuracy from other experiments (Table 4-1); the fourth term is the π -mesic K -shell binding energy; and α is the fine structure constant.

The method is as follows: 330-Mev protons which strike an internal target—usually chosen to be a heavy element (thorium)—produce negative mesons that are stopped in a high-pressure vessel filled with hydrogen. The resulting γ -rays form pairs in the converter of a pair spectrometer, and the energy of the pair fragments is determined by measuring their curvature in a magnetic field. A γ -ray spectrum consists of the monochromatic spike at ~ 130 Mev plus a distributed spectrum from the decay γ -rays from neutral mesons produced in the competing reaction



The continuous spectrum is analyzed below to determine the π^0 mass.

The mass of the π^- has been obtained in two experiments. Panofsky, Aamodt, and Hadley (22) obtain

$$M_{\pi^-} = (275.2 \pm 2.5) m \text{ [PF]} \quad (4-31)$$

with an energy resolution of approximately 9 per cent full-width at half-maximum. These measurements were continued by Crowe and Phillips (23), who obtain

$$M_{\pi^-} = (272.74 \pm 0.27) m \text{ [PF]} \quad (4-32)$$

with an energy resolution of approximately 1.6 per cent. In the process of analyzing the more accurate result it was discovered that a small ionization-loss correction of the outgoing pairs had been overlooked in the earlier measurement (22). Inclusion of this correction would increase the value of M_{π^-} given in equation (4-31) by approximately 2.6 m . A thorough reevaluation of this measurement has not been made, primarily because the main object of the later measurement was to eliminate errors this large by improving the basic resolution. Both pion-capture experiments are similar in many details. The major improvement results from a relocation of the spectrometer detectors to gain additional focusing properties against multiple Coulomb scattering in the converter.

The orbits that the positron-electron pair follow are calculated from measurements of the magnet field: in a nearly uniform field, the deviations from circular orbits are small, and by taking successive small segments of an arc one can find the orbit to high accuracy; if the field varies rapidly the problem is more difficult. The technique adopted by Crowe and Phillips (23) was to map the field in the median (horizontal) plane in the region of interest on a rectangular grid; the size of the grid was chosen small enough to allow numerical-interpolation methods to give the field to the desired accuracy at any arbitrary point. With this information, integration of the equations of motion for several cases in the median plane was performed, and the other orbits deviating from these central orbits were obtained by perturbation techniques. The converted particles share the total energy such that one member will have an approximately uniform energy distribution. On the way out of the converter they ionize and radiate. The sum of the energies of the pair thus has an apparent reduction of energy that varies with the depth of the point of production in the converter. The particles produced at various points on the converter and having various angles of multiple scattering will have energy aberrations. The change in the apparent energy for a given aberration is determined by the resulting horizontal displacement at the detector. These are obtained from the perturbation orbit calculations. The pairs enter the counter array, and are recorded in energy channels that are accurately defined by the Geiger-tube edges. Electron-positron coincidences are observed, and are sorted and combined such that the sum of the energies of the pairs falls into equal γ -ray

energy channels. All the instrumental effects were calculated and folded together to obtain the effective resolution. This can be compared to the observed width of the spectrum. The final spectrum and resolution are shown in Figure 4-2. The errors of the energy scale are shared equally among the statistics for the location of the

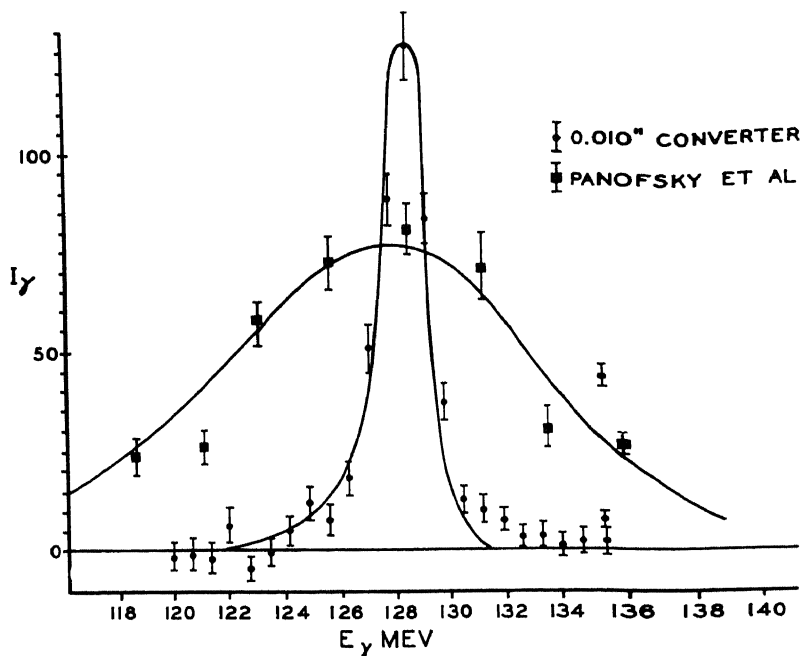


Figure 4-2. Capture spectrum measured by Crowe and Phillips (23). The high-resolution data as well as the early data from reference 22 are shown with their theoretical resolution curves.

mean, the accuracy of the field measurements, and all the uncertainties of the calculated aberrations.

c. π -Mesic X-Rays

The possibility of obtaining accurate meson-mass data as well as information about nuclear charge distribution from the study of the x-rays resulting from transitions of μ mesons between various Bohr orbits was first pointed out by Wheeler (24). The binding energy of a pion in the Bohr orbit of a nucleus (Z, A) with quantum numbers

n and l , calculated from the energy levels given by the point-charge Klein-Gordon relativistic wave equation together with various corrections, is

$$M_{\pi'} c^2 \frac{Z^2 \alpha^2}{2} \cdot \frac{1}{n^2} \left[1 + \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{l + 1/2} - \frac{3}{4} \right) + \dots \right] \quad (4-33)$$

where $M_{\pi'}$ is the reduced mass of the pion and the nucleus. The radius R_{π} of the mesic Bohr orbit will be well within the K -shell electron radius but well outside the nuclear radius R_0 for the lighter element series chosen for this measurement:

$$\begin{aligned} R_{\pi} &= \left(\frac{m n^2}{M_{\pi}} \right) \frac{a_0}{Z} \doteq \frac{n^2}{(M_{\pi}/m) \alpha^2} \left(\frac{r_0}{R_0} \right) \frac{R_0}{Z} \\ &\doteq \frac{n^2 (137)^2 2.82 R_0}{273 \times 1.25 A^{1/3} Z} \doteq n^2 \left(\frac{155}{A^{1/3} Z} \right) R_0 \end{aligned} \quad (4-34)$$

Pi-mesic x-rays were first observed by Camac *et al.* (25). An experiment was done by Stearns *et al.* (26) on the Carnegie Tech. synchrocyclotron by observing the discontinuity of the absorption coefficient for π -mesic x-rays with cells of various materials. For example, a π^- -meson beam is stopped in a phosphorus target and the x-rays from the $4F-3D$ transition are counted with a broad-resolution NaI scintillation crystal spectrometer. Absorption cells containing a series of neighboring elements are inserted, and it is observed that there is a sharp break in the absorption coefficient between Ce and Pr. Therefore it is inferred that the absorption edge for Ce is below the energy of the phosphorus transition. By using the energy-level equation (4-33) for the mesic x-ray energy and making a suitable correction for the vacuum polarization (27), one can obtain directly the limits for the mass of the pion. Corrections to the point-charge Klein-Gordon equation due to finite nuclear size, nuclear polarization, and electronic screening are found to be less than 10 ev in the cases considered. The energy shifts due to pion-nucleon interactions have been observed (26); for these transitions, however, this correction is entirely negligible. Table 4-2 shows the actual targets and absorption-edge limits that have been established.

The uncertainties of the limits thus obtained are extremely small. The locations of the K -edges are known to high precision. As an additional verification, the absorption cells were checked directly

Table 4-2. Mesic X-Ray Upper and Lower Limits on the π^- -Meson Mass.

Transition	K-Absorption Edges ^a	Vacuum Polarization	Mass Limit
P: $4F-3D$	Above Cc 40.440 ± 0.006 keV	+0.100 keV	$\geq (272.2 \pm 0.03) m$
Al: $4F-3D$	Below Sb 30.489 ± 0.004 keV	+0.065 \pm 0.003 keV	$\leq (273.51 \pm 0.04) m$
K: $4F-3D$	Below Hf 65.347 ± 0.003 keV	+0.190 \pm 0.010 keV	$\leq (273.52 \pm 0.04) m$
$\therefore (272.2 \pm 0.03) m \leq M_{\pi^-} \leq (273.51 \pm 0.04) m$			

^a See reference 28.

by Shacklett and DuMond (28) to assure that no chemical effects (~ 10 ev out of 50 keV) might have been overlooked. The accuracy of these measurements far exceeds the spread between the limits.

The number of transitions has not been exhausted as yet. It appears, however, that the intensities of mesic x-rays are not yet sufficient to allow more precise determinations by, for example, curved-crystal spectrometry methods.

d. π^+ Lifetime

The decay in flight of π^+ mesons spiraling in a magnetic field can be observed by measuring the ratio of the numbers of particles that survive in a spiral over several radians. Pions are lost by decay to muons in the reaction (4-25). Recent measurements by Steinberger (29) show that π - β decay occurs less than 6×10^{-4} of the time. Richardson (30) and Martinelli and Panofsky (31) obtained mean lives for the positive and negative pions. The quantities measured were the mean lives in number of revolutions N in the cyclotron magnetic field, where the mean proper life is

$$\tau_{\pi} = \left(\frac{2\pi}{\omega}\right) R = \left[\frac{2\pi}{(eH/mc)}\right] \left(\frac{M_{\pi}}{m}\right) N \quad (4-35)$$

Notice that by expressing the result in terms of the number of turns the result does not have any pion-energy dependence or time-dilation factor. Richardson (30) obtained from 48 events

$$N_{\pi^-} = (1.53 \pm 0.44) \text{ revolutions [SD]} \quad (4-36)$$

or

$$\tau_{\pi^-} = \left(1.04 \begin{array}{c} +0.30 \\ -0.21 \end{array} \right) \times 10^{-8} \text{ sec [SD]} \quad (4-37)$$

Martinelli and Panofsky (31) obtained from 230 events over 720°

$$N_{\pi^+} = (2.84 \pm 0.20) \text{ revolutions} \quad (4-38)$$

giving

$$\tau_{\pi^+} = \left(1.93 \begin{array}{c} +0.22 \\ -0.25 \end{array} \right) \times 10^{-8} \text{ sec [SD]} \quad (4-39)$$

(Both of these mean-life measurements have been recalculated from the lifetime in revolutions, the measured magnetic field, and the pion-mass value adopted later.) These measurements included a solid-angle calibration by means of α particles in the identical geometry. The small number of events and the possibility of missing tracks in the low-yield plates made this an extremely difficult experiment.

The decay of the π^+ to a μ^+ meson has been observed by Wiegand *et al.* (32) by allowing pions to stop in a scintillator. Each event was identified by the muon- β^+ decay pulse. The delay between the entering π^+ and the characteristic 4.2-Mev μ^+ has been measured by photographing the pulses on an oscilloscope and comparing the delay to a known frequency oscillator. A total of 1419 pulses was observed, giving, corrected for background (~ 10 per cent),

$$\tau_{\pi^+} = (2.60 \pm 0.13) \times 10^{-8} \text{ sec [SD]} \quad (4-40)$$

554 muon pulses were resolved from the pions into the differential time distribution shown in Figure 4-3. From these data, Wiegand obtains

$$\tau_{\pi^+} = (2.56 \pm 0.14) \times 10^{-8} \text{ sec [SD]} \quad (4-41)$$

These pulses are distributed over ~ 7 mean lives and have a negligible background (~ 1 pulse). The dominant uncertainties of this measurement are ~ 2 per cent for measuring the pulse separation and ~ 4 per cent for the statistical error. This experiment was repeated by Jakobson *et al.* (33). In connection with improvement in the pion-counting techniques by delayed coincidences they scaled

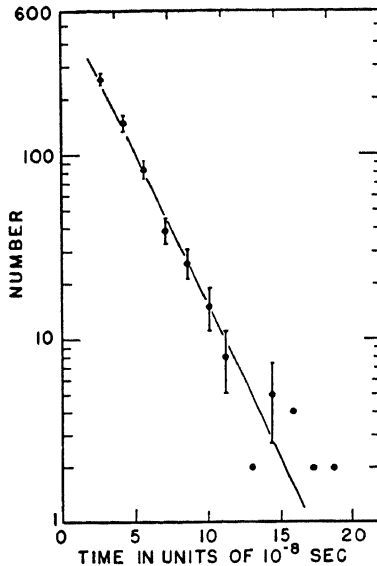


Figure 4-3. Differential time distribution of muon pulses obtained by Wiegand (32).

the delayed coincidences and calibrated the lengths of the cable delay on an oscilloscope to ~ 0.5 per cent. Their result,

$$\tau_{\pi^+} = (2.54 \pm 0.11) \times 10^{-8} \text{ sec [SD]} \quad (4-42)$$

is based on 5641 mesons, and agrees well with earlier work, although the measured background of accidental events was ~ 20 per cent of the maximum rate. Kraushaar (34) has also measured the lifetime of the π^+ . The final result, based on 670 resolved $\pi\text{-}\mu\text{-}\beta$ events, gave

$$\tau_{\pi^+} = (2.53 \pm 0.10) \times 10^{-8} \text{ sec [SD]} \quad (4-43)$$

Lederman *et al.* (35) were able to measure the π^- lifetime by the decay in flight of pions in a cloud chamber, by observing the fractions of decays in which the angle between π and μ tracks was greater than 5° . Correcting for the number that decay with angle less than 5° and for the contamination of muons and electrons in the beam, they obtained

$$\tau_{\pi^-} = (2.72 \pm 0.25) \times 10^{-8} \text{ sec} \quad (4-44)$$

The ratio of the π^- to the π^+ decay periods was measured by reversing the cyclotron magnetic field. For a lifetime ratio they obtained

$$\tau_{\pi^-}/\tau_{\pi^+} = 1.01 \pm 0.14 \quad (4-45)$$

Durbin, Loar, and Havens (36) have also measured the lifetime of the π^+ and π^- mesons by observing the attenuation by decay in flight over a path length of ~ 75 inches. By counting a total of 39,000 π^+ mesons and 54,000 π^- mesons, they obtain

$$\tau_{\pi^-} = (2.55 \pm 0.19) \times 10^{-8} \text{ sec} \quad (4-46)$$

$$\tau_{\pi^+} = (2.44 \pm 0.18) \times 10^{-8} \text{ sec} \quad (4-47)$$

The errors are divided among five sources, so that without more information about possible systematic errors which may be correlated in the results [equations (4-46), (4-47)], we obtain the ratio

$$\tau_{\pi^-}/\tau_{\pi^+} = 1.04 \pm (\sigma \leq 0.11) \quad (4-48)$$

The standard deviation of this ratio is probably somewhat smaller than the value 0.11 which is calculated on the assumption of independent errors in the positive and negative mean-life measurements.

Table 4-3. Pion Mean Lifetimes

No.	Value (10^{-8} sec)	Method	Reference
1	$\tau_{\pi^-} = 1.04$ $+ 0.30$ $- 0.21$	Spiral (360°) plates; 48 events (scanning losses appreciable)	30
2	$\tau_{\pi^+} = 1.93$ $+ 0.22$ $- 0.25$	Spiral (360° and 720°) nuclear plates; ~ 230 events (scanning losses probably underestimated)	31
	$\tau_{\pi^+} = 2.29$ $+ 0.87$ $- 0.50$	Spiral (360° only) plates; 241 events	
3	$\tau_{\pi^+} = 1.65 \pm 0.33$	Delayed coincidences; 57 events (preliminary)	34
	$\tau_{\pi^+} = 2.53 \pm 0.10$	Differential data; 670 events	
4	$\tau_{\pi^+} = 2.60 \pm 0.13$	Delayed coincidences; 1277 pulses (integral data)	32
	$\tau_{\pi^+} = 2.56 \pm 0.14$	Differential data; 557 pulses	
5	$\tau_{\pi^+} = 2.54 \pm 0.11$	Delayed coincidences; 5641 counts (background $\sim 20\%$ minimum)	33
6	$\tau_{\pi^-} = 2.72 \pm 0.25$	Cloud chamber; ~ 188 events	35
	$\tau_{\pi^+} = 2.70 \pm 0.30$	$\tau_{\pi^-}/\tau_{\pi^+} = 1.01 \pm 0.14$	
7	$\tau_{\pi^-} = 2.55 \pm 0.19$	Decay over variable path	36
	$\tau_{\pi^+} = 2.44 \pm 0.18$	$\tau_{\pi^-}/\tau_{\pi^+} = 1.04 \pm 0.11$	
Average of Nos. 3-7:		$\tau_{\pi^-} = (2.56 \pm 0.05) \times 10^{-8}$ sec	

The combination of Nos. 3 to 7 of the pion-lifetime measurements shown in Table 4-3 gives the following mean lifetime:

$$\tau_{\pi} = (2.56 \pm 0.05) \times 10^{-8} \text{ sec} \quad (4-49)$$

e. π^0 Mass

The absorption reaction at rest in hydrogen



provides a monochromatic beam of π^0 's. The π^0 velocity causes both a Doppler shift and an angular aberration of the emitted γ -rays. Both have been measured. The spectrum of the π^0 has been determined by Panofsky *et al.* (22) and the location of the end points or the width gives a $\pi^- - \pi^0$ mass difference, as follows: If the velocity of the π^0 is βc , the spectrum of γ -rays is a uniform distribution from

$$E_{\gamma} = \frac{1}{2} M_{\pi^0} c^2 (1 - \beta)(1 - \beta^2)^{-\frac{1}{2}} \quad (4-50)$$

to

$$E_{\gamma} = \frac{1}{2} M_{\pi^0} c^2 (1 + \beta)(1 - \beta^2)^{-\frac{1}{2}} \quad (4-51)$$

The width ΔE_{γ} is the momentum of the π^0 :

$$\Delta E_{\gamma} = 2\beta(M_{\pi^0} c^2 / 2)(1 - \beta^2)^{-\frac{1}{2}} \equiv P_{\pi^0} c \quad (4-52)$$

If $\Delta(n, p)$ is the neutron-proton mass difference, then

$$\begin{aligned} M_{\pi^-} - M_{\pi^0} \\ = \Delta(n, p) + \frac{1}{2} \frac{(M_p + M_{\pi})}{[M_{\pi} - \Delta(n, p)]} \frac{\Delta E_{\gamma}^2}{M_{\pi} c^4} - \frac{\alpha^2 M_{\pi}}{2} + \dots \end{aligned} \quad (4-53)$$

Even a small mass difference results in a large energy broadening. Panofsky *et al.* (22) observed a width of (31.4 ± 4.0) Mev, and found

$$M_{\pi^-} - M_{\pi^0} = (10.6 \pm 2.0) m \text{ [PF]} \quad (4-54)$$

The minimum correlation angle between the two emitted γ -rays in the reaction (4-30) is

$$\theta_{\min} = \cos^{-1}(2\beta^2 - 1) \quad (4-55)$$

The mass difference can be written in terms of the velocity of the π^0 :

$$M_{\pi^-} - M_{\pi^0} = \Delta(n, p) + (\beta^2/2)[M_{\pi^-} + (M_{\pi^-2}/M_{\pi})] + \dots \quad (4-56)$$

Chinowsky and Steinberger (37) have measured the angular correlation of the γ -rays, and, after folding in their angular resolution, they find the mass difference

$$M_{\pi^-} - M_{\pi^0} = (8.8 \pm 0.6) m \text{ [SD]} \quad (4-57)$$

The errors of the measurements of the mass difference are mainly statistical.

Measurements of the Panofsky type [equation (4-53)] were repeated with the Liverpool pair spectrometer by Kuehner, Merrison, and Tornabene (37a) with a result

$$M_{\pi^-} - M_{\pi^0} = (9.0 \pm 0.3) m \text{ [SD]} \quad (4-58)$$

By using the pion mass we shall adopt later, we obtain

$$M_{\pi^0} = (264.27 \pm 0.32) m \text{ [SD]} \quad (4-59)$$

f. π^0 Lifetime

Anand (38) summarized the evidence on the π^0 lifetime.

The internal pair conversion of π^0 's permits an observation of very short lifetimes. The reaction

$$\pi^0 \rightarrow e^+ + e^- + \gamma \quad (4-60)$$

was calculated by Dalitz (39) to have a branching ratio of 1.24 per cent. Lindenfeld, Sachs, and Steinberger (40) have observed that the π^0 decays into a γ -ray and an electron positron pair

$$\left(\begin{array}{c} 1.45 \\ -0.45 \end{array} \begin{array}{c} +0.80 \\ -0.45 \end{array} \right)$$

per cent of the time. Anand (38) has traced the narrow-angle pairs to their origins in the vicinity of cosmic-ray stars in emulsions; and by observing the gap in the tracks between the star and the pair origin, he observed a mean gap distribution corresponding to a mean life of

$$\tau_{\pi^0} = \left(\begin{array}{c} 5.0 \\ -2 \end{array} \begin{array}{c} +5 \\ -2 \end{array} \right) \times 10^{-15} \text{ sec} \quad (4-61)$$

The unresolved pairs can be compared to approximately twice-minimum ionizing star prongs; and it is found that the probability that they have the same gap distribution—i.e., zero lifetime—is less than 0.1 per cent.

Harris, Orear, and Taylor (38a) have studied the gap distribution of π^0 pairs produced by the decay of K_{π^2} mesons (see Section 4.3). Their results indicate a mean gap of 0.02 ± 0.16 micron, which corresponds to a significantly lower mean life than Anand's previous limits. There is no lower limit on the lifetime, and the upper limit corresponds to a mean life

$$\tau_{\pi^0} < 4.0 \times 10^{-16} \text{ sec} \quad (4-61a)$$

The probability is $\sim 1/30$ that the mean life is greater than 10^{-15} sec.

g. Parity and Spin of the Pion

The parity (41) of the negative pion is known to be odd from the following consideration: In the reaction



the conservation of angular momentum and parity places a restriction on the states of the $(\pi^- + d)$ system. Most of the time the meson drops into the K -shell, and since the orbital angular momentum of the pion is zero and the pion spin will be shown to be zero, the total angular momentum is equal to the spin of the deuteron. The only allowed final state of the two neutrons is thus a 3P_1 with odd parity. In order to conserve parity, since the deuteron is in an even-parity state, the pion must have an odd intrinsic parity if the reaction (4-62) is allowed.

From the γ -capture experiment, Panofsky (22) has inferred that this is the case. The rate of occurrence is measured relative to the radiative capture reaction as follows:

$$\frac{\text{Rate } (\pi^- + d \rightarrow 2n + \gamma)}{\text{Rate } (\pi^- + p \rightarrow n + \gamma) + \text{Rate } (\pi^- + p \rightarrow n + \pi^0)} \quad (4-63)$$

$$= 0.30 \pm 0.05$$

where the number of pions stopping is the same for deuterium and hydrogen under identical bombardment conditions. Thus,

$$R = \frac{\text{Rate } (\pi^- + d \rightarrow 2n)}{\text{Rate } (\pi^- + d \rightarrow 2n + \gamma)} = 2.4 \pm 0.6 \quad (4-64)$$

Neutrons from this reaction were later observed directly by Chinowsky and Steinberger (42). The ratio was measured to be

$$R = 1.5 \pm 0.8 \quad (4-65)$$

Recent pair-spectrometer results from Liverpool give (37a)

$$R = 2.35 \pm 0.35 \text{ [SD]} \quad (4-65a)$$

From the study of the interaction of pions with deuterium together with the measurements of pion production in proton-proton collisions, it is possible to measure the spin (43) of the positive pion.

The total cross section for the reactions

$$\sigma_{\pi^+,d} (p + p \rightarrow \pi^+ + d) \quad (4-66)$$

$$\sigma_{p,p} (\pi^+ + d \rightarrow p + p) \quad (4-67)$$

can be related by the principle of detailed balancing (44):

$$\frac{(2I_{\pi^+} + 1)(2I_d + 1)}{2P_{p,p}^2} \sigma_{p,p} = \frac{(2I_p + 1)^2}{P_{\pi^+,d}^2} \sigma_{\pi^+,d}, \quad (4-68)$$

where $P_{\pi^+,d}$ and $P_{p,p}$ are the center-of-mass momenta of the $(\pi^+ + d)$ and $(p + p)$ systems, respectively. Measurements of the production processes were made by Cartwright *et al.* (45). The π^+ interaction with deuterium was observed by Clark *et al.* (46) and by Durbin *et al.* (47). The results are given in Table 4-4. By comparing $\sigma_{\pi^+,d}$ directly with the inverse reaction $\sigma_{p,p}$, the unknown spin factor is found. The region of overlap is limited owing to the ranges of pion and proton energies available to the experimenters. Interpolation is made by using the experimental excitation function (52). The result is clearly that the spin factor $(2I_{\pi^+} + 1) = 1 \pm 10$ per cent; hence, $I = 0$.

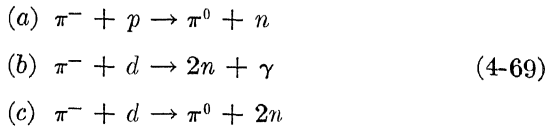
The charge symmetry of nuclear forces ($n-n = p-p$) is well established, for example, from the energy levels of mirror nuclei (10, 44). For this reason, it follows that the positive and negative pions have the same spin and parity. More generally, there is evidence for charge independence of nuclear forces ($n-n = n-p = p-p$); and specifically, the pion-production reactions and pion-nucleon interactions satisfy charge independence (10). The π^0 would thus have the same spin and parity as the charged pions. The spin and parity of the π^0 meson are not easily measured directly. Yang (53) showed that since the π^0 decays into two γ -rays, the spin must be even-

Table 4-4. Pion Spin—The Total Cross Sections for the Pion Production and Absorption Reactions

The absorption cross sections have been converted to $\sigma_{\pi^+,d}$ with equation (4-68). To compare the production and absorption cross sections, multiply each of the $(\pi^+ + d \rightarrow p + p)$ entries by $(2I_{\pi^+} + 1)$. The value of the spin is solved for each pair of measurements with approximately equal pion energy in the center of mass.

No.	T_{π} (Mev)	$\sigma_{\pi^+,d}$ from $p + p \rightarrow \pi^+ + d$ (millibarns)	$\frac{\sigma_{\pi^+,d}}{(2I_{\pi^+} + 1)}$ from $\pi^+ + d \rightarrow p + p$ (millibarns)	Ref.	Spin
a	21.5	0.269 ± 0.026	...	48	$a + b = 0.05 \pm 0.11$
b	22.7	...	0.284 ± 0.05	46	$a + c = 0.30 \pm 0.09$
c	25.0	...	0.22 ± 0.02	47	$b + d = 0.22 \pm 0.11$
d	22.3	0.184 ± 0.06	...	45	$c + d = 0.02 \pm 0.16$
e	53	...	0.97 ± 0.10	47	$e + f = 0.00 \pm 0.06$
f	63	1.23 ± 0.07	...	49	
g	72	1.54 ± 0.16	...	50	
h	76	...	1.39 ± 0.23	51	$g + h = 0.07 \pm 0.10$
i	93	2.1 ± 0.2	...	50	
j	94	...	2.04 ± 0.22	51	$i + j = 0.04 \pm 0.07$

integral, i.e., 0, 2, 4, etc. The parity, on the other hand, seems to be odd. The argument is weaker than for the charged meson because it depends on the relative rates for the reactions



If the π^- and π^0 have the same parity, the last reaction is allowed only if the final neutrons are in a 3P state and the π^0 in a P state relative to the center-of-mass system. Since the energy available is small, this effectively constitutes a strong selection rule against the π^0 reaction (c). If the parities are different, the two neutrons can be in a 1S state. Here the phase space factor reduces the reaction by about 1/20. The rate observed by Chinowsky and Steinberger (54) is

$$R = \frac{\text{Rate } (\pi^- + d \rightarrow 2n + \pi^0)}{\text{Rate } (\pi^- + d \rightarrow 2n + \gamma)} = -0.0034 \pm 0.0043 \tag{4-70}$$

The expected ratio would be $\sim 0.05 \pm 0.02$ with opposite parities, the uncertainty arising from the error of the $\pi^- - \pi^0$ mass difference (4-57). The error of the expected ratio can be further reduced from their value using the new mass difference (4-58). It therefore seems likely that the parities are the same.*

h. μ^+ Mass

The cosmic-ray information on muon masses obtained by Fretter (55) and by Retallack and Brode (56) was collected in 1949 (13). The cloud-chamber technique was used, and in one of the several modifications there was a magnetic field over the top chamber

* It should be noted that the intrinsic parity of a particle does not have a unique meaning; rather, one must define the parity relative to a standard, (54a), e.g., the proton can be defined to be even. The neutron is defined to have the same parity as the proton in the convention adopted here. The opposite convention—taking the neutron and proton to have opposite parities—results in having the π^- even and the π^0 odd. It can be shown that the choice of convention cannot basically effect, for example, the current models for pion-nucleon interactions. However, for the decay of K mesons, the second definition leads to changes in assignment, but they do not result in any different conclusions concerning the θ - τ “paradox,” etc.

where the curvature and hence the momentum of the entering muon could be measured. A series of absorber plates was placed in a second chamber where the same muons stopped. From the momentum and range, in his analysis of 78 events selected from three different experiments, Brode (13) obtained an average muon mass

$$M_{\mu} = (215 \pm 2) m \text{ [PE]} \quad (4-71)$$

Ascoli (57) has measured the range and momentum of 48 cosmic-ray muons, from which he obtains the mass

$$M_{\mu} = (207.4 \pm 2.4) m \text{ [PE]} \quad (4-72)$$

Barkas *et al.* (21) have measured the mass ratio of the pion to the muon as part of the experiment described for the pion-proton mass ratio, and obtained

$$M_{\pi^+}/M_{\mu^+} = 1.321 \pm 0.002 \text{ [PE]} \quad (4-73)$$

From this mass ratio and the π^+ mass obtained in the pion-proton ratio (4-23), one obtains

$$M_{\mu^+} = (206.9 \pm 0.4) m \text{ [PE]} \quad (4-74)$$

The most accurate determination of the μ^+ mass is obtained from the π - μ decay. From the kinematics, if one assumes zero rest mass for the neutrino, the mass difference is

$$M_{\pi} - M_{\mu} = \frac{2(M_{\pi}/M_{\mu})(p_0/c)}{1 + (M_{\pi}/M_{\mu})} \quad (4-75)$$

Birnbaum (21) has measured the momentum p_0 of the μ^+ coming from the decay of the π^+ in a nuclear-emulsion experiment. He measured the momenta and the ranges of the muons coming from those pions that stopped in the production target. Only those muons are chosen that have a momentum less than p_0 by the amount corresponding to the small energy loss in the target. These particles can be compared with muons from pions that have stopped and decayed within the emulsion. The comparison is made over as narrow an interval as possible in order to minimize the errors due to uncertainties in the range-energy relation in emulsions. For the absolute momentum one needs to know the magnetic field intensity; Birnbaum measured this with a nuclear-resonance technique. The momentum he obtains is

$$p_0 = (29.80 \pm 0.04) \text{ Mev}/c \text{ [PE]} \quad (4-76)$$

By combining this momentum and equation (4-73) for the ratio in (4-75), one obtains

$$M_{\pi^+} - M_{\mu^+} = (66.41 \pm 0.07) m \text{ [PE]} \quad (4-77)$$

The π^+ mass from the earlier pion-proton measurement (4-23) combined with this mass difference gives

$$M_{\mu^+} = (206.9 \pm 0.2) m \text{ [PE]} \quad (4-78)$$

It should be mentioned that although the accuracy of this value is considerably better than that obtained with the π^+/μ^+ ratio (4-73), it does depend on assuming the neutrino rest mass to be zero. If one assumes the neutrino of μ decay to have the same rest mass as the limit found for neutrinos of nuclear β decay (58), the change in muon mass given in (4-78) is not significant. However, if one assumes that the neutral particle may not be the same as the neutrino of ordinary β decay, it is possible to obtain an indication of its mass. The accuracy of such a determination is poor because the neutral particle mass must be calculated from the differences between meson masses. The most probable value of the neutral particle mass is $1.4 m$ but a zero mass is only slightly less probable. The probability is 0.33 that the mass exceeds $7.9 m$ and the 95% confidence limit is $0 < M_\nu < 11 m$.

The kinetic energy of the decay muon is determined to be

$$T_\mu = (4.123 \pm 0.016) \text{ Mev [PE]} \quad (4-79)$$

assuming a zero-rest-mass neutrino. If this is not assumed, the value is

$$T_\mu = (4.12 \pm 0.02) \text{ Mev [PE]} \quad (4-80)$$

i. μ - β Decay

The β decay of the positive muon has been studied by many observers (59-61). The β spectrum in the reaction

$$\mu^\pm \rightarrow \beta^\pm + \nu + \bar{\nu} \quad (4-81)$$

has an end point (total energy) E which is $[(M_\mu c^2/2) - (m^2 c^2/2M_\mu)]$ if the neutral particles are neutrinos. The most accurate determination of this end point is obtained by Sagane *et al.* (59),

$$E = (52.8 \pm 0.2) \text{ Mev} \quad (4-82)$$

giving

$$M_\mu = (206.6 \pm 0.8) m \text{ [PE]} \quad (4-83)$$

The experiment has been repeated by the same group and new results will appear soon.

The shape of the μ - β decay spectrum is of interest because it will provide a stringent test of the hypothesis that all β -decay processes have the same coupling scheme. If this is assumed to be the case, μ - β decay should provide additional data to determine the relative sizes of the interactions. At this time the experimental results are no longer in violent disaccord, and it is clear that when the different experimenters have published their results the situation will be improved.

The limits on the neutrino masses involved in μ - β decay are not sufficiently accurate to compare with nuclear β -decay information. No analysis of the recent studies has yet been reported.

j. μ^- Mass

The negative muon can be observed only when a negative pion decays in flight, so that ratio experiments analogous to those for the μ^+ are not possible. Lederman *et al.* (35, 62) observed the decay in flight of π^- 's in a cloud chamber that was in a magnetic field. They obtain from the momentum measurement a mass difference

$$M_{\pi^-} - M_{\mu^-} = (66.3 \pm 1.8) m \quad (4-84)$$

The negative-muon mass obtained with this difference and the pion mass [(4-26) or (4-32)] is

$$M_{\mu^-} = (206.5 \pm 1.8) m \quad (4-85)$$

k. μ -Mesic X-Rays

The mesic x-ray experiment was done with μ^- mesons by Koslov *et al.* (63). By using K -edge filters analogous to those discussed for pions, they obtained limits that are summarized in Table 4-5.

The energy levels are calculated with an analogous Dirac energy-level solution. In equation (4-33), M_π is replaced by M_μ , and l by $l \pm 1/2$. Vacuum-polarization corrections (27, 68) and finite-nuclear-size corrections (69) (necessary only for carbon) are accurately taken into account. If one uses the best π - μ difference [equation (4-77)] and assumes that the positive and negative meson masses are identical, one has the results expressed for both particles in Table 4-6. From this it is seen that the limits obtained from mesic x-rays just overlap each other.

Table 4-5. Mesic X-Ray Upper and Lower Limits on the μ^- -Meson Mass

Transition	K-absorption edges	Vacuum polarization	Mass limit	Reference
C: $2P-1S$	Below Ir 76.123 \pm 0.015 kev	+0.38 kev	\leq (208.95 \pm 0.04) m	64, 65
P: $3D-2P$	above Pb 88.015 \pm 0.002 kev	+0.325 \pm 0.016 kev	\geq (206.77 \pm 0.04) m
Si: $4F-3D$	Above Cd 26.713 \pm 0.006 kev	+0.045 kev	\geq (206.47 \pm 0.04) m	66, 67
\therefore (206.77 \pm 0.04) $m \leq M_{\mu^-} \leq$ (208.95 \pm 0.04) m				

Table 4-6. Pion- and Muon-Mass Summary

Limits obtained from mesic x-rays are compared with other measurements. The π - μ difference [equation (4-77)] has been used to convert pion measurements to muon values, and vice versa. All errors are standard deviations. Values are quoted in electron-mass units m .

π	μ		Method	Reference (this paper)	Ref.
$272.2 \pm 0.03 - 273.51 \pm 0.04$	$205.8 \pm 0.10 - 207.10 \pm 0.11$		π -mesic x-rays	Table 4-2	26
$273.18 \pm 0.11 - 275.36 \pm 0.10$	$206.77 \pm 0.04 - 208.95 \pm 0.04$		μ -mesic x-rays	Table 4-5	63
$\therefore (273.18 \pm 0.11) m \leq M_{\pi} \leq (273.51 \pm 0.04) m$ $(206.77 \pm 0.04) m \leq M_{\mu} \leq (207.10 \pm 0.11) m$					
$(\pi^+) \quad 273.34 \pm 0.33$	206.93 ± 0.35		Plate experiments	Eq. (4-23)	21
$(\pi^-) \quad 272.8 \pm 0.45$	206.3 ± 0.47		Plate experiments	Eq. (4-26)	21
$(\pi^-) \quad 272.74 \pm 0.40$	206.33 ± 0.41		π^- -capture spectrum	Eq. (4-32)	23
273.34 ± 0.13	206.93 ± 0.13		Mesic x-rays (combined)	Eq. (4-87)
273.27 ± 0.11	206.86 ± 0.11		Adopted value	Eqs. (4-89), (4-90)

The values of the x-ray limits given in Table 4-6 differ slightly from those published. The published lower limit was based on the experimentally determined lead K edge measured in 1927 by Mack and Cork (65) with an estimated error of ± 0.07 per cent. However, a more accurate value of the K edges can be found by using the measurements of the L edges and the K_{α} lines. As a result of re-

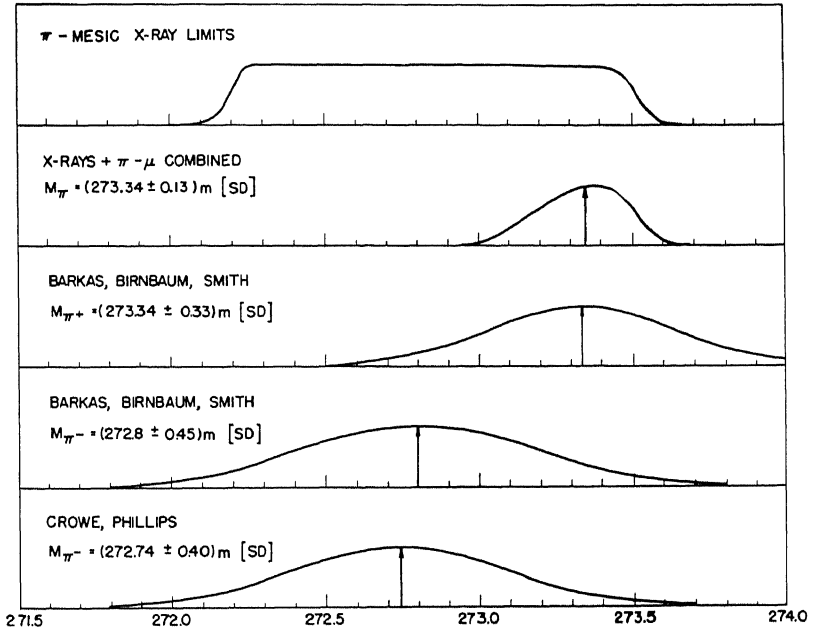


Figure 4-4. Graphical summary of the data on the light-meson masses.

evaluating the K edges, we find that the errors due to the x-ray measurements correspond in all cases to less than $\pm 0.04 m$ in the meson limits. This error includes as well the estimated uncertainty in the vacuum-polarization corrections. In the pion and muon mass limits the main uncertainty is in the limit involving the π - μ mass difference and its error, $\pm 0.10 m$.

To summarize the situation with regard to the masses, we have plotted most of the information for pions in Figure 4-4. The x-ray limits using the π - μ difference and the uncertainties of the edges are shown. The nuclear-plate data of Barkas *et al.* (21) and the high-

energy x-ray data of Crowe and Phillips (23) are sketched in with the error distributions indicated.

It is possible to give here a useful limit for the masses of the light mesons:

$$\begin{aligned} M_{\pi} &= (273.23 \pm 0.36) m \text{ [Limit]} \\ M_{\mu} &= (206.82 \pm 0.36) m \text{ [Limit]} \end{aligned} \quad (4-86)$$

The probability that the masses exceed these limits is less than 2×10^{-2} because one is required to exceed more than two standard deviations of two independent measurements, or 2.8 standard deviations of the mass difference.

The mean values of the meson masses and their standard deviations can be calculated from the x-ray limits:

$$\begin{aligned} M_{\pi} &= (273.34 \pm 0.13) m \text{ [SD]} \\ M_{\mu} &= (206.93 \pm 0.13) m \text{ [SD]} \end{aligned} \quad (4-87)$$

The mean value and standard deviation, using *all* the mass data, can be calculated as follows: Combining the three pion-mass measurements, (4-23), (4-26), (4-32), one obtains

$$M_{\pi} = (273.05 \pm 0.22) m \text{ [SD]} \quad (4-88)$$

Finally, combining (4-87) and (4-88), one obtains a best value of the pion mass, and the corresponding best value of the muon mass:

$$M_{\pi} = (273.27 \pm 0.11) m \text{ [SD]} \quad (4-89)$$

$$M_{\mu} = (206.86 \pm 0.11) m \text{ [SD]} \quad (4-90)$$

These are our adopted light-meson mass values.

1. Spin, Magnetic Moment, and Gyromagnetic Ratio of the Muon

The spin of the muon has been measured indirectly and has very probably a value of $1/2$. The situation can be summarized as follows:

1). The evidence on burst production (bremsstrahlung of energetic muons observed in cosmic rays) favors $1/2$ over zero or one (70).

2). The decay of the pion (spin-zero) into a muon and the usual (spin- $1/2$) neutrino leads to half-integral muon spin; the neutral particle, of course, is never identified (as discussed in Section 4.2*h*).

3). The success of universal β decay in explaining the shape and rate of μ decay is evidence for the simplifying assumption that the muon is simply a heavy Dirac particle.

4). There is conflicting evidence that muons may have anomalous (excessive) large angle scattering (71).

5). The existence of electromagnetic μ -pair production (72) is confirmation of the spin-1/2 theory, the Bethe-Heitler theory extended to particles with the muon mass. The theory of pair production of particles with spin greater than 1/2 has not been shown to give unambiguous prediction of the cross section. However, the effect of an anomalous magnetic moment has been studied (72a). From the magnitude of the absolute cross section (72), the magnetic moment is that of the Dirac particle within about 30 per cent ($1.2 < g < 2.4$).

6). Garwin, Lederman and Weinrich (72b) have reported a preliminary determination of the gyromagnetic ratio of the free muon. Briefly, the experiment consists of stopping the μ^+ beam produced by cyclotron-produced π^+ mesons which have decayed in flight. The decay β^+ is detected in a gate about 1.25- μ sec long, delayed by 0.75 μ sec after the μ^+ stops. By applying a magnetic field perpendicular to the initial muon direction, the μ^+ 's precess with the Larmor frequency:

$$\omega = \frac{\mu H}{S\hbar} = g \frac{e}{2M_{\mu}c} \cdot H \quad (4-90a)$$

The magnetic field is varied, and the counting rate varies periodically. By rotating the counter, they measure directly the precession frequency and the direction of rotation:

$$g = +2.0 \pm 0.1 \quad (4-90b)$$

[They state that work is in progress (72c) to determine the value to $\pm 0.03\%$.] Their value agrees with the Dirac theory for spin-1/2. For spin-3/2 the value of g is expected to be 2/3 on theoretical grounds.* A backwards peaking of the β decay (fore-aft asymmetry) is observed. They assert that this asymmetry can be accounted for only

* A theory for spin-3/2 particles has been formulated by Fierz and Pauli. Belinfante (72d) has shown that if the Fierz-Pauli theory applies to positive muons the g factor would be 2/3. If the particle is not a "bare" particle, but has a complex structure, this argument does not apply.

by assuming that parity is not conserved in both the reactions $\pi^+ \rightarrow \mu^+ + \nu$ and $\mu^+ \rightarrow \beta^+ + \nu + \nu$. (See Section 4.3g for a further discussion of the sequence leading to this remarkable experiment.) The angular distribution for correlation in $\mu^+ \rightarrow \beta^+$ decay deduced from the data is

$$W(\theta^+) = 1 - \frac{(0.33 \pm 0.03) \cos \theta^+}{R} \quad (4-90c)$$

where θ^+ is the angle between the incident muon velocity direction and the β -decay direction; R , which measures both the degree of polarization of the stopping muon beam and the extent of its depolarization during the delay time, is not known. Garwin *et al.* conclude that there is a "very strong probability" that the μ^+ spin is $1/2$. For the μ^- , their preliminary result is that the g value is the opposite sign and "roughly equal" in magnitude to the g value of the μ^+ equation (4-90b).

7). The evidence reported by Fitch and Rainwater (73) on the fine-structure splitting in μ -mesic x-rays has as yet not been confirmed by other experimenters (73a). The splitting in the $2P$ -to- $1S$ transitions in lead is not adequately resolved by the NaI spectrometer to determine the multiplicity. One can conclude, however, that the possibility of fine-structure splitting a factor of three greater is ruled out by the Fitch-Rainwater results. Since the total fine-structure splitting is proportional to $g(2S + 1)$, the width then probably excludes spins higher than $1/2$, providing, of course, that there is not some other effect that might obscure the splitting or seriously deplete several of the lines.

m. Muon Lifetime

The muon lifetime has been observed in cosmic-ray studies by Rossi and others (see Table 4-7). The decay in flight of muons has been observed as a change in cosmic-ray muon flux with altitude. The results of Rossi (74) and of Seymour and Swann (75) give mean lives in agreement with the counter results. The delayed-counting techniques are all similar: the two events for which these delayed coincidences are observed are (1) the arrival of the μ^+ , and (2) the emission of the β^+ when the muon decays [equation (4-81)]. The most recent and accurate measurement of the μ^+ lifetime was made by Bell and Hincks (76). Their method was to

Table 4-7. Muon Lifetimes

Particle	Reference	τ Mean Life (μsec)	Description
μ	74	2-3	Cosmic rays, decay in flight
μ	75	2.3 ± 0.5	
μ^+	77	3.1 ± 1.5	
μ^+	78	2.15 ± 0.07	Cosmic rays, delayed coincidences
μ^+	79	2.11 ± 0.10	
μ^+	80	2.33 ± 0.15	
μ^+	76	2.22 ± 0.02	
μ^+	81	2.28 ± 0.10	
μ^+	82	2.07 ± 0.04 (?)	Accelerator; μ^- not clearly separated.

Adopted value Eq. (4-91), this paper $\tau_\mu = (2.22 \pm 0.02) \times 10^{-6}$ sec

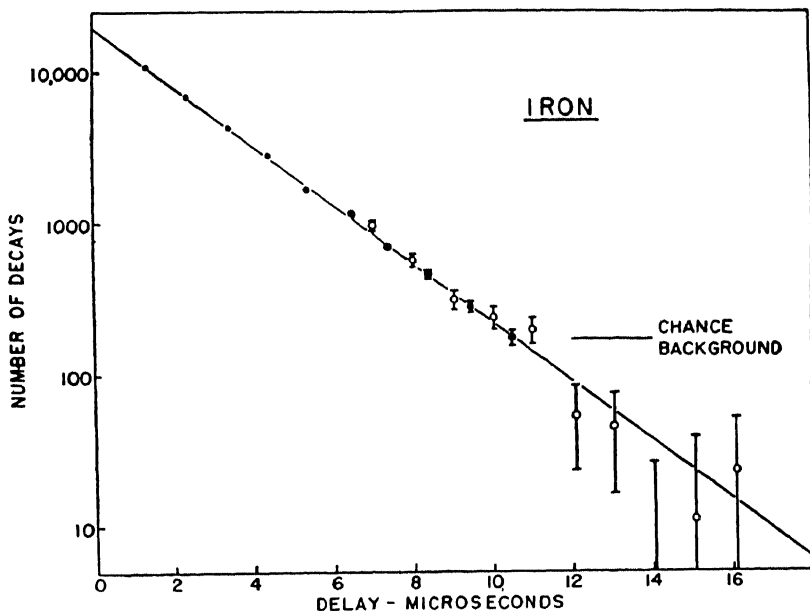


Figure 4-5. Differential time distribution of positron pulses obtained by Bell and Hincks (76). The circles and dots show the results of two runs with different initial delays. The random background has been subtracted.

scale the delayed coincidences associated with cosmic-ray muons; the data are shown in Figure 4-5. The experimental result is

$$\tau_{\mu^+} = (2.22 \pm 0.02) \times 10^{-6} \text{ sec [SD]} \quad (4-91)$$

with the quoted error based upon statistics. Systematic errors are believed to be less than 0.3 per cent. All the previous measurements, as seen from Table 4-7, are in good agreement with their result.

The μ^- lifetime is altered because of the competition due to capture by nuclei when the muon is stopped in material. Keuffel *et al.* (83) have studied the capture in heavy elements. Bell and Hincks (81) have studied the lifetime in Li, Be, and C; in Be they obtain

$$\tau_{\mu^+} - \tau_{\mu^-} = (0.07 \pm 0.09) \times 10^{-6} \text{ sec} \quad (4-92)$$

The nuclear absorption corrects this by 0.01 μsec , so that the undisturbed μ^- lifetime is equal to the μ^+ lifetime within the error:

$$\frac{\tau_{\mu^+} - \tau_{\mu^-}}{\tau_{\mu^+}} = \frac{0.06 \pm 0.09}{2.22} = (2.8 \pm 4.3)\% \text{ [SD]} \quad (4-93)$$

4.3 MASSES AND PROPERTIES OF K MESONS

Because of the rapid growth in the subject of K -meson physics, the discussion of both this and the following section on hyperons will be seriously restricted. Most of the data are preliminary, and many revisions are to be expected as techniques improve. The objective here is to present the data as they exist at this writing; no attempt has been made to include data on either the interactions of K mesons with nuclei or the production mechanisms, nor will any attempt be made to discuss details of the theory of these particles.

For orientation in the subject, the reader is referred to articles by Leprince-Ringuet (84), Dilworth *et al.* (85), Powell (86), Marshak (87), Thompson (88, 89) and Bridge (89a), and to the reports and proceedings of conferences held at Bagnères (90), Padua (91), Pisa (92), and Rochester (93); articles by A. M. Shapiro (93a) and M. M. Shapiro (93b) giving tables of the properties of elementary particles have appeared in 1956.

a. Nomenclature

The nomenclature for K mesons is summarized in Table 4-8. K mesons are restricted to particles of masses between pions and

nucleons; in particular, their masses fall around 966 *m*. To identify the decay mode, *K* mesons can be named with subscripts for the type of decay product— π , μ , β —together with a further subscript for the number of decay products—2 or 3. The convention of naming with Greek letters mesons whose decay schemes are well established was suggested at the Bagnères Conference (90, 94). Both the K_{μ_2} and the K_{β_3} , however, seem to lack Greek-letter “Christian names” at this date.

Table 4-8. *K*-Meson Nomenclature and Modes of Decay

Mode of Decay	Names in Use	
$\theta^0 \rightarrow \pi^+ + \pi^- \dots \dots \dots$	$\theta^0, V_4^0, \theta_1$	} Thetons
$\theta^0 \rightarrow \pi^0 + \pi^0 \dots \dots \dots$	$\theta^0 (2\pi^0)$	
$\theta^0 \rightarrow \pi^\pm + \mu^\mp + \nu \dots \dots \dots$	} $\theta_2,$	
$\theta^0 \rightarrow \pi^\pm + e^\mp + \nu \dots \dots \dots$		
$\theta^0 \rightarrow \pi^0 + \mu^\pm + e^\mp \dots \dots \dots$		
$\chi^\pm \rightarrow \pi^\pm + \pi^0 \dots \dots \dots$	$\chi, \theta, K_\pi, K_{\pi_2}$	} K_L^a
$K_{\mu^\pm}^\pm \rightarrow \mu^\pm + \nu \dots \dots \dots$	K_μ, K_{μ_2}	
$\kappa^\pm \rightarrow \mu^\pm + \pi^0 + \nu \dots \dots \dots$	κ, K_{μ_3}	
$\tau^\pm \rightarrow \pi^\pm + \pi^+ + \pi^- \dots \dots \dots$	τ	} Tauons
$\tau'^\pm \rightarrow \pi^\pm + \pi^0 + \pi^0 \dots \dots \dots$	τ', K_{π_3}	
$\tau^0 \rightarrow \pi^+ + \pi^- + \pi^0 \dots \dots \dots$	τ^0, V_3^0	
$K_{\beta^\pm}^\pm \rightarrow \beta^\pm + \pi^0 + \nu \dots \dots \dots$	$K_\beta, K_e, K_{e_3}, K_{\beta_3}$	

^a K_L is also used to describe decays with a lightly ionizing secondary that is not identified.

Throughout the following discussion, there will be the question: How many of the *K* mesons are really alternate modes of the same particle? From analysis of the angular correlation and energy distribution of the pions of the decay of the τ meson, Dalitz (95) has shown that it is very probable that the spin and parity of the τ are such that the K_{π_2} disintegration is forbidden (see Section 4.3g, below). The *K*-meson mean lives have been measured electronically, and the results indicate that $\tau_\tau, \tau_{K_{\mu_2}}$, and $\tau_{K_{\pi_2}}$ are approximately equal (see Section 4.3f, below). There is some theoretical speculation (96) as to how these data can be made consistent by having, for example, the τ decay branch into the K_{π_2} with the subsequent K_{π_2} decay being much faster than the τ .

Lee and Yang (96a) have also argued that one explanation of this

paradoxical situation might well indicate that parity may not be conserved in the weak-decay interactions. They have shown that this very weak mixing of parity states would have no consequences in the usual strong interactions involved in nuclear processes. In particular, they outline how experiments can be performed to check this hypothesis; for example, in the β decay of polarized nuclei (i.e., aligned with a definite orientation). These experiments are being carried out by Wu, Ambler, *et al.* (96b). Preliminary results have been presented which confirm the Lee-Yang parity-non-conservation hypothesis. Furthermore, Garwin *et al.* (72b) have reported work on the π - μ - β decay process which also gives confirming evidence (see Section 4.2*l*). The Lee-Yang hypothesis, if extended to the θ - τ decay problem, suggests that all the K -meson decay schemes can be and probably are alternate modes of decay of a single K meson.

b. Mass of the τ Meson — Q -Value Determination

Since its discovery in Bristol in 1949 (97), the decay at rest of the τ^+ meson has been observed many times. The energy of the fragments is low enough so that often the ranges of the three decay pions can be measured in the stacks of stripped emulsions. These events, called τ completes, give the most accurate mass measurements.

The Q value of cosmic-ray tauons was summarized at Padua in 1954 (98): In nuclear plates 14 events collected from many groups gave an average Q value

$$Q_{\tau^+} = (75.2 \pm 1.5) \text{ Mev} \quad (4-94)$$

In stripped emulsions, 25 events gave

$$Q_{\tau^+} = (74.7 \pm 0.3) \text{ Mev} \quad (4-95)$$

At Pisa (1955) (92), over 100 tauons in stripped emulsions were reported; the result of averaging all cosmic-ray tauons was

$$Q_{\tau^+} = (75.0 \pm 0.2) \text{ Mev} \quad (4-96)$$

The error quoted is statistical and does not contain uncertainties arising from inaccuracies in emulsion range-energy relations, i.e., densities, moisture content, shrinkage, and calculations using different mean ionization potentials. Amaldi (99), in summarizing the results, increased the error to approximately ± 1.5 Mev.

With the emulsion stacks exposed to the Bevatron K^+ beam, the systematic errors can be all but eliminated. Haddock (100) reported

$$Q_{\tau^+} = (75.13 \pm 0.20) \text{ Mev [SD]} \quad (4-97)$$

based on 67 tauons. With 27 tauons, Barkas *et al.* (101) have obtained

$$Q_{\tau^+} = (75.08 \pm 0.20) \text{ Mev [SD]} \quad (4-98)$$

These measurements are in progress at this writing, and possibly some changes may be made in the final results. However, combining the Berkeley values, we find

$$Q_{\tau^+} = (75.11 \pm 0.14) \text{ Mev [SD]} \quad (4-99)$$

This gives for the mass of the τ^+ meson, using the best value for the pion mass [equation (4-89)],

$$M_{\tau^+} = (966.80 \pm 0.43) m \quad (4-100)$$

The error here includes the uncertainty in the pion mass.

In a few cases the τ^- has been observed to decay in flight in a cloud chamber. Aggson *et al.* (102) reported a positive and negative τ decay in flight; the Q values were measured to be

$$Q_{\tau^+} = (84 \pm 6) \text{ Mev} \quad (4-101)$$

$$Q_{\tau^-} = (77 \pm 9) \text{ Mev} \quad (4-102)$$

The analysis of four decays in flight of negative tauons in the 10-in. Berkeley hydrogen bubble chamber gives (102a)

$$Q_{\tau^-} = (73.6 \pm 5) \text{ Mev} \quad (4-102a)$$

Van Lint and Trilling (103) report an event which permits an accurate Q -value measurement:

$$Q_{\tau^-} = (70 \pm 3) \text{ Mev} \quad (4-103)$$

giving

$$M_{\tau^-} = (956.8 \pm 6) m \quad (4-104)$$

c. Masses of the K_L^+ Mesons— Q -Value Determination

The accuracy with which the Q values for the $K_{\pi_2^+}$ and $K_{\mu_2^+}$ mesons are known has increased considerably with stacks exposed to the Bevatron K beam. The early cloud-chamber S events (de-

cays at rest giving rise to monoenergetic secondaries) gave low Q values for the $K_{\mu_2}^+$ (104-106); these have not been verified. All the K stacks, including the cosmic-ray G -stack (107), have been analyzed by Barkas *et al.* (101). These results appear in Table 4-9. The masses obtained from these Q values using our best pion and muon masses [equations (4-89) and (4-90)] are

$$M_{K_{\tau_2}^+} = (965.5 \pm 2.2) m \text{ [SD]} \quad (4-105)$$

$$M_{K_{\mu_2}^+} = (962.2 \pm 2.8) m \text{ [SD]} \quad (4-106)$$

The errors include statistics and uncertainties of the range-energy relations; the values are also subject to slight changes as the number of events increases.

The differences between the τ , $K_{\tau_2}^+$, and $K_{\mu_2}^+$ values involve uncertainties in the pion- and muon-mass measurements. However, these are small compared with the statistical errors.

Table 4.9. Masses of K Particles Relative to Tauon Mass

Values shown are $M_K - M_\tau$. Standard deviations are given.

Particle	From Q Values		From Range-Momentum		Combined
	Value	Ref.	Value	Ref.	
K_{μ_2}	-4.0 ± 6.0	107			
	-2.0 ± 3.4	108	$+1.2 \pm 2.9$	108	
	-4.0 ± 6.1	109	$+0.8 \pm 5.9$	111	
	-11.8 ± 4.8	110			
Average	-4.6 ± 2.9	$+1.1 \pm 2.6$	-1.45 ± 1.9
K_{τ_2}	$+1.5 \pm 4.0$	107			
	-2.6 ± 2.3	108	$+0.2 \pm 2.8$	108	
	-4.1 ± 4.0	109	$+0.0 \pm 7.9$	111	
	$+4.3 \pm 4.5$	110			
Average	-1.5 ± 2.2	$+0.2 \pm 2.7$	-0.83 ± 1.7
τ'	$+1.4 \pm 4.5$	108a	
K_{μ_3}	$+1.0 \pm 5.8$	108	
	-11.8 ± 15.6	111	-1.2 ± 5.2
K_{β_3}	-3.3 ± 10	108	
	-14.9 ± 8.5	111	-8.7 ± 6.4

d. Masses of the K^\pm Mesons—Direct Measurements

The masses of the K^+ mesons have been measured directly by Birge *et al.* (108, 108a), Heckman *et al.* (111), and Fung *et al.* (109). The mesons are produced by the Berkeley Bevatron, analyzed by a strong-focusing analyzing magnet system, and detected in nuclear-emulsion stacks. The mass is obtained by measuring simultaneously the momentum as defined by the analyzing system and the range in the emulsion for each type of K meson. The results for various K^+ -meson masses appear in Table 4-9. The τ^+ -meson mass is used as a normalizing unit, as discussed above; its Q value is known accurately. The τ^+ can be compared to the proton by comparing its range to the extrapolated proton range. The results are:

$$\text{(Birge } et al.) M_{\tau^+} = (966.3 \pm 2.7) m \text{ [SD]} \quad (4-107)$$

$$\text{(Heckman } et al.) M_{\tau^+} = (961.8 \pm 2.6) m \text{ [PE]} \quad (4-108)$$

The direct measurements of the differences between the various K and τ mesons have less possible systematic error. By combining the mass differences from the direct measurements and using the τ mass from the Q -value measurement (4-100), the K_{π_2} and K_{μ_2} are accurately determined to be:

$$M_{K_{\pi_2}} = (967.0 \pm 2.7) m \text{ [SD]} \quad (4-109)$$

$$M_{K_{\mu_2}} = (967.9 \pm 2.6) m \text{ [SD]} \quad (4-110)$$

The Q -value masses can be combined with the direct measurements to obtain the best mass values for the K_{π_2} and K_{μ_2} :

$$M_{K_{\pi_2}} = (966.0 \pm 1.7) m \text{ [SD]} \quad (4-111)$$

$$M_{K_{\mu_2}} = (965.3 \pm 1.9) m \text{ [SD]} \quad (4-112)$$

Clearly there is no significant difference in the K -meson mass measurements to a precision of $\sim 2 m$.

Hornbostel and Salant (112) have measured the K^- mass by momentum and range to be

$$M_{K^-} = (931 \pm 24) m \text{ [SD]} \quad (4-113)$$

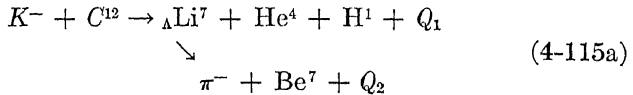
Webb, Chupp, Goldhaber, and Goldhaber (113) have measured the ratio of the masses of the K^- to the K^+ by measuring the ratios of their momenta and ranges; they obtain

$$M_{K^-}/M_{K^+} = 0.998 \pm 0.013 \quad (4-114)$$

Taking the K^+ to have the τ mass, (4-100), one obtains

$$M_{K^-} = (963 \pm 12) m \text{ [SD]} \quad (4-115)$$

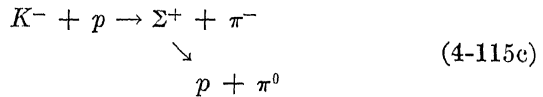
Gilbert, Violet, and White (113a) report a K^- -capture star believed to be an example of the reaction



From the measurements on the six particles and their masses, they can determine the Q 's and deduce a K^- mass:

$$M_{K^-} = (966 \pm 5) m \quad (4-115b)$$

Fry *et al.* (113b) report a K^- meson believed to follow the reaction



It is assumed that this occurs at rest since the Σ^+ and the pion are closely colinear ($\sim 1/2^\circ$). Since the Σ^+ mass is known [see discussion in Section 4.3c, equation (4-157)], a K^- mass can be deduced,

$$M_{K^-} = (966.7 \pm 2) m \quad (4-115d)$$

in excellent agreement with that of the τ^+ [equation (4-100)] (113c).

e. θ^0 Mass— Q -Value Determination

The decay of the neutral K meson (θ^0) has been observed in cloud chambers (88, 89). The Q value has been measured by Thompson (114) from 24 events to be

$$Q_{\theta^0} = 213.9 \begin{array}{l} \pm 1.4 \text{ Mev (external)} \\ \pm 2.8 \text{ Mev (internal)} \end{array} \quad (4-116)$$

Known systematic uncertainties increase the error to ± 3.0 Mev. In their article, the experimenters have increased the error to ± 5.0 Mev on the basis of their belief that "the curvature discrepancies between views may conceal an unknown systematic error." Their result is then

$$Q_{\theta^0} = (214 \pm 5) \text{ Mev [PE]} \quad (4-117)$$

giving

$$M_{\theta^0} = (965 \pm 10) m \text{ [PE]} \quad (4-118)$$

For our purposes it is conventional to take only the known or measured errors into account; using the external-consistency error, the uncertainty of the absolute field, and our best pion mass, (4-89), we obtain

$$Q_{\theta^0} = (214.0 \pm 2.5) \text{ Mev [SD]} \quad (4-119)$$

and from this

$$M_{\theta^0} = (965.1 \pm 5.0) m \text{ [SD]} \quad (4-120)$$

There have been several other recent measurements of Q_{θ^0} . The Princeton group has reported (115)

$$Q_{\theta^0} = 212 \begin{array}{l} \pm 3 \text{ (external)} \\ \pm 4 \text{ (internal)} \end{array} \text{ Mev [SD]} \quad (4-121)$$

Fretter has reported (116) a measurement

$$Q_{\theta^0} = (222.6 \pm 3.7) \text{ Mev [PE]} \quad (4-122)$$

The endings of K^- mesons in liquid hydrogen have yielded θ^0 mesons. At this writing, three have been found by the Berkeley group (116a). The kinetic energies were measured to be 10 ± 2 , 9 ± 2 , and 1.5 ± 1 Mev. Some or all of the events may arise from the interaction in flight. If the first two arise from stopped K 's of mass $966.8m$, the Q value is

$$Q_{K^-(\pi,\pi)} = (200.2 \pm 2.3) \text{ Mev} \quad (4-122a)$$

This is 4.6 standard deviations lower than Thompson's Q -value measurement (4-119). More events of this type should establish definitely if neutral θ 's come from the interaction of K^- 's at rest.

f. K-Meson Lifetimes

The K -meson lifetime has been observed by several experimenters (see Table 4-10). The data are increasing rapidly and therefore references to individual results will be brief.

The early cloud-chamber estimates of the lifetime of the K_{μ_2} gave limits (117-119)

$$\tau_{K_{\mu_2}} = (4 - 10) \times 10^{-9} \text{ sec} \quad (4-123)$$

Table 4-10. K-Meson Lifetime Measurements

Particle	Mean Life (10^{-9} sec)	Method	Reference
K^\pm	(4-10)	Cloud chamber.....	118
K^\pm	>(5-20)	Cloud chamber.....	119
K^+ (short)	0.52 $\begin{matrix} + 0.33 \\ - 0.15 \end{matrix}$	Cloud chamber.....	120
K^- (short)	0.42 $\begin{matrix} + 0.38 \\ - 0.12 \end{matrix}$	Cloud chamber.....	120
K^- (short)	0.13 \pm 0.06	Cloud chamber.....	121
K^+	6.7 $\begin{matrix} + \infty \\ - 5.5 \end{matrix}$	Cloud chamber.....	122
$K_{\mu_2^+}$ (mostly)	8.7 \pm 1.0	Čerenkov counter, cosmic rays...	123
$K_{\mu_2^+}$	11 $\begin{matrix} + 4.1 \\ - 2.4 \end{matrix}$	Cloud chamber and counters, cosmic rays.....	124
$K_{\mu_2^+}$	8.05 \pm 0.66	Counters, cosmic rays.....	125
τ^+	10 $\begin{matrix} + 7 \\ - 3 \end{matrix}$	Plates, variable distance, accelera- tor.....	126
τ^+	8 $\begin{matrix} + 5 \\ - 2 \end{matrix}$	Plates, variable distance, accelera- tor.....	127
$K_{\tau^+}^+$	7 $\begin{matrix} + 1.5 \\ - 1.0 \end{matrix}$	Plates, variable distance, accelera- tor.....	127
$\tau + \tau'$	13.0 \pm 3.3	Plates, variable distance, accelera- tor.....	127a
K_{μ_3}	8.8 \pm 2.3	Plates, variable distance, accelera- tor.....	127a
K_β	14.4 \pm 4.6	Plates, variable distance, accelera- tor.....	127a
$K_{\pi_2^+}$	13 \pm 2	Electronic, accelerator.....	128
$K_{\mu_2^+}$	14 \pm 2	Electronic, accelerator.....	128
$K_{\mu_2^+}$	11.7 $\begin{matrix} + 0.8 \\ - 0.7 \end{matrix}$	Electronic, accelerator.....	129
$K_{\pi_2^+}$	12.1 $\begin{matrix} + 1.1 \\ - 1.0 \end{matrix}$	Electronic, accelerator.....	129
τ^+	11.7 $\begin{matrix} + 0.8 \\ - 0.7 \end{matrix}$	Electronic, accelerator.....	130
K^-	9.5 $\begin{matrix} + 3.6 \\ - 2.5 \end{matrix}$	Plates, decay in flight, accelerator.	131
K^+	10.1 $\begin{matrix} + 3.3 \\ - 2.1 \end{matrix}$	Plates, decay in flight, accelerator.	132

The existence of a short-lived K component has been reported (120, 121*). However, Fretter (122) finds no evidence under similar conditions.

There are three cosmic-ray electronic lifetime measurements on the K -meson. A delayed-coincidence method was used where the decay mode was identified, either as a relativistic up-going secondary, mainly the K_{μ_2} , or by observing the secondary in a cloud chamber.

Alvarez and Goldhaber (126) and Harris, Orear, and Taylor (127) report the decay of the τ^+ by observing in nuclear plates the number of τ mesons that survive various lengths of path from the production target.

Alvarez *et al.* (128) counted K_L mesons in the Bevatron K beam and report an electronic determination. Fitch and Motley (129) have also counted K_L 's, and their lifetime for the τ has been reported (130); preliminary values are

$$\tau_{\tau^+} = \left(\begin{array}{c} 11.7 + 0.8 \\ -0.7 \end{array} \right) \times 10^{-9} \text{ sec} \quad (4-124)$$

$$\tau_{K_{\pi_2}} = \left(\begin{array}{c} 12.1 + 1.1 \\ -1.0 \end{array} \right) \times 10^{-9} \text{ sec} \quad (4-125)$$

$$\tau_{K_{\mu_2}} = \left(\begin{array}{c} 11.7 + 0.8 \\ -0.7 \end{array} \right) \times 10^{-9} \text{ sec} \quad (4-126)$$

The results are equal within the errors and strongly suggest that either the τ and the K_{π_2} are different modes of decay of the same particle or that if one decays to the other by cascade, the second particle has a shorter life.

Hoang, Kaplan, and Yekutieli (127a) report an emulsion study of the τ and τ' , K_{μ_3} and K_{β} lifetimes by observing the reduction in flux due to decays in flight; their preliminary results are:

$$\tau_{(\tau+\tau')} = (13.0 \pm 3.3) \times 10^{-9} \text{ sec} \quad (4-126a)$$

$$\tau_{K_{\mu_3}} = (8.8 \pm 2.3) \times 10^{-9} \text{ sec} \quad (4-126b)$$

$$\tau_{K_{\beta}} = (14.4 \pm 4.6) \times 10^{-9} \text{ sec} \quad (4-126c)$$

* Professor Leighton has informed us (private communication) that it is difficult to choose between a K meson and a hyperon, but that he suspects that the particle may actually be a Σ^- .

Table 4-11. Lifetime Measurements of the θ^0

Number of Events	Mean Life (10^{-10} sec)	Method	Reference
11	4 \pm 3	Cloud chamber, cosmic rays.....	134
11	1.6 $\begin{matrix} + 2.2 \\ - 0.6 \end{matrix}$	Cloud chamber, cosmic rays.....	135
9	2.3 $\begin{matrix} + 2.1 \\ - 0.7 \end{matrix}$	Cloud chamber, cosmic rays.....	136
6 ^a	0.9 $\begin{matrix} + 1.6 \\ - 0.3 \end{matrix}$	Cloud chamber, cosmic rays.....	137
8 ^a	0.6 $\begin{matrix} + 0.4 \\ - 0.2 \end{matrix}$	Cloud chamber, cosmic rays.....	133
14 ^a	0.7 $\begin{matrix} + 0.3 \\ - 0.2 \end{matrix}$	Cloud chamber, cosmic rays.....	138
29 ^a	0.8 $\begin{matrix} + 0.3 \\ - 0.2 \end{matrix}$	Cloud chamber, Cosmotron produced.....	139
35 ^a	0.8 $\begin{matrix} + 0.4 \\ - 0.2 \end{matrix}$	Cloud chamber, cosmic rays....	140
18 ^a	1.2 $\begin{matrix} + 7.6 \\ - 0.2 \end{matrix}$	Bubble chamber, Cosmotron produced.....	140a
.....	1.7	Counter experiment, Cosmotron..	140b
.....	1.9 $\begin{matrix} + 0.2 \\ - 0.3 \end{matrix}$	Counter experiment, Bevatron...	140c

^a The average of the six entries so marked is $0.78 \begin{matrix} + 0.17 \\ - 0.11 \end{matrix} \times 10^{-10}$ sec.

It is possible to obtain a K^- lifetime by observing decay in flight in emulsions. Several groups have combined their data (131) and obtain

$$\tau_{K^-} = \left(9.5 \begin{matrix} +3.6 \\ -2.5 \end{matrix} \right) \times 10^{-9} \text{ sec} \quad (4-127)$$

For positives (not including τ 's), Iloff *et al.* (132) obtain (using the same method)

$$\tau_{K^+} = \left(10.1 \begin{matrix} +3.3 \\ -2.1 \end{matrix} \right) \times 10^{-9} \text{ sec} \quad (4-128)$$

The θ^0 lifetime has been calculated by Gayther (133); the revised data are shown in Table 4-11. The early cloud-chamber data

probably contain a bias toward the longer-lived events. Cloud-chamber results by the Columbia group (139) at Brookhaven give

$$\tau_{\theta^0} = \left(0.8 \begin{array}{c} +0.3 \\ -0.2 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-129)$$

Cloud-chamber cosmic-ray studies at Purdue (140) give a mean life:

$$\tau_{\theta^0} = \left(0.8 \begin{array}{c} +0.4 \\ -0.2 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-130)$$

A recently-reported bubble-chamber experiment by Budde *et al.* (140a) gives a mean life based on 18 events:

$$\tau_{\theta^0} = \left(1.2 \begin{array}{c} +7.6 \\ -0.2 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-131)$$

the larger upper error results from the small dimensions of the chamber.

Two counter experiments have been analyzed to give mean lives for θ^0 's which decay via the reaction



The experiments by Ridgeway, Berley, and Collins at Brookhaven, (140b) and by Osher (140c) at Berkeley consist of detecting γ -rays produced as follows: A target bombarded with protons of several-Bev energy makes θ^0 's and Λ^0 's; these may decay in flight, producing neutral mesons that subsequently decay rapidly [equation (4-61)] into γ -rays. The direct π^0 γ -rays from the target can be absorbed with an appropriately-placed baffle, so that only γ -rays produced by particles which survive a few centimeters before decaying are counted in the shadow cast by the absorber. The analysis of the spatial origin of these high-energy γ -rays gives a mean life for the θ^0 : Ridgeway *et al.* obtain

$$\tau_{\theta^0} = 1.7 \times 10^{-10} \text{ sec} \quad (4-131b)$$

Osher obtains

$$\tau_{\theta^0} = \left(1.9 \begin{array}{c} +0.2 \\ -0.3 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-131c)$$

The decay equation (4-131a) is not observed directly in bubble

chambers. Budde *et al.* (140a), by studying associated $\Lambda^0 - \theta^0$ production, conclude that the usual charge decay proceeds

$$\alpha_{(\theta^0 \rightarrow \pi^+ + \pi^-)} = \begin{pmatrix} 0.3 & +0.19 \\ & -0.12 \end{pmatrix} \quad (4-131d)$$

of the time. This ratio depends upon the Λ and θ lifetimes. The remaining θ 's either decay via the $2\pi^0$ reaction, or live long enough to escape detection.

The counter experiments discussed in connection with the θ^0 lifetime are regarded as strong evidence that this decay mode occurs. In particular, the upstream γ -rays produced by 6-Bev protons on copper cannot arise kinematically from hyperon decay (140c) without assuming a pathological momentum distribution. Previously unobserved shortlived charged- K decays into π^0 's and τ^0 decays (140d) with comparable lifetimes ($\sim 10^{-10}$ sec) are considered possible (but improbable) explanations, also. Further experiments on the existence of the neutral decay mode are planned.

g. Spin and Parity of the τ Meson

Dalitz (95) and Fabri (141) have shown that the three-body decay can be analyzed to determine the spin and parity of the τ^+ meson. If strong pion interactions are ignored, the phase space factors for decay of various assignments of spin and parity can be computed.

The analysis can be seen as follows: When one can identify the decay products, one can separate them into a pair of identical pions and an odd pion. Since the wave function of the identical pions is symmetric, the parity of the τ is $(-1)^{L+1}$, where L is the angular momentum of the unlike (negative) pion relative to the center of mass of the two π^+ 's. The spin j of the τ is the sum of L and l . The relative angular momentum l of the positive pions must be even since the pions are Bosons. When the relative momentum of the unlike pion is low the distributions are sensitive to L , i.e., the higher the L , the less phase space for the π^- . At the other extreme, the very-high-energy π^- corresponds to low relative energy of the like pions, and hence measures l . Similarly, the angular correlation between the odd pion and the pair of like pions depends on the assignment of L .

The analysis of the data—see, e.g., references 100, 101, 142–145—on τ 's indicates that of the possible K_{τ^+} assignments— 0^+ , 1^- , 2^+ , 3^- ,

etc.—the 0^+ is forbidden if parity is conserved in the decay process, the 1^- and 2^+ are extremely improbable, and 3^- and 4^+ are relatively unlikely. Above a spin of 4, there are not enough events to be informative. Of the other states that cannot decay into two pions, the choice of 0^- is likely, 1^+ is ruled out in all but the M.I.T. data (142), but 2^- and 3^+ are satisfactory. The conclusion is that if the spin is less than 4, the τ and K_{τ_2} cannot be the same particle; if the spin is less than 2, the τ is a pseudoscalar (0^-). The reader should be cautioned, however, about the various assumptions made in this analysis; i.e., we have neglected any strong pion-pion interaction in the final state and assumed that parity is strictly conserved in the decay process. In the light of the recent evidence (72b, 96b) on the violation of parity in the β -decay process, this argument together with the apparent experimental identity of the K mesons, may be regarded as evidence that parity is also not conserved in the K -particle decays.

h. Status of K Mesons

At this writing, the evidence can be summarized as follows:

1). The measured masses of the K mesons (τ , K_{τ_2} , K_{μ_2}) are equal within $\pm 2m$. An accidental equality of masses is, of course, possible, but it seems highly unlikely. Lee and Yang (146) discuss this problem and suggest a theory of parity conjugation that would lead to such a mass degeneracy.

2). The experimental lifetimes of the charged K mesons are equal within 10 to 15 per cent, which is within the experimental uncertainty (128a). It is difficult to reconcile this with the predictions of a parity-conjugation scheme (146).

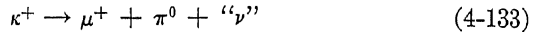
3). The analysis of the decay of the τ meson makes it unlikely that the K_{τ_2} can be an alternate mode of decay of the same particle unless parity is not conserved in the decay.

4). There is no experimental evidence for cascade decay of one K meson into another with emission of one or more low-energy gamma rays, e.g.,



Alvarez (147) reported a search for gamma rays from reaction (4-132), and the preliminary results indicate that none exists of energy above ~ 500 kev.

5). The information regarding the less frequently produced K mesons is accumulating rapidly. The κ^+ meson decays by the reaction



The energy distribution of muons will have an upper limit depending upon the mass of the neutral particles. Crussard (148) summarized the data on approximately 20 κ decays, and the results are not inconsistent with the $(\pi^0 + \nu)$ decay mode. The strongest evidence supporting this assignment is obtained in the two cases where the π^0 has been observed (149) to convert internally giving an electron-positron pair (see Section 4.2f). The neutral particle is shown to have a mass less than 150 m . To avoid a new particle, one concludes the neutral particle to be a neutrino or gamma ray. Again, if the κ is a Boson like the χ and τ , the gamma ray is excluded.

One of the most remarkable examples of internal conversion of the π^0 is that obtained from the decay of the χ^+ meson into a π^+ and π^0 with the π^0 converting into four particles, i.e., two electron-positron pairs. Assuming this decay scheme, the π^0 is measured to be

$$M_{\pi^0} = \left(\begin{array}{c} 255 + 15 \\ -10 \end{array} \right) m \quad (4-134)$$

in good agreement with our adopted value [equation (4-59)]. The cloud-chamber picture of this rare event was obtained by Hodson *et al.* (150).

The χ^- meson is probable. Several cloud-chamber events are consistent with the decay scheme. The measurements on one event reported by Reynolds (151) give a mass

$$M_{\chi^-} = (954 \pm 30) m \quad (4-135)$$

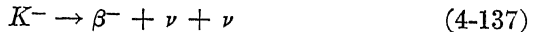
Each of these events may be κ decay, although this is improbable. In the decay in flight of K^- mesons from the Bevatron K^- beam, a χ^- event has been observed (152). The mass obtained is

$$M_{\chi^-} = (957 \pm 40) m \quad (4-136)$$

This event gives a charged meson with a mass $(265 \pm 30) m$; it is therefore unlikely that the secondary is a muon, and hence the κ -decay process does not seem a likely explanation of this event.

The β decay of the K^+ meson was first observed by Friedlander *et al.* (153) at Bristol. Similarly, the energy spectrum should reflect the masses of the neutral particles. However, there is inherently poor accuracy in the determination of the end point of the high-energy β particle. The combined spectrum for all K_β 's was formed in the analysis of the G -stack (107) and more recently by Crussard (148). No internal conversion of the π^0 particles from K_β 's has been reported to date.

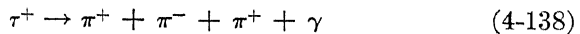
The β decay of the K^- has been observed twice. The event observed in emulsions by Williams *et al.* (154) appears to come from a stopped K^- . The K mesons are strongly coupled to nucleons, so that either this is a rare event (155) or perhaps this K^- may be a Fermion weakly bound to the nucleus and decaying via the scheme



The second event is a decay in flight from the Bevatron K^- beam, also observed in emulsions (152).

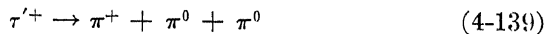
The possible decay $\theta^0 \rightarrow \beta^- + \pi^+ + \nu$ has been reported by Peyrou (156).

A possible example of radiative decay of the τ meson,

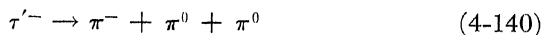


has been observed. Daniel and Pal (157) observed an event consistent with a gamma-ray energy of (32.1 ± 2.7) Mev.

The τ' decay,



was first reported by Crussard *et al.* (158). The τ' has a reasonable abundance (~ 20 per cent of all τ 's) and many have been observed. Heckman *et al.* (111) have reported an internal pair from this decay. The charged pion should have an energy less than ~ 53.3 Mev. No single identified pion has been reported that exceeds this value that is not consistent with the χ decay. The energy distribution is in good agreement with this assignment of neutral particles. Amaldi *et al.* (159) report a cosmic-ray K meson with a single light meson product which forms a star. They conclude that the event is a K^- decaying at rest to a π^- and at least two neutrals. One neutral is excluded from the measured kinetic energy of the pion. This may be the negative counterpart of the τ' :



The event can be explained in several other ways. The event may be a K^- star rather than a decay. The decay at the end of their ranges of K^- mesons in emulsions is a relatively rare event (155). The neutrals in reaction (4-140) are not identified.

There are measurements on two-pion decay of the neutral K or θ^0 meson that lead to "anomalous" Q values, i.e., values not equal to the accepted 214- m value within the experimental errors. The status of these "anomalous θ^0 's" has been reviewed by Thompson (88, 89) and others (160).

The decay scheme

$$\tau^0 \rightarrow \pi^+ + \pi^- + \pi^0 \quad (4-141)$$

would have a Q of ~ 80 Mev. Some of the magnetic-cloud-chamber events are consistent with this scheme (161). Bridge *et al.* (106) have observed a multiplate cloud-chamber event of this type; Deutschmann *et al.* (162) have observed a nuclear-plate event.

The Columbia cloud-chamber group (162a) at the Cosmotron has observed a number of anomalous charged V events that are not colinear with the θ beam direction. The decays are presumably a mixture of $\pi^\pm + \mu^\pm + \nu$, $\pi^\pm + e^\pm + \nu$, and $\mu^\pm + e^\pm + \pi^0$; assuming that their production cross sections are of the same order as the other K^0 mesons in order to explain the frequency of observations, their lifetime must be $10^{-6} > \tau > 3 \times 10^{-9}$ sec. The data on the decays are consistent with a mass of $\sim 1000 m$. These events are presumed to be θ_2 particles for which the $\theta_1 \rightarrow 2\pi$ decay is forbidden. Light mesons from the decay of neutral particles (θ_2 's) have been counted electronically by Fitch and Panofsky and their coworkers (162b). Unfortunately, the theoretical bases of these particles and their "startling" properties are beyond the scope of this discussion (162c), and the implications of the parity nonconservation of these results (162d) must be omitted.

4.4 MASSES AND PROPERTIES OF HYPERONS

a. Nomenclature

Hyperons are unstable particles whose masses are greater than that of the proton and less than that of the deuteron. The nomenclature and modes of decay are given in Table 4-12. The decay reactions imply that hyperons are Fermi particles. The spins are as yet unknown.

Table 4-12. Modes of Decay and Nomenclature of Hyperons

Mode of Decay		Names in Use
$\Lambda^0 \rightarrow p + \pi^-$	Λ^0, V_1^0	[Lambda]
$\Sigma^\pm \rightarrow \pi^\pm + n$	$\Sigma^\pm, Y_{L^\pm} (L = \text{light meson}), V_1^\pm$	
$\Sigma^0 \rightarrow \Lambda^0 + \gamma$	Σ^0	[Sigma]
$\Sigma^+ \rightarrow p + \pi^0$	Σ^+, Y_{p^+}	
$\Xi^- \rightarrow \Lambda^0 + \pi^-$	Ξ^- (cascade)	[Xi]

b. Λ^0

The Λ^0 has been observed to decay in cloud chambers and nuclear stacks by the reaction

$$\Lambda^0 \rightarrow p + \pi^- \tag{4-142}$$

The Q values obtained in chamber studies are shown in Table 4-13. The average of these results is

$$Q_{\Lambda^0} = (36.26 \pm 0.39) \text{ Mev} \tag{4-143}$$

giving a mass value

$$M_{\Lambda^0} = (2180.4 \pm 0.8) m \tag{4-144}$$

The Q value obtained with emulsion events was reported by Friedlander (167):

$$Q_{\Lambda^0} = (36.92 \pm 0.22) \text{ Mev} \tag{4-145}$$

The error is based on internal consistency and does not include the systematic errors; Amaldi (168) estimated the errors to be $\sim \pm 1$

Table 4-13. Measurements of the $\Lambda^0 Q$ Value

Q (Mev)	Method	Reference
37 \pm 1	Magnetic chamber	163
43 \pm 3	Magnetic chamber	164
43 \pm 2		
35.9 \pm 1	Magnetic chamber	165
34.7 \pm 1	Magnetic chamber	166
36.7 \pm 1.0	Magnetic chamber	134
37 \pm 2	Multiplate chamber	137
36 \pm 1	Magnetic chamber	115
36 \pm 1	Magnetic chamber	139

Mev owing to uncertainties and errors in the emulsion range-energy relations. Friedlander (169) has reexamined the errors, however, and in the same plates π - μ calibration was made; no change has been made in (4-145). Several more events have been reported by Daniel and Lal (170):

$$Q_{\Lambda^0} = (37.40 \pm 0.27) \text{ Mev} \quad (4-146)$$

An optimistic average of the nuclear-emulsion determinations and the cloud-chamber results gives

$$Q_{\Lambda^0} = (36.97 \pm 0.16) \text{ Mev} \quad (4-147)$$

giving a mass

$$M_{\Lambda^0} = (2181.74 \pm 0.35) m \quad (4-148)$$

The measurements of the Λ^0 lifetime are given in Table 4-14. The early data have been analyzed by Page (173), who reports

$$\tau_{\Lambda^0} = \left(3.7 \begin{array}{c} +0.6 \\ -0.5 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-149)$$

Table 4-14. Lifetime Measurements of the Λ^0

Number of Events	Mean Life (10^{-10} sec)	Reference
22	10 \pm 7 ^a	134
37 ($0 < Q < 50$ Mev)	2.9 \pm 0.8	171
21	3.5 \pm 1.2	137
22	4.8 $\begin{array}{c} + 2.6 \\ - 1.3 \end{array}$	136
21	4.0 $\begin{array}{c} + 3.7 \\ - 1.2 \end{array}$	133
26	3.7 $\begin{array}{c} + 3.9 \\ - 1.3 \end{array}$	172
23	3.6 $\begin{array}{c} + 1.1 \\ - 0.7 \end{array}$	173
65	2.8 $\begin{array}{c} + 0.5 \\ - 0.4 \end{array}$	139
23	2.8 $\begin{array}{c} + 1.2 \\ - 0.7 \end{array}$	140
25	3.3 \pm 0.6	116a
23	2.0 $\begin{array}{c} + 1.3 \\ - 0.7 \end{array}$	140a
<i>Final Average</i>	3.25 \pm 0.33

^a Selection may be biased and is excluded from average.

A cosmic-ray mean life has been obtained by the Purdue cloud-chamber group (140):

$$\tau_{\Lambda^0} = \left(2.8 \begin{array}{c} +1.2 \\ -0.7 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-150)$$

The Columbia cloud-chamber group (139) has also obtained a mean lifetime for Λ^0 's produced by the Brookhaven Cosmotron:

$$\tau_{\Lambda^0} = \left(2.8 \begin{array}{c} +0.5 \\ -0.4 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-151)$$

The Berkeley bubble-chamber group (116a) obtains a mean life for Λ^0 's produced by K^- captures in hydrogen:

$$\tau_{\Lambda^0} = (3.3 \pm 0.6) \times 10^{-10} \text{ sec} \quad (4-151a)$$

Budde *et al.* (140a) have obtained a mean life for Λ^0 's produced by π^- mesons:

$$\tau_{\Lambda^0} = \left(2.0 \begin{array}{c} +1.3 \\ -0.7 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-151b)$$

By combining the data, we obtain for the lifetime of the Λ^0

$$\tau_{\Lambda^0} = (3.25 \pm 0.33) \times 10^{-10} \text{ sec} \quad (4-152)$$

The data do not exclude a mixture of Λ^0 's with not too different lifetimes. The alternative mode of decay,

$$\Lambda^0 \rightarrow n + \pi^0 \quad (4-152a)$$

is not observed directly. However, from the assumption that there is always associated production in (π^-, p) production of θ^0 's, the branching ratio can be estimated from the number of Λ^0 's observed with the θ^0 . The fraction of charged decays is given by Budde *et al.* (140a) to be

$$\alpha_{\Lambda^0} = \left(0.3 \begin{array}{c} +0.15 \\ -0.12 \end{array} \right) \quad (4-152b)$$

The remaining Λ^0 's decay into neutral particles or have a long enough life to escape detection.

c. Σ Hyperons

The mass of the Σ^\pm reported at Padua (174) was obtained from Q -value determinations in nuclear plates:

$$Q_{\Sigma^\pm(\pi^\pm, n)} = (110 \pm 10) \text{ Mev} \quad (4-153)$$

$$Q_{\Sigma^+(p, \pi^0)} = (116 \pm 2) \text{ Mev} \quad (4-154)$$

Ceccarelli *et al.* (175) report an example of a Σ^+ decaying into a neutron and π^+ with the pion coming to rest giving the $\pi\text{-}\mu\text{-}e$ decay event. From the range of the π^+ they obtain a Q value

$$Q_{\Sigma^+(\pi^+,n)} = (107.8 \pm 3.5) \text{ Mev} \quad (4-155)$$

An accurate value of the Σ^+ mass has been obtained by Fry *et al.* (176) by measuring the proton range of ten $\Sigma^+(p, \pi^0)$ decays and calibrating the emulsion with muons from $\pi\text{-}\mu$ decay at rest:

$$Q_{\Sigma^+(p,\pi^0)} = (116.08 \pm 0.47) \text{ Mev} \quad (4-156)$$

With this, the Σ^+ mass becomes

$$M_{\Sigma^+} = (2327.4 \pm 1.0) m \quad (4-157)$$

In addition to the ten events reported by Fry *et al.*, Barkas *et al.* (176a) and Gilbert *et al.* (176b) have obtained additional events in emulsions whose density is well known. Gilbert *et al.* obtain 7 events, and the resulting mass

$$M_{\Sigma^+} = (2329.5 \pm 1.0) m \text{ [SD]} \quad (4-157a)$$

Barkas *et al.* report 13 events which give

$$M_{\Sigma^+} = (2327.8 \pm 0.7) m \text{ [SD]} \quad (4-157b)$$

Combining these three measurements we obtain

$$M_{\Sigma^+} = (2328.3 \pm 0.5) m \text{ [SD]} \quad (4-157c)$$

The evidence on the Σ^- comes from the decay in flight observed in cloud chambers by groups at Brookhaven (177),

$$Q_{\Sigma^-} = \left(130 \begin{array}{c} +25 \\ -15 \end{array} \right) \text{ Mev} \quad (4-158)$$

at Turin (178),

$$Q_{\Sigma^-} = (107 \pm 15) \text{ Mev} \quad (4-159)$$

and at Berkeley (179),

$$Q_{\Sigma^-} = (121 \pm 11) \text{ Mev} \quad (4-160)$$

Chupp *et al.* (180) reported evidence concerning the Σ^+ and Σ^- hyperons resulting from the capture at rest

$$K^- + p \rightarrow \Sigma^\pm + \pi^\pm \quad (4-161)$$

These four events observed in nuclear emulsions were analyzed under different assumptions. If they assume that the K^- that stops in the emulsion (the Σ and π are colinear to better than 0.5°) has the mass of the τ^+ meson, they obtain

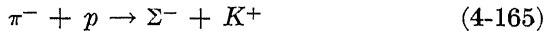
$$M_{\Sigma^+} \leq (2324 \pm 4) m \quad (4-162)$$

$$M_{\Sigma^-} = (2338 \pm 4) m \quad (4-163)$$

The observed difference in the masses depends only on the assumption that the K^- mesons producing the Σ^+ and Σ^- have the same mass:

$$M_{\Sigma^-} - M_{\Sigma^+} \geq 14 \pm 5.5 m \quad (4-164)$$

Steinberger *et al.* (181) report a propane bubble-chamber experiment (no magnetic field) that has yielded information on the mass and lifetime of Σ^- hyperons. The Σ^- 's are produced by pions in the reaction



The pion energy is measured on events where the K^+ stops. The sign of the Σ hyperon is assumed to be negative, a result that is borrowed from the theory discussed in Section 4.4f, below. One event thus far of a Σ^- decaying in flight in which the π^- comes to rest making a star has been measured in detail:

$$\Sigma^- \rightarrow \pi^- + n \quad (4-166)$$

$$Q_{\Sigma^-(\pi^-+n)} = (118 \pm 2.6) \text{ Mev [SD]} \quad (4-167)$$

From this the Σ^- mass can be calculated:

$$M_{\Sigma^-} = (2343 \pm 5.2) m \quad (4-168)$$

Combining this with the Σ^+ data, the mass difference is

$$M_{\Sigma^-} - M_{\Sigma^+} = 14.5 \pm 5.3 m \text{ [SD]} \quad (4-169)$$

Subsequently several groups have obtained events in which K^- capture on hydrogen in nuclear emulsions [equation (4-161)] produced Σ^\pm that came to rest. The π^\pm in some cases also stops. Fry *et al.* (113b) have recently reported two events of each type (4-161) where the Σ^+ and Σ^- stop. The Σ^+ was analyzed for a K^- mass (4-115d); the Σ^- event gives a mass

$$M_{\Sigma^-} = (2343.3 \pm 3.1) m \text{ [SD]} \quad (4-169a)$$

By comparing directly the ranges they obtain an accurate mass difference, independent of both the emulsion stopping power and the K^- mass:

$$M_{\Sigma^-} - M_{\Sigma^+} = (15.9 \pm 2.9) m \quad (4-169b)$$

Chupp *et al.* (181a) report four new events which yield the $\Sigma^- - \Sigma^+$ mass difference:

$$M_{\Sigma^-} - M_{\Sigma^+} = (13.9 \pm 1.8) m \text{ [SD]} \quad (4-169c)$$

the Σ^- mass derived from the range of the two negative Σ 's is

$$M_{\Sigma^-} = (2342.7 \pm 1.3) m \text{ [SD]} \quad (4-169d)$$

Gilbert *et al.* (176b) have analyzed two events in detail:

$$M_{\Sigma^-} = \begin{matrix} (2347.4 \pm 3.5) m \\ (2341.8 \pm 1.5) m \end{matrix} \quad (4-169e)$$

Freden and Ticho (181b) have a particularly good event which yields an excellent mass value:

$$M_{\Sigma^-} = (2340.7 \pm 1.3) m \text{ [SD]} \quad (4-169f)$$

Combining these we obtain a value:

$$M_{\Sigma^-} = (2341.9 \pm 0.7) m \text{ [SD]} \quad (4-169g)$$

The Σ mass difference from these data (113c), equations (4-157c) and (4-169g), is

$$M_{\Sigma^-} - M_{\Sigma^+} = (13.6 \pm 0.9) m \text{ [SD]} \quad (4-169h)$$

York *et al.* (119) have reported a lifetime for Σ hyperons:

$$\left[\left(\begin{matrix} 1.5 & +1.3 \\ & -0.3 \end{matrix} \right) < \tau_{\Sigma} < \left(\begin{matrix} 2.8 & +2 \\ & -0.6 \end{matrix} \right) \right] \times 10^{-10} \text{ sec} \quad (4-170)$$

Two observations of the life of the Σ have been reported by emulsion groups: Davies *et al.* (182) have found

$$\tau_{\Sigma(+ \text{ and } -)} = \left(\begin{matrix} 0.35 & +0.15 \\ & -0.11 \end{matrix} \right) \times 10^{-10} \text{ sec} \quad (4-171)$$

Fry *et al.* (183) combine all the decays in flight and obtain mean lifetimes:

$$\tau_{\Sigma(+ \text{ and } -)} = \left(\begin{matrix} 0.34 & +0.14 \\ & -0.08 \end{matrix} \right) \times 10^{-10} \text{ sec} \quad (4-172)$$

$$\tau_{\Sigma(+ \text{ and } -)} = \left(\begin{matrix} 1.41 & +0.19 \\ & -0.27 \end{matrix} \right) \times 10^{-10} \text{ sec}$$

The latter value is obtained by combining all the events which decay in flight with those which decay at rest (Σ^+) or make stars (Σ^-). These data indicate a lifetime for the Σ^- at least 3 to 5 times longer than that of the Σ^+ .

The mean life obtained by Fry (183) by assuming all Σ 's that decay in flight to be Σ^+ 's and using the Σ^+ 's which decay at rest is

$$\tau_{\Sigma^{(+)}} = \left(0.76 \begin{array}{c} +0.2 \\ -0.15 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-173)$$

On the other hand, the definitely identified events from $\Sigma^+ \rightarrow p + \pi^0$ decay give a mean life which, owing to the large statistical error, includes both the shortest and longest lifetimes obtained with the unknown mixtures. Snow (183a) has summarized all the emulsion Σ^+ events and obtained a mean life

$$\tau_{\Sigma^+} = \left(0.89 \begin{array}{c} +0.14 \\ -0.10 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-173a)$$

With 16 Σ^- decays, Steinberger (181) has obtained a mean life

$$\tau_{\Sigma^-} = \left(1.4 \begin{array}{c} +1.6 \\ -0.5 \end{array} \right) \times 10^{-10} \text{ sec} \quad (4-174)$$

It is difficult to obtain a reliable Σ^+ mean life from Fry's data until one understands what if any bias causes disagreement between the two shortest lived samples which are certainly composed of almost all Σ^+ hyperons. A larger statistical sample may, of course, be the solution.

The lifetimes measured by the Berkeley bubble-chamber group (116a) are: with 44 Σ^- decays in flight and 6 stopped events,

$$\tau_{\Sigma^-} = (1.83 \pm 0.26) \times 10^{-10} \text{ sec} \quad (4-174a)$$

with 27 Σ^+ events,

$$\tau_{\Sigma^+} = (0.86 \pm 0.17) \times 10^{-10} \text{ sec} \quad (4-174b)$$

The possibility of more than one Σ lifetime is not excluded by the data. However, if the components are approximately equal in magnitude, then a difference in lifetime by more than a factor of about three or four is unlikely.

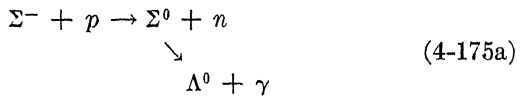
There are to date few accurate data on the mass of the Σ^0 . Evidence concerning the existence of this particle has been obtained at Brookhaven and Berkeley by Fowler *et al.* and by Walker (184), and by Steinberger (181). The mass obtained from the momentum unbalance agrees with the Σ^\pm mass with an error $\pm 60 m$ (184).

The Σ^0 is believed to decay rapidly into the Λ^0 :



An event was observed in the Bevatron neutron beam by Fowler *et al.* (184) in which the γ -ray internally converted. The cloud-chamber picture consists of a proton recoil with an electron-positron pair at the origin, and a nearby Λ^0 decay. From the absence of a gap in the pair origin, they obtain an indication for a Σ^0 lifetime limit of the order of 10^{-12} sec.

Two events have been seen in the Berkeley 10-in. bubble chamber (with magnetic field) with a K^- meson stopping in hydrogen [reaction (4-161)] (116a). The Σ^- comes to rest in hydrogen, and a low-energy Λ^0 is observed. The kinetic energies of the two Λ^0 's are measured as 4.5 ± 0.5 and 2.8 ± 0.5 Mev. The events are interpreted as



With this assignment, the $\Sigma^- - \Sigma^0$ mass difference is

$$\sim 44.5m \leq [M_{\Sigma^-} - M_{\Sigma^0}] \leq \sim 3.4m \quad (4-175b)$$

Plano *et al.* (184a) have seen several events in which Σ^0 's are produced with θ^0 's by energetic pions of well-determined momentum. The γ -ray converts in the propane bubble chamber and the two neutral particles decay; their momenta are determined by the curvature in the magnetic field. The angles agree with the reaction assigned. The average Q value of the Σ^0 decay is measured to be

$$Q_{\Sigma^0(\Lambda^0, \gamma)} = 73.0 \pm 3.5 \text{ Mev} \quad (4-175c)$$

The corresponding Σ^0 mass,

$$M_{\Sigma^0} = (2324.6 \pm 6.9)m \quad (4-175d)$$

as obtained using the Λ^0 mass [equation (4-148)] and this Q value, falls within the limits given by (4-175b) and falls somewhat below the lighter (Σ^+) mass by $(3.7 \pm 7.0)m$.

d. Ξ^- Cascade Particle

The mass of the Ξ^- particle is known from cloud-chamber observations. The decay observed so far is



Table 4-15. Q -Value Measurements of Ξ^- Cascade Particles

Q (Mev)	Method	Reference
$15 < Q < 60$	Cloud chamber	185
60 ± 15	Cloud chamber	186
75 ± 15	Cloud chamber	186
67 ± 12	Cloud chamber	187
66 ± 6	Cloud chamber	188
63 ± 9	Cloud chamber	189
59 ± 11	Emulsions	190
63 ± 27	Emulsions	191
72 ± 20	Emulsions	192
71 ± 5	Emulsions	193
66.6 ± 3.0	Average of these values

Reported Q -values are listed in Table 4-15. In the emulsion events the Λ^0 is not identified. The combined Q value is

$$Q_{\Xi^-} = (66.6 \pm 3.0) \text{ Mev} \tag{4-177}$$

giving a mass

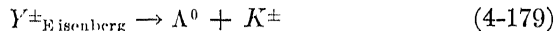
$$M_{\Xi^-} = (2585.0 \pm 5.9) m \tag{4-178}$$

The observation of cascade particle decays in cloud chambers indicates a lifetime of the order of 10^{-10} sec (186).

e. "Anomalous" Particles and Hyperfragments

The individual hyperons and K mesons for which the measured mass falls outside the well-established groups by more than the estimated experimental errors are often called "anomalous." The reader should refer to the current literature as well as to work mentioned earlier—for example, references 84 through 93, and 160—for the status of this very important problem. The frequency of such anomalies may be decreasing somewhat as estimates of measurement errors improve and as these "anomalies" achieve the status of well-established particles.

There are a few examples of a charged particle decaying into a K meson. The events observed by Eisenberg (194) may be a heavier hyperon that decays as follows:



The neutral is not observed so that only a crude estimate based on multiple scattering measurements gives 3160 m for the primary mass.

An alternative explanation might be a decay of a heavy K meson:



Fry *et al.* (195) report a possible event of this type. Evidence for the reaction



has been reported by van Lint *et al.* (196).

Unstable hyperfragments are observed in which a hyperon is apparently bound to a nucleus. Many examples of Λ hyperfragments have been reported and the binding energy of the Λ^0 in various nuclei can be measured. Fry, Schneps, and Swami (197) have given in their article an excellent bibliography as well as a summary of the measured binding energies.

Ruderman and Karplus (198) have made an analysis of the mesic versus nonmesic decays of hyperfragments, and conclude that the Λ^0 has spin 1/2 or 3/2; if the spin is 3/2 the parity is the same as that of the proton. Early results on angular correlations of the production plane and the decay plane of the Λ^0 implied a high value for the Λ^0 spin. The status of these experiments is at present ambiguous (199, 181, 177).

f. Strange Particles

The intention of this chapter is not to discuss the details of theories of the new elementary particles. There is, however, a growing body of facts that can be shown to fall within a rather general framework. To explain the early observations that the new unstable particles— K mesons and hyperons—were produced with relatively large cross sections and yet had long lifetimes against decay into strongly interacting pions and nucleons, Gell-Mann and Pais (200) have proposed a theory of associated production by which only pairs of these particles may be made in nuclear collisions. Furthermore, they postulate that the decay proceeds slowly because it is a “forbidden” transition. The rule takes the form of a new quantum number called “strangeness” which characterizes the new particles. The charge Q of the particle is given in terms of the Z component of the isotopic spin I , the number N of nucleons minus antinucleons, and the strangeness classification S , by the relation

$$Q = I_z + \frac{N}{2} + \frac{S}{2} \quad (4-182)$$

Table 4-16. Gell-Mann Classification of Particles

Strangeness	-2		-1		0		+1		+2	
	$ I = 1/2$	$ I = 1$	$ I = 0$	$ I = 1/2$	$ I = 1/2$	$ I = 1$	$ I = 1/2$	$ I = 0$	$ I = 1$	$ I = 1/2$
$I_z:$										
+1	Σ^+	π^+	Σ^-
$+1/2$	Ξ^0	p, n	K^+	Ξ^-
0	Σ^0	Λ^0	π^0	Λ^0
$-1/2$	Ξ^-	\bar{n}, \bar{p}	K^0	Σ^0
-1	Σ^-	π^-	Σ^+	Ξ^0
Hyperonic charge U	-1	0	0	-1	+1, -1	0	+1	0	0	+1
Baryon or nucleon number N	+1	+1	+1	0	+1, -1	0	0	-1	-1	-1

Table 4-16 shows the relative positions of all the particles which have been discussed; similar assignments have been made by Nishijima (201), Sachs (202), Goldhaber (203), and others (204).

D'Espagnat and Prentki (204a) show that the Gell-Mann scheme is a natural consequence of the rotation and reflection invariance in isotopic spin space. A new constant U (or Y) is introduced, the "isofermionic" or "hyperonic" charge, or simply "hypercharge." The value of U is defined to be the net charge in each isotopic spin multiplet; the particle charge Q is then given by

$$Q = I_z + \frac{U}{2} \quad (4-183)$$

U takes the value 0, ± 1 , in analogy to 0, $\pm e$ for the charge. The strangeness S is related to the hypercharge by

$$S = U - N \quad (4-184)$$

It can be seen by inspection of Table 4-16 that this assignment is in accord with the Gell-Mann assignment. The location of antiparticles is fixed as follows: Since I_z is conserved for annihilation, a strong interaction, I_z goes to $-I_z$, so that U goes to $-U$ and S goes to $-S$ under charge conjugation operation ($Q \rightarrow -Q$, $N \rightarrow -N$).

One advantage of this scheme is that there is no unfilled or additional vacancy: $S = \pm 3$, or $N = +1$ and $S = +2$, etc., are not possible unless one introduces $U = \pm 2$, departing from the charge analogy (there are no multiply-charged elementary particles). There is one exception in this model: for $N = 0$, the isotopic singlet is not known. It therefore follows that if any other elementary particle is established (see Sec. 4.4e), this scheme cannot be adequate.

The selection rules are that the allowed processes are those for which $\Delta S = 0$, the slow processes for which $\Delta S = \pm 1$. The evidence supporting this assignment has accumulated steadily. There are no observed violations of the rules in the interaction or production processes.

Associated production has been amply demonstrated. There have been systematic searches for single production without success. Production in which $\Delta S \neq 0$ —i.e., $\Lambda^0 + \Lambda^0$, $\Sigma + \Sigma$, $\Sigma + \Lambda^0$, $\Sigma + K^-$, $\Lambda^0 + K^-$ —have not been observed. The ratio of positive to negative K mesons near threshold favors positives since less energy is

Table 4-17. Summary of the Masses of the Unstable Particles
References, unless otherwise noted, are to the text.

Particle	Mass (<i>m</i>)	Reference	Mean Life (sec)	Reference
μ	206.86 ± 0.11	Eq.(4-90)	$(2.22 \pm 0.02) \times 10^{-6}$	Eq.(4-91)
π	273.27 ± 0.11	Eq.(4-89)	$(2.56 \pm 0.05) \times 10^{-8}$	Eq.(4-49)
π^0	264.27 ± 0.32	Eq.(4-59)	$< 4 \times 10^{-16}$	Eq.(4-61a)
$K_{\mu 2}^0$	965.3 ± 1.9	Eq.(4-112)	$\left(\begin{array}{l} 11.7 + 0.8 \\ - 0.7 \end{array} \right) \times 10^{-9}$	Eq.(4-126)
$K_{\pi 2}^0$	966.0 ± 1.7	Eq.(4-111)	$\left(\begin{array}{l} 12.1 + 1.1 \\ - 1.0 \end{array} \right) \times 10^{-9}$	Eq.(4-125)
τ	966.80 ± 0.43	Eq.(4-100)	$\left(\begin{array}{l} 11.7 + 0.8 \\ - 0.7 \end{array} \right) \times 10^{-9}$	Eq.(4-124)
θ^0	965.1 ± 5.0	Eq.(4-120)	$(0.6 \text{ to } 2) \times 10^{-10}$	Table 4-11
ρ	1836.12 ± 0.02	Table 8-7	stable: $> 3 \times 10^{28}$	^b
η	1838.65 ± 0.02	Table 8-7	$(1.04 \pm 0.13) \times 10^3$	^c
Λ^0	2181.74 ± 0.35	Eq.(4-148)	$(3.25 \pm 0.33) \times 10^{-10}$	Eq.(4-152)
Σ^+	2328.3 ± 0.5	Eq.(4-157c)	$(0.86 \pm 0.17) \times 10^{-10}$	Eq.(4-174b)
Σ^0	2341.9 ± 0.7	Eq.(4-169g)	$(1.83 \pm 0.26) \times 10^{-10}$	Eq.(4-174a)
Σ^0	2324.6 ± 6.9	Eq.(4-175d)	$\ll 10^{-12}$	Eq.(4-184)
Ξ^-	2585.0 ± 5.9	Eq.(4-178)	$\sim 10^{-10}$	^d

^a Note that the masses of these *K* mesons, as well as of other types of *K* mesons not listed, are not significantly different from that of the τ (see Table 4-9).

^b See reference 205.

^c See reference 206.

^d See references 185-189.

required for the associated production by the allowed reaction of $K^+ + (\Lambda^0 \text{ or } \Sigma)$ than for $K^- + K^+$.

The interaction of K mesons with nucleons shows complete charge asymmetry. K^+ mesons according to the scheme can only scatter elastically or charge exchange, whereas the K^- can also form Σ 's or Λ 's. This is in agreement with observation.

Table 4-17 gives a summary of the masses of the unstable particles.

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$$M_{\Sigma^-} = (2341.6 \pm 1.0) m$$

$$M_{\Sigma^-} - M_{\Sigma^+} = (14.1 \pm 1.2) m$$

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History of the Atomic Constants

A clear-cut definition of the subgroup which we shall call the atomic constants is difficult to formulate. R. T. Birge was one of the first to use the term atomic constants in his 1929 review (reference 1, Chapter 1). An important part of this review was concerned with determining the "best" values of e , the electronic charge, m , the electronic mass, and h , Planck's constant of action, three quantities which indisputably deserve the name, atomic constants. It was clear in 1929 that many of the most important sources of information for determining e , m , and h were indirect in nature. For example, one way by which Birge arrived at a value of h was by combining measured values of four quantities, e , c , e/m , and $R_\infty = 2\pi^2e^6h^{-3}c^{-2}(e/m)$ and then solving for h . With the passage of time more and more of these indirect ways involving other measured physical quantities made their appearance, and it soon became clear that in order to obtain a *consistent* set of values of all the constants which could be so determined (consistent, that is, with all the accepted theoretical relationships connecting them) it was unavoidably necessary to determine a considerable number of interrelated constants simultaneously. Thus it developed as time went on that a discussion of the atomic constants required careful study and discussion of measurements of an ever-increasing number of physical magnitudes such as the velocity of light, c , the Faraday, F , and the Sommerfeld fine structure constant, α . These all had to be studied with about equal care and from the mathematical point of view were so intimately interrelated that the entire group came to be called the atomic constants. About the only general physical constant that is not related in some known way to the atomic constants is the Newtonian constant of gravitation discussed in Section 3.1.

At present a large group of important, fundamental, experimen-

tally measured, numerical values, each known with high precision, is available to yield information pertinent to the atomic constants. These directly measured quantities which constitute our input data are so interlaced with well-established theoretical relationships that a precise knowledge of only a small number of them (the group which we shall call our unknowns) fixes all the others. Once the unknowns have been determined, a few "auxiliary constants" suffice to compute the values of a very long list of convenient constants and conversion factors of physics. The choice of *which* particular set of atomic constants shall constitute the unknowns to be adjusted in this way is to some extent arbitrary or dictated by mathematical convenience. The choice has changed from time to time, and this is another reason why the meaning of the term atomic constants has become increasingly inclusive and indefinite.

The experimentally measured numerical values which constitute our input data are each to be equated to a function of the unknowns which represents the interpretation of that particular experiment. The set of equations which results from this process will in general contain more equations than there are unknowns. In such a situation it becomes immediately interesting to inquire how *consistent* the overdetermined set is. If some few of the input data are glaringly inconsistent with the remainder, this may indicate that hitherto unsuspected systematic errors afflict those data. Aside from the exercise of vigilance in the experiments themselves, this test of consistency is in fact the only safeguard we possess against systematic errors. A maximum degree of overdetermination is therefore always to be sought.

At the outset (in his 1929 paper) Birge found himself confronted with a confusing mass of overdetermined and woefully inconsistent data. The discrepancies from consistency were so large relative to the estimated accuracy of the individual measurements that the situation did not lend itself to any straightforward analytic conclusion. He therefore used the subjective method of judiciously selecting certain subgroups of data, each sufficient to solve for some chosen atomic constant (e , m , or h), and calculating values of that constant by a number of such just-determinate paths. In the course of his analysis of each individual experiment Birge often corresponded privately with the research workers in an effort to detect hidden mistakes or overlooked corrections, and then reanalyzed

the primary observational data using improved statistical methods. In this way he succeeded in isolating one discrepancy after another.

Undoubtedly the greatest single contribution to the progress of our knowledge of the atomic constants is to be found in these monumental pioneer efforts. His 1929 and 1942 general reviews (reference 1, Chapter 1; reference 12, Chapter 2) are all-time models of patient and meticulous care in the study and gradual organization of a huge mass of primary data. In this winnowing of the chaff from the wheat Birge occasionally encountered some astonishing discrepancies and oversights coming from the work of outstanding authorities, whose great prestige had placed their reliability quite beyond question.

Since some of these discrepancies have been shown to have their roots in errors connected with historically important experiments, and indeed in experiments still frequently cited in textbook accounts of how such atomic constants as e , h , and m were first measured, it is valuable to retrace the history of the progress of our knowledge of the atomic constants in order to clarify the record up to the present. After correcting these earlier methods for their systematic errors, their results have been shown to be not inconsistent with those of the later and more indirect, but far more precise, methods. These earlier methods were of great value for the progress of knowledge in their time and still possess immense historical importance, even though they do not now make contributions of significant weight in a present-day precision least-squares evaluation of the atomic constants.

5.1 THE VELOCITY OF LIGHT

The measurements of the velocity of light, perhaps the most important of all the constants fixed by Nature, have a long history starting in 1676 with the work of the Danish astronomer Ole Römer on the fluctuations in his observations of the time of arrival of the eclipses of Io, Jupiter's first satellite. A series of observations by the Italian astronomer, Cassini, had earlier permitted an accurate evaluation, for the chosen satellite, of the average eclipse period, T_0 . A modern determination gives this period as 42 hours, 28 minutes, 16 seconds. The distance between Jupiter and the earth varies because of the different orbital periods of these two bodies, the difference between the maximum and minimum distances being

the diameter of the earth's orbit. Römer found a secular variation in the period with an amplitude of approximately 20 seconds and a period of 13 months. This 13-month period is just the time required for the earth to move in its orbit from one closest approach to Jupiter to the next. Thus starting at a time when the earth was closest to Jupiter and trying to infer the time of occurrence of an eclipse $6\frac{1}{2}$ months later (when the earth was its full orbital diameter more distant), Römer found a delay which he estimated to be of the order of 22 minutes. He correctly inferred from this that light travels with a finite velocity. This interpretation was not accepted, however, until an entirely independent determination of light velocity based on the effect known as the aberration of light, a displacement of the apparent position of the stars in the direction of the earth's orbital velocity, was discovered in 1727 by the English astronomer, James Bradley.

In 1849 the French physicist, H. L. Fizeau, first succeeded in measuring c , the velocity of light, by a method not involving astronomical observations. He measured the time of transit of light flashes between two hills, Montmartre and Suresnes, about 8.6 km apart, near Paris. The beam of light was modulated into flashes by means of a wheel with 720 teeth, and Fizeau measured the successive critical speeds of rotation at which the returning flash of light was just eclipsed by rotation of succeeding teeth into the path. The experimental conditions of this experiment were later improved by Cornu and by Young and Forbes with more accurate results.

The famous rotating mirror method was first suggested by the French astronomer, D. F. J. Arago, and first applied successfully by Fizeau and by J. L. Foucault working independently in 1850. In these experiments a pencil of light from a point source was reflected from a rapidly rotating plane mirror, and after traversing a path to a stationary mirror about 20 meters distant returned to the rotating mirror. During the time of transit this mirror was found to have rotated sufficiently to displace the focused image of the light source 0.7 mm. Foucault's result for the velocity of light was roughly $298,000 \text{ km sec}^{-1}$. This method was greatly improved by Cornu, by Simon Newcomb, and by A. A. Michelson, who increased the path distance and utilized rotating polygonal mirrors with very accurately polished optically plane faces and with optically correct mutual orientations. In a series of experiments performed in Cali-

fornia and published in 1926, Michelson (1) used a light path of 44 miles, from Mt. Wilson to Mt. San Antonio and return; the average value of 200 determinations varying between extremes of 299,756 and 299,803 km sec⁻¹ yielded, after correction for the group velocity refractive index of air to obtain the vacuum value,

$$c = 299,798 \pm 4 \text{ km sec}^{-1} \quad (5-1)$$

The toothed wheel, rotating mirror, and similar methods of modulating a light beam all yield values of the *group* velocity of light in the medium employed. In a dispersive medium the group velocity and phase velocity are, however, not identical, and therefore the group refractive index of air is the one which must be used in correcting the results to find the vacuum value of *c*. Actually Michelson had incorrectly used the phase velocity refractive index of air instead of the group velocity refractive index in reducing his 1926 results. R. T. Birge detected this error, and for this reason made a correction upward of 2 km sec⁻¹ in Michelson's value obtaining the result (5-1). As Table 5-1 below shows, this point was overlooked by several other workers also. Birge refers to this oversight on Michelson's part as "one of the most inexplicable errors" he ever encountered (reference 12, Chapter 2), since Michelson had in earlier work shown himself to be completely familiar with the distinction between group and phase velocity indices.

The light path for Michelson's Mt. Wilson determinations was measured by the U. S. Coast and Geodetic Survey in a remarkably accurate triangulation from a 40-km base line. The length of this base was determined to an estimated error of 1 part in 11 million. The result (5-1), within its estimated error range, is in accord with the results of the best modern measurements.

A rotating mirror experiment, begun in 1929 by Michelson, Pease, and Pearson (2) but not completed until after Michelson's death in 1931, was conducted over a light path in a 1 mile long evacuated pipe on the Irvine Ranch near Laguna Beach in California. Successive to-and-fro reflections between plane mirrors were used to give a total light path of some 10 miles. A plot of the statistical frequency distribution of the results of nearly 3000 measurements with this equipment showed a distribution with a strong symmetrical peak centered at the mean value

$$c = 299,774 \text{ km sec}^{-1} \quad (5-2)$$

The distribution exhibited, however, rather widely spreading, more or less symmetrical wings or plateaus on either side of the central peak which were decidedly non-Gaussian in character. The computed "probable error" of this array of results was ± 0.2 km sec⁻¹, but this apparently overestimates the true accuracy considerably, and in the light of our present knowledge the mean result (5-2) is almost certainly 18 or 19 km sec⁻¹ too low. It is perhaps significant that the value now strongly indicated as correct by modern and very accurate methods, namely, 299,793 km sec⁻¹, or even Michelson's slightly higher value (5-1), falls well inside the non-Gaussian plateau on the statistical distribution curve of the Irvine Ranch results. A posteriori reasons to account for the systematic errors in this Michelson, Pease, and Pearson determination are not hard to find. The base line was on very unstable alluvial soil. A correlation between fluctuations in the results and the tides on the sea coast was reported. A far greater number of measurements with the rotating mirror than measurements of the admittedly fluctuating base length were made. Base length measurements, it appears, were all made in the daytime, whereas a great majority of the rotating mirror measurements were made at night.

Beams of light modulated at high frequencies in the megacycle range by Kerr-cell methods have in the most modern work of Bergstrand, with the equipment which he calls the "geodimeter," far surpassed the accuracy attained with rotating mirrors. Bergstrand's value of 299,793 km sec⁻¹ is in accord with an impressive array of other evidence. Karolus and Mittelstaedt in 1925 were the first to develop this Kerr-cell method, and W. C. Anderson in 1937 and in 1941 improved upon it (3). Nearly 3000 observations in 1941 by Anderson, however, yielded the mean value

$$299,776 \pm 6 \text{ km sec}^{-1} \quad (5-3)$$

which agrees very well with the Michelson, Pease, and Pearson value, the one which we now regard as almost certainly 19 km sec⁻¹ too low. The different transit times of the electrons in the detecting tube in Anderson's work constituted a possible source of systematic error which he recognized clearly himself. This latter objection is avoided in Bergstrand's geodimeter.

These two measurements, (5-2) and (5-3), with their impressively large number of replicated observations and their excellent (but

apparently fortuitous) agreement, have misled physicists, including R. T. Birge, for about a decade. Not until C. I. Aslakson in 1949, using "Shoran," a radar method of measuring the distance of an airplane from a ground station by the time of flight of a radio signal, reported a higher value, was suspicion cast on the value $c = 299,776$ km sec⁻¹. When signals were measured using Shoran, as the airplane approached a position of exact alignment between two ground stations separated by a known distance, Aslakson obtained limiting results indicating a value, $c = 299,792 \pm 3.5$ km sec⁻¹. Since then other measurements of the constant c for electromagnetic radiation have been made by many observers and by much more accurate methods, all supporting the higher value, $c = 299,793$. We defer discussion of these to Section 6.2, however, and restrict the present Section to measurements of c for light of optical frequency.

The geodimeter of Bergstrand (4) is an improved Kerr-cell modulation method for measuring the time of flight of a light pulse over outdoor paths of order several kilometers. It was developed primarily for use in precision geodetic surveying. A frequency of 8.33 Mc with amplitude of 2000 volts is used to modulate the light source by means of a Kerr cell, and the same high-frequency oscillator also modulates the detecting photomultiplier tube which receives the returning light from the distant mirror. A 50 cps alternating bias voltage of 5000 volts with square waveform is also applied to the Kerr cell so that the 8.33 Mc oscillations swing to and fro over the steepest and most linear region of the Kerr cell's characteristic curve of light intensity versus applied voltage. Thus one set of alternate half-waves of the H.F. oscillator give high light transmission during one entire half cycle of the 50 cps square-wave bias voltage, while the other H.F. half cycles give low transmission so as to yield a nearly pure sinusoidal variation of light intensity at 8.33 Mc sec⁻¹. During the next half cycle of the 50 cps square wave the reversed bias causes the oscillations of light intensity to occur with the high light transmission maxima 180° of the 8.33 Mc sec⁻¹ frequency out of phase with respect to their phase during the preceding half cycle of the low frequency. If the oscillations of intensity of the returning light are in suitable phase coincidence with the electrical H.F. which modulates the plate voltage of the photomultiplier tube, the latter will supply 50 cps rectified pulses of a maximum amplitude during one set of alternate

half cycles. These furnish a rectified pulsating signal to an amplifier. A shift in relative phase between incoming light pulsations and R. F. modulating voltage on the photomultiplier tube away from this optimum phase will reduce this signal. During the other set of alternate half cycles of the 50 cycle square-wave biasing voltage, practically no rectified signal will be available from the photomultiplier tube because the 8.33 Mc modulating voltage applied to its plate is in the wrong phase. Clearly, however, a shift in phase of the sinusoidal light intensity can modify this condition of extreme unbalance between the rectified signals from the two sets of alternate 50 cycle half-waves. Two vacuum tubes controlled from the 50 cps square-wave supply serve to switch alternate pulses of this amplified signal from the photomultiplier through a D.C. meter of long period. Reversing switches permit the operator to reverse the phases of the 50 cps which the switching tubes select and also to reverse the phase of the 8.33 Mc voltage applied to the photomultiplier tube plate. There will be some distance for the remote mirror such that the phase delay of the returning oscillations of light intensity will just yield a zero reading on the D.C. meter and, for the selected frequency of 8.33 Mc, there will occur another such zero for every increase or decrease in distance of the mirror of about 9 meters.

Bergstrand explains in his published articles (4) the means he has provided to correct for the systematic error occasioned by the fact that "different parts of the image"—of the light source at the distant mirror—"have different phases, dependent on the part from which the light is emanating in the space between the Kerr cell plates."

Bergstrand's measurements with his geodimeter are seen in Table 5-1 to yield a value of c about 19 km sec^{-1} higher than the Michelson, Pease, and Pearson or the Anderson values. The geodimeter has also been independently used by Mackenzie in Scotland (5) with results which do not differ significantly from Bergstrand's.

We give in Table 5-1 a list of all the significant determinations of the velocity of light of optical frequencies. The first twelve are taken from Birge's 1941 review (reference 12, Chapter 2).

For reasons to be explained in Chapter 7, the root-mean-square or "standard" error is uniformly adopted as an index of precision in this tract. For this reason whenever "probable errors" were

Table 5-1. Determinations of the Velocity of Optical Light

Author	Method	Year	Corrected Result (km sec ⁻¹)	Standard Deviation (km sec ⁻¹)	Corrected by	Corrected for
Cornu-Helmert	TW	1875	299990	±300		
Michelson	RM	1879	299910	± 75		
Newcomb	RM	1883	299860	± 45		
Michelson	RM	1883	299853	± 90		
Perrotin	TW	1902	299901	±104		
Rosa-Dorsey ^a	REU	1906	299784	± 15	R. T. Birge, 1941	Elect. conv. factor
Michelson	RM	1927	299798	± 22	R. T. Birge, 1941	Group vel. Index refr. air
Mittelstaedt	KC	1928	299786	± 15	R. T. Birge, 1941	Group vel. Indices of opt. path
Michelson, Pease, and Pearson	RM	1933	299774	± 6		
Anderson	KC	1937	299771	± 15	R. T. Birge, 1941	Group vel. Indices of opt. path
Hüttel	KC	1937	299771	± 15	R. T. Birge, 1941	Group vel. Index refr. air
Anderson	KC	1941	299776	± 9		
Bergstrand	KC	1951	299793.1	± 0.32		
Mackenzie	KC	1953	299792.4	± 0.5		

TW = toothed wheel; RM = rotating mirror; REU = ratio electrical units; KC = Kerr cell

^a The Rosa-Dorsey determination is listed here for purposes of comparison. It is not a determination of the velocity of optical light but of the constant, c , in Maxwell's equations. We have no reason to believe that the two should differ in value, however.

given we have converted them to standard errors in Table 5-1 by dividing each probable error by 0.6745. For purposes of comparison we include in this list also the indirect determination of c by Rosa and Dorsey (6), obtained by measuring the ratio of an electrical charge in absolute esu to the same charge in absolute emu. This experiment, very carefully carried out at the U. S. National Bureau of Standards, has been characterized by Birge (1941) as "one of the most beautifully executed pieces of precision research in the entire history of science." It is to be noted that the Rosa and Dorsey value, $c = 299,784 \pm 15 \text{ km sec}^{-1}$, is about at the mid-point of the above-mentioned 19 km sec^{-1} discrepancy interval. Its precision is insufficient to discriminate clearly in favor of either the old 299,774 value or the modern 299,793 value, but it should be noted that this meticulously careful piece of work is not inconsistent with the modern high value since the difference, 9 km sec^{-1} , has an expected standard deviation of $\pm 15 \text{ km sec}^{-1}$. In fact, if the Michelson, Pease, and Pearson and the Anderson values are excluded, the remaining data of Table 5-1 including the work of Rosa and Dorsey and the Mt. Wilson work of Michelson are not at all inconsistent with the newer, much more accurate high value. Further strong support for this high value comes from microwave cavity resonance and interferometer measurements made since 1949 with very superior precision. These will be described in Section 6.2. We therefore defer discussion of the value of c to be adopted in this text to that Section.

A more detailed account of the history and classical methods of measuring c may be found in standard optics texts (7, 8).

5.2 MILLIKAN'S OIL-DROP EXPERIMENT

Undoubtedly the most important key experiment in the evolutionary process which has led to our present precise knowledge of the atomic constants was the justly famous oil-drop experiment of R. A. Millikan. This experiment served both to establish the "unitary" or discrete nature of electrical charge and to measure the magnitude of that charge. It was developed by Millikan as a logical outgrowth from the earlier work of Townsend (9), J. J. Thomson (10), and H. A. Wilson (11), using clouds of water droplets. Millikan conceived the idea of working with single droplets of watch oil, this substance being chosen to minimize changes in size of the droplet

by evaporation or condensation during the observations. Millikan's own detailed description (12) of these and related experiments is one of the great scientific classics and should be consulted for those details which cannot be included here.

In this experiment, whose apparatus is illustrated in Figure 5-1 a droplet of watch oil is kept suspended in air in a homogeneous electric field of intensity, F , between the plates of an electrical condenser. The droplet, strongly illuminated, is observed in the field of a micro-

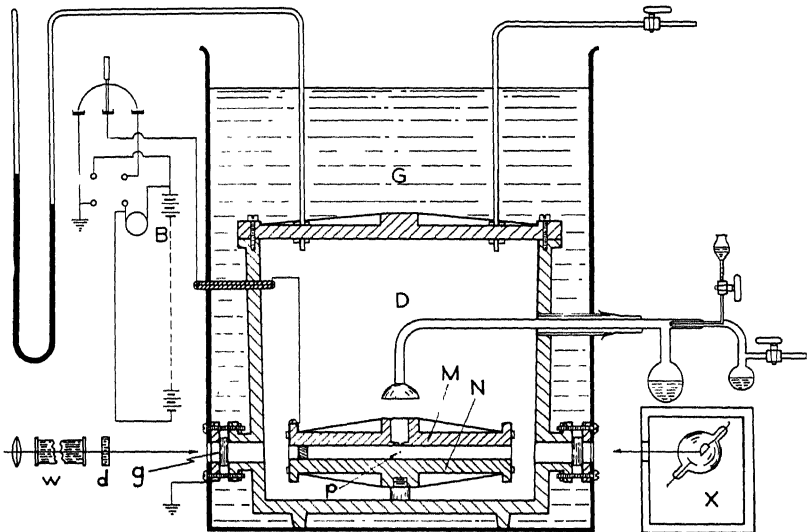


Figure 5-1. R. A. Millikan's oil-drop apparatus for measuring the electronic charge.

scope provided with cross hairs. If F is made zero by short-circuiting the condenser plates, the droplet falls at a uniform terminal speed, v , calculable, to first approximation, by equating the gravitational force, mg , to Stokes' formula for the viscous resistance of a spherical particle under nonturbulent flow, $6\pi\eta av$. The mass, m , of the droplet is $(4/3)\pi a^3\rho$. In these formulas a is the radius of the spherical droplet, ρ its density, η the viscosity of air, and g the local acceleration of gravity. By measuring the time of transit across the fixed distance defined by the cross hairs, the terminal speed of fall, v , was ascertained and this together with a knowledge of η , ρ , and g

permitted calculation of the radius of the droplet, a . It is easy to see that*

$$a^2 = \frac{9}{2} \frac{\eta}{\rho} \frac{v}{g} \quad (5-4)$$

The gravitational force on the droplet is then in principle known. It is

$$mg = 9\pi[2\eta^3v^3/(\rho g)]^{\frac{1}{2}} \quad (5-5)$$

In this way Millikan established that droplets of a wide variety of quite accurately calculable sizes and masses were obtained. However, without the necessity of knowing either the size, or the mass, or even Stokes' law of fall, but merely from the assumption that the viscous retarding force on a droplet is proportional to its velocity, Millikan gave a convincing demonstration of the unitary nature of electrical charge. This in itself was of greater fundamental importance to atomic theory than his measurement of that charge.

If v_1 is the terminal speed of fall under gravity alone and v_2 is the speed of the droplet (counted positive upward) when an electrostatic field, F , exists between the condenser plates, e_n being the charge on the droplet, then

$$\frac{v_1}{v_2} = \frac{m_g}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{F} \frac{v_1 + v_2}{v_1} \quad (5-6)$$

The droplets were found to be strongly charged by frictional effects incident to forming them with an atomizer. Millikan also introduced various artificial ionizing sources (x-rays and nuclear radiations) to create ions in the air between the condenser plates and thus to encourage changes in the electrical charge carried by the droplet. Whenever such a change in the charge, e_n , to a new value, e_n' , occurred, a change in the velocity of rise of the droplet under the applied field, F , would be observed. If, by the capture of an ion, the droplet changed its charge from e_n to a new value, e_n' , and its upward speed thereby changed from v_2 to v_2' , the value of the captured charge, e_i , would be given by

$$e_i = e_n' - e_n = \frac{mg}{F} \frac{v_2' - v_2}{v_1} \quad (5-7)$$

* A small correction is required for the buoyant force of the air. This introduces the factor $(1 - \rho_0/\rho)^{-3/2}$ into equation (5-5), where ρ_0 is the density of air.

and since mg/Fv_1 is a constant for each individual drop (so long as no evaporation or condensation takes place), any charge which it might capture would always be proportional to $v_2' - v_2$, the change observed in the droplet's upward speed under the field, F . As a droplet approached the upper condenser plate the field would be switched off and the droplet allowed to fall under gravity. These periods of fall served to check whether any appreciable change in droplet size and mass had occurred.

In this way Millikan showed that the changes in speed, and hence the charges captured, were always multiples, usually no greater than two or three, of a constant base value to within the uncertainty of his transit time measurements. To quote his own words, "Here then is direct, unimpeachable proof that the electron* is not a 'statistical mean,' but that rather the electrical charges found on ions all have exactly the same value or else small exact multiples of that value."

The reader should consult Millikan's text (12) for an account of the many refinements and precautions he introduced such as his magnificent study of the deviations from Stokes' law of fall for smaller droplets when the size approached comparability with the mean free path of the air molecules. Such effects led him also to important researches on the Brownian motion bearing on the value of Avogadro's number, N .

Millikan's final value, the mean result of observations extending over a period of two years on 25 droplets varying in size from 23.4×10^{-5} cm to 12.2×10^{-5} cm radius at air pressures varying from about normal atmospheric to 20.5 cm of mercury, was

$$e = (4.770 \pm 0.005) \times 10^{-10} \text{ abs esu} \quad (5-8)$$

The entire work appeared to be a supreme example of attentive care in every conceivable detail, and yet we now know that one essential factor used in Millikan's calculations of the charge, e , was incorrect. This was η , the viscosity of air.

5.3 HARRINGTON'S DETERMINATION OF THE VISCOSITY OF AIR

It is clear from our equations (5-5) and (5-6) that in the evaluation of the charge, e_n , the coefficient of viscosity, η , enters to the

* Millikan preferred to use the word electron to denote a quantity of electrical charge of either sign rather than the name of the negative particle, as is now the common usage.

$3/2$ power. The methods then available for measuring η were (1) the rate of flow of air through capillary tubes or pipes, (2) damping of oscillating cylinders or pendulums, (3) torque transmission between rotating cylinders. This last method uses two vertical coaxial metal cylinders with a small air gap between them. One of these cylinders is hung from a fine axial suspending fiber while the other cylinder is caused to rotate relative to the first at an accurately measured speed. The viscous drag coming from the transfer of momentum by the air molecules across the air gap from the moving cylinder to the stationary cylinder exerts a torque on the latter which can be measured by its steady angular deflection from the equilibrium position against the restoring torque of the fiber. Millikan gave great weight to the results of one of his colleagues, E. Harrington (13), working at the Ryerson Physical Laboratory of the University of Chicago with this constant deflection method. Later criticism and more careful measurements (14), however, have shown that Harrington's value of η was biased by several serious systematic errors. W. V. Houston showed (14) that Harrington had overlooked a correction which must be applied for the viscous drag exerted on the ends of the suspended cylinder, a drag exerted through the clearance opening between the suspended cylinder and the stationary guard cylinders adjacent to each end. Furthermore, Houston showed the necessity for another correction overlooked by Harrington—a correction for the effect of the air entrained by the suspended cylinder on the apparent moment of inertia of the latter. This introduced an error in Harrington's inference of the restoring torsional constant of the fiber. Actually Harrington's η was too low by about 0.4 per cent, and as a result Millikan's value of e was too low by about 0.6 per cent. This systematic error remained completely unsuspected for a period of about 15 years (1916 to 1931). Because of the great importance of e and its close relationship to many other atomic constants this error had quite far-reaching effects.

5.4 RELATIONSHIP OF THE CONSTANT, e , TO OTHER ATOMIC CONSTANTS

Millikan was fully aware of the importance of the constant he had measured. A precise knowledge of e furnishes one way of establishing the scale factor connecting all the atomic magnitudes with

macroscopic magnitudes accessible to measurement by ordinary means. The quotient of the Faraday constant by e gives us Avogadro's number (Section 3.6) and hence the absolute masses of all atoms (in grams). If we know the absolute mass of any atom, we can compute the volume in cubic centimeters occupied by the "unit cell" of the atomic lattice of a crystal from the crystal's measured macroscopic density, once the geometry of the structure has been established by x-ray diffraction studies. From this we can determine the interatomic spacings (interplanar grating constant, d) of the lattice. With d known, Bragg's law of selective x-ray reflection from the crystal atom planes, with appropriate corrections for refractive index, combined with the measured angles of selective reflection, permits one to compute the wavelengths of characteristic x-ray spectral lines in absolute centimeter units. Sir William Bragg in England was the first to do this, and he was followed by A. H. Compton in the United States and by Manne Siegbahn in Sweden. Siegbahn using this method set up a scale of x-ray wavelengths in terms of a unit intended to be equal to a milliangstrom (10^{-11} cm) but which he very wisely chose to call by a different name, the x-unit. (See Section 5.6.) These wavelengths and corresponding frequencies lead to information about a host of atomic magnitudes involved in the Bohr-Sommerfeld theory of the atom.

The calculation of a great number of other atomic magnitudes requires a knowledge of e . Examples of such are Boltzmann's constant, $k = R_0/N = R_0 e/F$; Planck's constant, $h = e(h/e)$ (see Section 5.11 for experiments leading to values of h/e); the rest-mass, m , of the electron (by combining e with the results of spectroscopic or deflection methods of determining e/m); the Bohr radius, $a_0 = h^2/(4\pi^2me^2)$. Though not all the constants which depend on the electronic charge were known in 1916, the far-reaching effect of the one systematic error in Harrington's determination of η can thus be easily appreciated. Perhaps the most important effect of this error concerned the establishment, by the method mentioned above, of the absolute scale of x-ray wavelengths. In fact it was the eventual development of a more accurate and direct independent method of establishing the scale of x-ray wavelengths in absolute cgs units (the study of x-ray diffraction at grazing incidence by ruled gratings) which finally revealed the systematic error in Harrington's η and Millikan's e .

5.5 RULED GRATING MEASUREMENTS OF X-RAY WAVELENGTHS

The discrepancy between Siegbahn's x-unit and the milliangstrom unit began to be manifest when the wavelengths of certain soft x-ray lines which had been measured in x-units by the methods of crystal diffraction were also precisely measured with artificially ruled gratings whose grating constants had been calibrated using known optical wavelengths. The reproducibility and precision in the measurements by crystal diffraction are such that the accuracy with which we know the *ratios* of the wavelengths of characteristic x-ray spectral lines to each other is very high indeed, of the order of a part in 10^5 in many cases. The uncertainty regarding the absolute value of x-ray wavelengths therefore concerns only the value of a single conversion factor, $\Delta = \lambda_g/\lambda_s$, the ratio of a given wavelength expressed in milliangstroms, λ_g (i.e., on the "grating scale") to the same wavelength expressed in x-units, λ_s (i.e., on the Siegbahn scale).

The first to note a discrepancy was Erik Bäcklin in his thesis dissertation at Uppsala (1928). Because of the great prestige of R. A. Millikan and the rather obscure nature of the true source of error, more than a decade elapsed before there was general acceptance that Millikan's value (5-8) was seriously erroneous. During this period there was much discussion of the "discrepancy" between the "oil-drop" and the "x-ray" values of e . Several rather far-fetched proposals to explain this discrepancy were made by proponents of the Millikan value before the error in η was definitely established as the chief source of the trouble: (1) It was proposed that a mosaic structure or that impurities in the crystals might be responsible. (2) It was suggested that the laws of optics might not be applicable to the diffraction of x-rays from ruled gratings at grazing incidence; a careful analysis by C. Eckart (15) refuted this. (3) The grating constant measured with x-rays might not be the same as the grating constant throughout the bulk of the crystal lattice. The third criticism was the most tenacious and the most difficult to refute. The Bragg reflection from atomic planes parallel and very close to a boundary surface was always used in precision determinations, and since the surface is admittedly a highly specialized locality, the atomic structure and hence the grating constant might conceivably have a special value there.

(An analogy might be made with surface tension in liquids.) The macroscopic density measurements of a crystal used by Sir William Bragg, A. H. Compton, or M. Siegbahn in their method of computing the grating constant, on the other hand, clearly must yield the average grating constant over the entire sample of crystal. The plausibility of this criticism and also that of the first one was greatly weakened by showing (16) that the measured densities and x-ray values of grating constants combined with molecular weights gave, for many different kinds of crystals of the perfect type, mutually consistent values of Avogadro's number, N . (As more fully discussed in Section 5.7, if we know from x-ray measurements the grating constant, d , of a crystal, its density, ρ , the molecular weight, M_μ , of its unit cell, and a dimensionless geometrical shape factor, ϕ , which is in fact the volume of a unit cell whose grating constant, d , is unity, we can calculate Avogadro's number, N , from $N = M_\mu/(\rho\phi d^3)$.) The third criticism persisted for a time nonetheless because of a suggestion by F. Zwicky that a superlattice structure, consisting of periodic local deviations of the lattice from the average grating spacing, might be a general property of all crystal lattices because of some very fundamental far-reaching and general "cooperative" effect extending over wide domains. Zwicky suggested that the boundary surface of a crystal might, by some considerations of minimum energy, be invariably the site of one of these abnormal grating constant regions. The third criticism was removed entirely, however, by two methods: (a) X-rays were reflected from crystals of the perfect type such as calcite using *internal* atomic planes for this purpose and the internal grating constant was shown to be the same as at the surface (17, 18). (b) Crystals such as calcite and quartz were powdered so finely that the penetration of x-rays through each grain was complete and not appreciably limited by "extinction." The grating constant for the powder was then measured with high precision using a Seeman-Bohlin spectrograph, and the density of the identical sample of powdered crystal was measured with a pycnometer. No significant deviation was observed in the inferred value of N from that obtained with macroscopic crystals used in Bragg surface reflection (17, 19).

Save for the case of extremely long x-ray wavelengths the great bulk of the ruled grating measurements of x-ray lines have been

made using plane gratings by the method of grazing incidence. Compton and Doan (20) and shortly afterward Thibaud (21) were the first to use this method. In grazing incidence far greater dispersion is obtainable with a grating of a specified number of rulings per unit distance than in the more familiar case of normal incidence.

A condition for sufficient intensity in the diffracted spectrum is that the angle of grazing incidence shall be less than the critical angle for total reflection. It should be recalled that the refractive indices of x-rays are in most cases less than unity. Total reflection occurs therefore in the less dense medium. Rather coarse gratings with a large ratio of flat intervening space to the width of the ruled

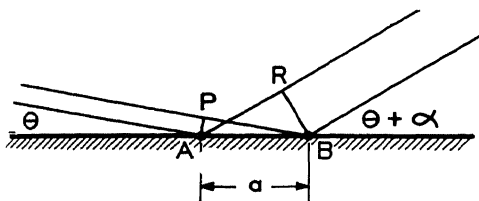


Figure 5-2. Illustrating the geometry of the path difference when ruled gratings are used in grazing incidence to measure x-ray wavelengths.

line are usually used and methods of ruling which are likely to produce a projection of the ruled material above the flat intervening surfaces are to be avoided.

The geometry controlling the path difference, $PB - AR = a[\cos\theta - \cos(\theta + \alpha)]$, is shown in Figure 5-2. It must be recalled that for x-rays no lenses are available to render a divergent beam parallel or to focus a parallel beam to a point, as in the case of ordinary optical light. Setting the path difference equal to a whole number of wavelengths, $n\lambda$, we have

$$n\lambda = a[\cos\theta - \cos(\theta + \alpha)] \quad (5-9)$$

In the simplest of all cases when θ can be regarded as negligible we have

$$n\lambda = a(1 - \cos\alpha) \cong a\alpha^2/2 \quad (5-10)$$

The dispersion for grazing incidence, $(d\alpha/d\lambda)_g$, is

$$(d\alpha/d\lambda)_g = \sqrt{n/(2a\lambda)} \quad (5-11)$$

This is to be compared with the dispersion for normal incidence, $(d\alpha/d\lambda)_n$, which is

$$(d\alpha/d\lambda)_n \cong n/a, \text{ for small } \alpha \quad (5-12)$$

The chief precision wavelength measurements of x-ray characteristic spectral lines by diffraction on ruled gratings have been made by four authors, J. A. Bearden, E. Bäcklin, M. Söderman, and F. Tyrén, between 1931 and 1938. The softer x-ray lines Cu $K\alpha$, β , Cr $K\alpha$, β , Al $K\alpha$ were chosen for study. The results are best expressed in terms of the conversion factor $\Lambda = \lambda_a/\lambda_s$ implied by the measurements and these will be found in Table 5-2 of Section 5.6, *c*.

5.6 SIEGBAHN'S SCALE OF WAVELENGTH; THE X-UNIT

a. Siegbahn's Definition of the X-Unit in Terms of Calcite

The wavelengths of x-ray spectral lines measured relative to each other by the high-precision methods of crystal diffraction are known with a precision of 1 part in 10^4 to 10^6 . This precision exploration and tabulation of the x-ray spectrum was first brought to high perfection by Manne Siegbahn (22) and his school. Later, with such further improvements as the two-crystal spectrometer and the curved crystal spectrometer, it was carried on even further by many others (23, 24). About 3000 of these precision wavelength measurements have been tabulated (25), and they constitute a very reproducible and well-defined natural scale of lengths in the range between about 10^{-9} and 4×10^{-6} cm. To express these wavelengths in centimeters or Angstrom units the method first adopted was that of Sir William Bragg (26), whose reasoning was as follows:

In the simple case of the cubic structure of a rock-salt crystal (see Figure 5-3), each atom (sodium or chlorine) is associated with a volume, d^3 , whose weight is ρd^3 , where $\rho = 2.17 \text{ g cm}^{-3}$ is the crystal density. Now 1 mole, that is to say $23.05 + 35.45 = 58.50 \text{ g}^*$ of rock salt, will contain $2 N$ molecules (where N is Avogadro's number) so that the mean weight per atom will be $58.50/(2 N) \text{ g}$. Equating this to ρd^3 , the mean weight of crystal associated with each atom, we have

$$\rho d^3 = 58.50/(2 N)$$

* These values are not the present international atomic weights but rather essentially the values used by Bragg in 1914 (with slight modification by Siegbahn (22) to obtain an accuracy of one additional significant figure). The present international atomic weight of rock salt is 58.454.

or

$$d = (58.50)^{1/3} / (2 N \rho)^{1/3} = 2.814 \times 10^{-8} \text{ cm}$$

provided we use for N the value Millikan obtained using Harrington's value of η .

The structure of rock salt is less perfect and less reproducible from sample to sample than certain other crystals; calcite, for instance. In 1925 Compton, Beets, and De Foe (27) made very careful measurements on the latter rhombohedral crystal to determine its density and the angles between its cleavage planes. This latter goniometric measurement permits calculation of the volume of a

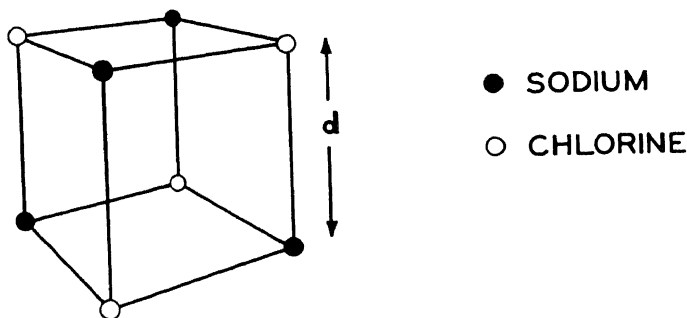


Figure 5-3. Cubic structure of a rock-salt crystal, illustrating Sir William Bragg's original method of computing the grating space d , given Avogadro's number, the crystal density, and its molecular weight.

calcite rhombohedron having unit separation between its three pairs of parallel faces. They found for this volume, $V = 1.09630 \pm 0.00007$. (In later work by J. A. Bearden referred to in Section 5.6 a slightly different numerical value has been obtained.) As a final result of their calculation, whose principle is the same as that described above for rock salt, they obtained for the true grating space a value which Manne Siegbahn *adopted* as the basis for calculating x-ray wavelengths. This calculated grating space was, however, erroneous chiefly because of the error in Harrington's value of η with its consequent effects on e , and thence on the value of $N = F/e$ which Compton, Beets, and DeFoe had used.

In view of these errors it is best to regard Siegbahn's system of wavelengths as a purely arbitrary system, and indeed Siegbahn

very wisely chose to call the unit of length in that system by a distinctive name, the x-unit, for although he had certainly intended to make the x-unit as nearly as possible equal to a milliangstrom, it seems highly likely that from the beginning he felt some insecurity about its absolute value. The *intention* was to express the grating spacing of calcite in milliangstrom units. For many years no distinction between x-units and milliangstrom units was suspected. The terms were used interchangeably. From our present point of view, however, it is preferable merely arbitrarily to *define*, as did Siegbahn, the "effective" grating space of calcite at 18° C for first order reflection as

$$d''_{18} = 3029.040 \text{ x-units} \quad (5-13)$$

b. Correction for Refractive Index of Crystal

The term "effective" grating space has the following meaning: Stenström showed by a precise comparison of Bragg reflections in different orders (28) that a small correction to the simple Bragg equation, $n\lambda = 2d \sin \theta$, is required. His corrected version of this equation is

$$n\lambda = 2d \left[1 - \frac{4d^2}{n^2} \left(\frac{\delta}{\lambda^2} \right) \right] \sin \theta_n \quad (5-14)$$

wherein $\delta = 1 - \mu$ is the "unit difference" of the index of refraction of the x-ray wavelength, λ , in the crystal, d is the crystal grating constant, n the order of reflection, and θ_n the grazing angle of selective reflection in the n^{th} order. Dispersion theory predicts and experiments have verified that save near absorption discontinuities δ/λ^2 is a constant of the material. For calcite $\delta/\lambda^2 = 3.69 \times 10^{10} \text{ cm}^{-2}$ and for practical purposes the bracketed term above may be taken as $[1 - 135 \times 10^{-6}/n^2]$ for the cleavage planes of calcite. The "effective" grating constant, d_n , is defined as the true grating constant multiplied by this correction term

$$\begin{aligned} d_n &= d[1 - 4d^2(\delta/\lambda^2)/n^2] \\ &= d[1 - 135 \times 10^{-6}/n^2] \quad (\text{for calcite} \\ &\quad \text{cleavage planes}) \end{aligned} \quad (5-15)$$

so that we may use the effective grating constant in an equation similar to the simple uncorrected Bragg equation. The effective

grating constant is of course not a constant but a function of the order of reflection, n ; it approaches d with increasing n . We may write then

$$n\lambda = 2d_n \sin \theta_n \quad (5-16)$$

The true grating space of the cleavage planes of calcite after this correction for index of refraction is

$$d_{18}' = 3029.449 \text{ x-units} \quad (5-17)$$

or at 20° C it is

$$d_{20}' = 3029.512 \text{ x-units} \quad (5-18)$$

c. The Conversion Factor, $\Delta = \lambda_g/\lambda_s$

R. T. Birge in his 1945 review (29) gave a summary of eight independent measurements in milliangstroms of the absolute wavelength, λ_g , of different x-ray spectral lines determined by diffraction on calibrated ruled gratings and expressed in the form of the ratio of λ_g , to the wavelength, λ_s , of the same line measured on the arbitrary Siegbahn crystal scale in x-units. Table 5-2 is reproduced from that paper.

Table 5-2. Comparison of Grating and Siegbahn Wavelengths of X-Rays

Author	X-Ray Line	$(\Delta - 1) \times 10^6$ The probable error is based on accidental errors only	Adopted Probable Error
Bearden ^a	Cu $K\alpha_{1,2}$	1980 \pm 31	\pm 52
Bearden ^a	Cu $K\beta_{1,3}$	2079 \pm 28	\pm 50
Bearden ^a	Cr $K\alpha_{1,2}$	2036 \pm 21	\pm 48
Bearden ^a	Cr $K\beta_{1,3}$	2017 \pm 28	\pm 48
Söderman ^b	Al $K\alpha_{1,2}$	2070 \pm 37	\pm 84
Bäcklin ^c	Al $K\alpha_{1,2}$	2000 \pm 14	\pm 60
Bearden ^d	Cu $K\alpha_{1,2}$	2087 \pm 55	\pm 130
Tyrén ^e	Al $K\alpha_{1,2}$	2024 \pm 5	\pm 48
	<i>Adopted average</i>	2030 \pm 20	

^a J. A. Bearden, *Phys. Rev.*, **37**, 1210 (1931).

^b M. Söderman, *Nature*, **135**, 67 (1935); Dissertation, Uppsala, 1934.

^c E. Bäcklin, *Z. Physik*, **93**, 450 (1935).

^d J. A. Bearden, *Phys. Rev.*, **48**, 385 (1935).

^e F. Tyrén, *Z. Physik*, **109**, 722 (1938).

Both Bearden and Birge arrived at the same conclusion for the most probable value of Λ from the data of Table 5-2. This value and the probable error assigned to it by Birge (29) was

$$\Lambda = 1.002030 \pm 0.000020 \text{ (Birge, 1945)} \quad (5-19)$$

A slightly lower value was "recommended for general adoption" (30) by Sir Lawrence Bragg in 1947 after consultation with M. Siegbahn, B. E. Warren, and H. Lipson with due consideration given to the analysis of various sources of primary data by R. T. Birge:

$$\Lambda = 1.002020 \pm 0.000030 \text{ (W. L. Bragg } et al., 1947)} \quad (5-20)$$

For many years the accuracy of our knowledge of Λ was so much superior to that of most of the experimental data on which our knowledge of the atomic constants is based that it was valid and convenient to regard this important conversion factor as a fixed auxiliary constant. This is now no longer true, however. In the least-squares adjustment of this text Λ is one of the unknowns to be adjusted. The direct observation of Λ yielding the value (5-20) (by comparison of λ_g and λ_s) of course furnishes one of the important equations which contribute in the least-squares adjustment to influence the adjusted output value of this unknown. The slight incompatibility of this equation (describing the direct observation) with the remainder of the set is such that the least-squares adjusted value of Λ is

$$\Lambda_{Adj} = 1.002039 \pm 0.000014 \text{ (DuMond and Cohen, 1955)} \quad (5-21)$$

It is clear, however, that this value is well within the "spread" of the observed values of Table 5-2. It differs from Birge's 1945 mean value (5-19) and from the Bragg 1947 value (5-20) used as "input value" in our 1955 adjustment as follows:

$$\Lambda(D' 55) - \Lambda(\text{Birge } 45) = 0.000009 \pm 0.000024^*$$

$$\Lambda(D' 55) - \Lambda(\text{Bragg } 47) = 0.000019 \pm 0.000027^*$$

* $\Lambda(D' 55)$ and $\Lambda(\text{Birge } 45)$ are observationally independent quantities. The standard deviation of their difference, $\sigma_{\Delta} = \pm 0.000024$, has therefore here been computed by the familiar formula

$$\sigma_{\Delta}^2 = \sigma_x^2 + \sigma_y^2$$

where σ_x^2 and σ_y^2 are the "variances" of any two observationally independent

The differences are seen to be so much smaller than their expected standard deviations as to be not at all disturbing.

5.7 AVOGADRO'S NUMBER BY THE XRCD METHOD AND THE ELECTRONIC CHARGE

The philosophy of the x-ray-crystal-density (XRCD) determinations of Avogadro's number, N , reverses the order of reasoning followed by Siegbahn (see Section 5.6, *a*). If the length of one edge of the unit cell in a cubic crystal is denoted by d , and the density of the crystal by ρ , then $d^3\rho$ is the mass of the unit cell. If there are f molecules in a unit cell and if M is the molecular weight, then $d^3\rho/f$ is the mass per molecule and Avogadro's number, N , the number of molecules in a gram mole, will be the ratio of these last two quantities, i.e., $N = Mf/(\rho d^3)$. Of course M and N must be expressed on the same scale of atomic weights. For crystals in general, the volume of a unit cell is given by ϕd^3 , where ϕ is the geometric factor already alluded to in Section 5.6, *a* as having been measured by Compton, Beets, and DeFoe (27). For the calcite rhomb, ϕ is the volume of a rhombohedron whose three equal obtuse dihedral angles, α , have the value, $105^\circ 3.5'$, and the distance between whose three parallel pairs of faces is unity. For this case J. A. Bearden obtained (31)

$$\phi = 1.09594 \pm 0.00001 \quad (5-22)$$

The general formula for Avogadro's number computed in this way is then

$$N = Mf/(\rho\phi d^3) \quad (5-23)$$

The grating constant, d , is to be measured by means of x-rays, that is to say, by measuring the Bragg angle for critical reflection of some x-ray spectral line of known wavelength reflected by the

variables, x and y , and σ_{Δ}^2 is the variance of $(x - y)$. $\Lambda(\text{DC } 55)$ and $\Lambda(\text{Bragg } 47)$, on the contrary, are the output and input values of the variable, Λ , in the DuMond and Cohen least-squares adjustment of 1955. Far from being observationally independent, they are for this reason observationally correlated in a very special way. For this case it can be shown that the *difference* rather than the sum of the variances gives the variance, σ_{Δ}^2 (of the difference between such output and input values. The standard deviation (± 0.000027) has therefore been computed using this relation

$$\sigma_{\Delta}^2 = \sigma_{B47}^2 - \sigma_{DC55}^2$$

atomic planes whose grating constant, d , is sought. The Bragg relationship, corrected for index of refraction (see Section 5.6, b), must be used, of course, for the calculation.

$$d = n\lambda / \left[2 \left\{ 1 - \frac{4d^2}{n^2} \frac{\delta}{\lambda^2} \right\} \sin \theta_n \right] \quad (5-24)$$

This has been done for many different crystals of determined macroscopic density, ρ , geometric factor, ϕ , and molecular weight, M . If the x-ray line wavelength, λ , has been measured on the Siegbahn nominal scale in x-units, we must use the conversion factor, Λ , to obtain N . As a result of the x-ray measurements, d will be expressed in x-units; if we use d_x to indicate that the crystal spacing is so expressed, we have:

$$N = Mf / [\rho\phi d_x^3 \Lambda^3] \quad (5-25)$$

It is convenient to introduce the quantity

$$N_s' = N\Lambda^3 = Mf / (\rho\phi d_x^3) \quad (5-26)$$

for which we might coin the name, the Siegbahn-Avogadro number, since it is the result of computing Avogadro's number from the measured properties of a crystal whose grating constant, d , has been measured on the Siegbahn nominal scale of x-units. Then clearly the true Avogadro number, N , is

$$N = N_s' \Lambda^{-3} \quad (5-27)$$

R. T. Birge has reviewed (29) the entire question involving the determination of N from five different crystals, and we present in

Table 5-3. Probable Errors in Parts Per Million for Factors of N_s' and the Resulting Values

Crystal	M	ρ_{20}	d_{20}^3	$\phi(\beta)$	Resulting Error in N_s'	N_s' (10^{23} mole $^{-1}$, chem)
Calcite	50	37	16.5	13	65	6.05989 ± 0.00039
NaCl	51	37	60		87	6.06077 ± 0.00052
Diamond	20	34	89		97	6.06018 ± 0.00059
LiF	32	45	120		132	6.05994 ± 0.00080
KCl	40	37	68		86	6.05999 ± 0.00052
<i>Adopted weighted mean</i>						6.06014 ± 0.00023

Table 5-3 an adaptation of his conclusions. (The data are his in essence although we have taken the liberty to reexpress them directly in terms of N_s' .) From the data of Table 5-3, the weighted mean value of N_s' on the chemical scale of atomic weights is

$$\begin{aligned} N_s' &= N\Lambda^3 \\ &= (6.06014 \pm 0.00023) \times 10^{23} \text{ (g mole)}^{-1} \text{ (chemical)} \end{aligned} \quad (5-28)$$

We convert this to the physical scale using Birge's value of r (see Section 5.8).

$$\begin{aligned} N_s' &= N\Lambda^3 \\ &= (6.06179 \pm 0.00023) \times 10^{23} \text{ (g mole)}^{-1} \text{ (physical)} \end{aligned} \quad (5-29)$$

We may now, if we wish, compute N , Avogadro's number, by combining the measured value of N_s' with the measured value of Λ . Such a value, however, derived from a combination of two or more experimental measurements, must be used with caution if the experimental measurements will also be combined individually with other data. We must therefore carefully distinguish such values, which are derived from a combination of arbitrarily selected experimental measurements, from (1) the directly observed values which are the results of single determinations, and (2) the least-squares adjusted values which result from a broad general analysis of all sources of information. Solving equation (5-29) for N and using the value $\Lambda = 1.002030 \pm 0.000020$, Birge then deduced the best value of Avogadro's number on the basis of the XRCD method

$$\begin{aligned} N &= (6.02338 \pm 0.00043) \times 10^{23} \text{ (g mole)}^{-1} \\ &\text{(chemical XRCD)} \end{aligned} \quad (5-30)$$

$$\begin{aligned} &= (6.02503 \pm 0.00043) \times 10^{23} \text{ (g mole)}^{-1} \\ &\text{(physical XRCD)} \end{aligned} \quad (5-31)$$

From this value of N and the electrochemically determined value of the Faraday constant, F , Birge obtained a value of the electronic charge, $F/N = e$. Using a value of F

$$F = 96487.7 \pm 10 \text{ abs coulomb per gram mole (chemical)} \quad (5-32)$$

Birge obtained

$$e = (4.8021 \pm 0.0006) \times 10^{-10} \text{ esu} \quad (5-33)$$

The estimated error of 125 ppm obtained in this calculation is to be compared with the estimated error in the same quantity when measured by Millikan's oil-drop method combined with the best and latest careful measurements of the viscosity of air. The latter method has been assigned a probable error by Birge (29) of 1560 ppm, of which 820 ppm come from the variance in the viscosity measurements and 1330 ppm from the variance in the oil-drop observations themselves. This overall probable error in e is over 12 times as great as that involved in the evaluation of e from the ratio, F/N . In forming a weighted average, F/N should therefore receive 150 times as much weight as the oil-drop value. It should be clear, therefore, why the oil-drop method no longer plays any practical role in contributing to our knowledge of the constant, e .

5.8 THE CHEMICAL AND PHYSICAL SCALES OF ATOMIC WEIGHTS

Two slightly different scales of atomic weights (or atomic masses) are in use, the "physical" and the "chemical" scales. The older of the two, the chemical scale, had its origin before the existence of isotopes was known. On the chemical scale the mean atomic weight of a mixture of the three isotopes of oxygen, O^{16} , O^{17} , and O^{18} "in their naturally occurring abundance ratios" is defined as having atomic weight 16.0000. On the physical scale the atomic weight of the O^{16} isotope has, by definition, the atomic weight exactly 16.

On the basis of the following assumed isotopic abundance ratio

$$O^{16} : O^{18} : O^{17} = (506 \pm 10) : 1 : (0.204 \pm 0.008) \quad (5-34)$$

and the masses $O^{16} = 16.0000$ (by definition), $O^{18} = 18.0049$, $O^{17} = 17.0045$, Birge (reference 12, Chapter 2) has computed the conversion factor, r , between the chemical and physical scales of atomic weight as

$$r = 1.000272 \pm 0.000005 \quad (\text{Birge, 1941}) \quad (5-35)$$

However, the definition of the chemical scale of atomic weights is an equivocal one because there is no exactly defined "naturally occurring abundance ratio" of the oxygen isotopes. A. O. Nier in a study (32) of the relative abundance of isotopes would revise Birge's value of r upward about 6 ppm, if the abundance ratio for atmospheric oxygen is taken as defining the chemical scale of atomic weights. Nier says that oxygen from limestone would agree with

this but if oxygen from iron ore or water were employed, the O^{18} content might be 4 per cent lower and the conversion factor, r , would be only about 1.000268, some 4 ppm lower than that chosen by Birge.

In a private communication from E. Wichers of the U. S. National Bureau of Standards we are informed that the International Commission on atomic weights has been considering redefinition of the chemical scale of atomic weights. The definition most probably will be based on the use of the exact number, 16, as the atomic weight of a mixture of the natural isotopes of oxygen whose average atomic mass is greater by an exact factor (probably 1.000275) than the mass of O^{16} . Wichers states that the reason for choosing 1.000275 is that it has been used by the International Commission since 1939 for converting to the chemical scale data reported on the physical scale. The difference of 3 ppm between this value of the conversion factor and that of Birge which we have used throughout this text makes no significant change in any of our output results.

Because of the unequivocal nature of its definition and because extremely accurate atomic weights can be derived in terms of it, as we have seen (Section 4.1) from measurements of nuclear reaction energies, we shall here base our calculations on the physical scale of atomic weights. Only in the calculations of Avogadro's number by the XRCD method (Section 5.6) have we employed the factor, r .

5.9 EXPERIMENTS BEARING ON e/m

The charge-to-mass ratio for electrons has been the object of a great variety of more or less precise determinations in the first half of the twentieth century before the era of much higher precision in the fundamental constants which followed World War II. None of these early e/m experiments were sufficiently accurate to remain as significant contributors to our knowledge of the atomic constants at the date of this writing. We discuss them here only because of the role they played in the development of our knowledge. Many of these experiments were beautiful and ingenious in conception, but because of their secondary importance for our objectives they can be mentioned here only briefly. Closely related to these were other experiments to test the relativistic variation of mass with velocity and experiments to test the equality of mass of

positive and negative electrons, neither of which will be described here. A more complete description of all such work may be found in collected form elsewhere (33, 34).

R. T. Birge distinguishes two large classes of e/m experiments as "deflection" and "spectroscopic" methods. Actually as Birge himself recognized (see Section 3.6 on the Faraday), the distinction between the two classes of measurement was really that, in the "deflection" experiments, beams of *free* electrons were accelerated and/or deflected by electric or magnetic fields or both, whereas in the spectroscopic measurements the charge-to-mass ratio was sought for *bound* electrons in atoms.

The spectroscopic methods were of two kinds. (1) The variation in the value of the Rydberg constant for different light atoms such as hydrogen and deuterium was measured by high-precision spectroscopic means to determine (by the "mitbewegung des kerns" effect) the ratio of the mass of the electron to the mass of the proton. This has already been alluded to in Section 4.1 under the discussion of methods of determining Nm , the atomic mass of the electron. By combining such a measurement of Nm with the electrochemically measured value of the Faraday (Section 3.6), $F = Ne$, a value of e/m can obviously be computed. We must be careful to recognize that *two* independent experiments are involved here to obtain e/m . That a systematic error was introduced into the inferred value of e/m by using the silver value of F in this calculation now seems almost certain, as we have already pointed out in Section 3.6, though this was not suspected until about 1940. We shall return to this point in Section 8.3. (2) The splitting of spectral lines emitted by a source in a strong magnetic field was measured to determine e/m by the Zeeman effect. It is known that the energy levels of an atom in a magnetic field of intensity, H , are displaced by an amount, $MgH\mu_0$, where M is the magnetic quantum number, $\mu_0 = eh/(4\pi mc)$ is the Bohr magneton, and g is the Landé g -factor. The shift $\Delta\bar{\nu}$ expressed in wave numbers (for the normal Zeeman effect, $g = 1$) is

$$\Delta\bar{\nu} = M H e / (4\pi mc^2) \quad (5-36)$$

By measuring the splitting, $\Delta\bar{\nu}$, and the field intensity, H , it is possible to compute e/m , if we have a reliable value of c , the velocity of light. For further details of the theory of this effect a text on

atomic spectra should be consulted (35, 36). A precision of the order of ± 400 ppm has been attained with this method by Kinsler and Houston (37) in the measurement of e/m .

Many but not all of the so-called deflection methods of measuring e/m involve a measurement of the speed, v , of the electron combined with a simultaneous determination of some other parameter such as the voltage used to impart its kinetic energy or the deflection produced by an electric or a magnetic field. Two classes of methods for measuring the speed were (1) transit time over a measured distance; (2) null deflection in crossed electric and magnetic fields perpendicular to each other and to the electron beam and so adjusted that the deflecting forces were balanced.

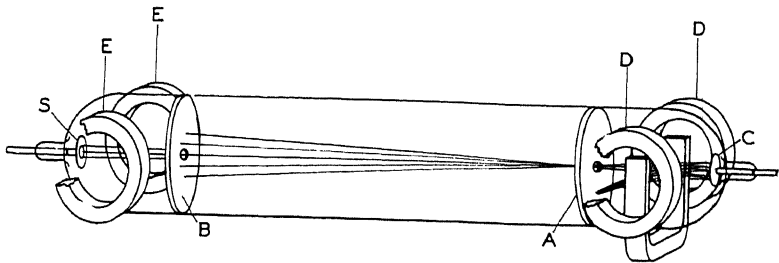


Figure 5-4. To illustrate Weichert's method of measuring electron speeds by deflecting the electron beam with alternating magnetic fields.

Weichert was the first to develop the time of transit method (38). His apparatus is schematically indicated in Figure 5-4. Electrons from a cathode, C , are projected down a vacuum tube. If no fields are present the electron beam is aligned so as to pass successively through two small holes in screens A and B and fall on a detecting fluorescent screen, S . A permanent magnet (not shown in Figure 5-4) provides a field which deflects the beam away from the hole in A . Two sets of coils, one D , between the cathode and screen A , the other, E , between screen B and the detecting screen, S , are supplied with high-frequency alternating current so as to give alternating magnetic fields normal to the beam and substantially in the same phase. The field from D is just sufficient to swing the beam back so that it passes through the aperture in A at its greatest deflection. For one critical speed of the electrons these will arrive beyond screen B in just the phase of the magnetic field of coil E

at which that field passes through zero and, if so, the beam will suffer no further deflection beyond *B* and will hit screen *S*. Clearly such electrons must have had a transit time between coil *D* and coil *E* of some odd whole number of quarter periods of the high frequency. Thus a knowledge of the frequency and the distance between coils *D* and *E* suffices to give the speed, *v*.

Another time of transit method used by Hammer (39) consisted in projecting the electron beam through two small condensers separated by a measured distance, *L*. High-frequency electric fields between the plates of these condensers were perpendicular to the beam and also to each other. In general this caused the beam beyond both plates to describe a Lissajous ellipse. At critical elec-

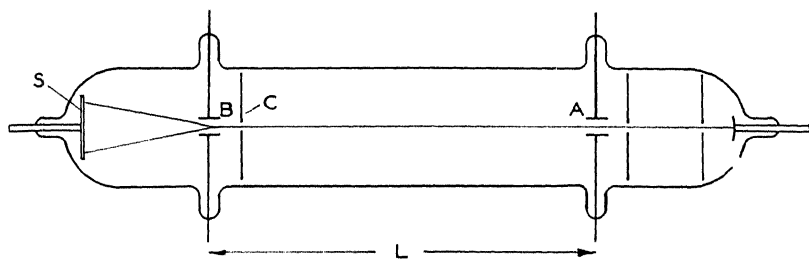


Figure 5-5. To illustrate Kirchner's method of measuring electron speeds by deflecting the beam with alternating electric fields.

tron speeds when the transit time over the distance, *L*, was just one-half period of the high frequency or any multiple thereof the ellipse degenerated into a straight line and this condition obviously permits calculation of the speed.

Kirchner has used a third modification (40) of this method of speed measurement. In Kirchner's method the electric fields from two condensers, *A* and *B*, separated a distance, *L*, along the beam, are parallel to each other as shown in Figure 5-5. Clearly the electrons can pass through both the condensers and hit the screen, *S*, without deflection only if they do so at instants when the two electric fields are just passing through zero. This means that the transit time over the distance, *L*, is just a whole number of half periods, if the alternating condenser fields are accurately in the same phase. Zero field at *A* is clearly necessary for passage of the beam through the hole in screen *C*. If at the time of arrival in *B* the field there is

slightly different from zero, this will cause two images of the beam to be projected at two different points on screen S , as shown; the two images being formed in alternate half cycles. When the time of transit has been accurately adjusted to a half period of the high frequency this will be evidenced by the two images coalescing into one at the center. Essentially this same method has also been used by Perry and Chaffee (see below).

Thomson was the first to use the method of null deflection in crossed electric and magnetic fields for measuring electron speed (41). If a beam of electrons traverses a region of homogeneous mutually perpendicular electric and magnetic fields, each of which is also perpendicular to the beam, the magnetic deflecting force Hev can be arranged so as just to balance the electric deflecting force, eE , and the critical velocity for null deflection must then clearly be given by the equation

$$Hev = Ee \quad \text{or} \quad v = E/H \quad (5-37)$$

This method has also been used by Bucherer in his famous experiment to test the relativistic law of variation of electron mass with velocity. The speed can of course also be determined if the two deflecting forces are not exactly balanced, provided we measure the deflections.

Methods of measuring e/m which involve a speed measurement of one of the two foregoing general types, either explicitly or implicitly, have been made by J. J. Thomson (41), W. Kaufman (42), A. H. Bucherer (43), K. Wolz (44), F. Kirchner (45), C. T. Perry and E. L. Chaffee (46), F. G. Dunnington (47), and A. E. Shaw (48) over a period from 1897 to 1938. In Thomson's original method the electrons passed out of the speed measuring electric and magnetic crossed fields into a region where the magnetic field alone was present. The beam deflection, that is to say, its radius of curvature, ρ , was then measured by means of a fluorescent screen. Since the magnetic deflecting force, Hev , is to be equated to the centrifugal force mv^2/ρ , the value of e/m is given by

$$e/m = v/(H\rho) \quad (5-38)$$

Kaufman in his method of measuring e/m used β -rays from radioactive materials which have a continuous spectral distribution over energies and therefore a continuous range of values of speed v . His

electric and magnetic fields, E and H , were normal to the beam but parallel to each other so that he obtained on a fluorescent screen an x deflection caused by the magnetic field and a y deflection perpendicular to the latter caused by the electric field. It is easy to verify that these two deflections will be

$$y = kEe/(mv^2) \quad (k \text{ a constant of the apparatus geometry}) \quad (5-39)$$

$$x = kHe/(mv) \quad (5-40)$$

These imply that with variation of the speed v , y is proportional to x^2 , except for the small effect of relativistic variation of mass with v . Thus on a fluorescent screen a parabolic locus of points of impingement of the beam is obtained. At any one point on the curve with coordinates, x , y , the value of e/m is given by the equation

$$e/m = (x^2/y) E/(kH^2) \quad (5-41)$$

This equation gives the value of e/m for the electron speed corresponding to the particular point on the parabola chosen. The method therefore afforded a rough way of investigating the relativistic variation of mass with speed. Simultaneous solution of equations (5-39) and (5-40) for v gives

$$v = (x/y)(E/H) \quad (5-42)$$

In Bucherer's method a small natural radioactive source of β -rays was placed at the center between two very closely spaced metal discs forming an electrical condenser. The entire apparatus was placed in a homogeneous magnetic field parallel to the plane of the plates. Figure 5-6 illustrates the arrangement schematically. In the region of the electric field between the plates the electric and magnetic deflecting forces must balance each other exactly if the particle is to escape. This will occur for some β -particle speed, v , which is a function of the azimuth angle θ at which the particle happens to be projected. Particles of no other speed can emerge at that azimuth. After emergence from between the plates the β -particle is deflected in the magnetic field alone and the result of many β -particles over a wide range of speeds selected by the foregoing mechanism at different angles θ forms a continuous curve on a cylindrical photographic film, P , concentric with the condenser plates. A typical curve is shown in Figure 5-6.

F. Kirchner first used his above-described time of transit method to determine the speed, v , combined with an $H\rho$ measurement by magnetic deflection to obtain e/m . In later work he abandoned the

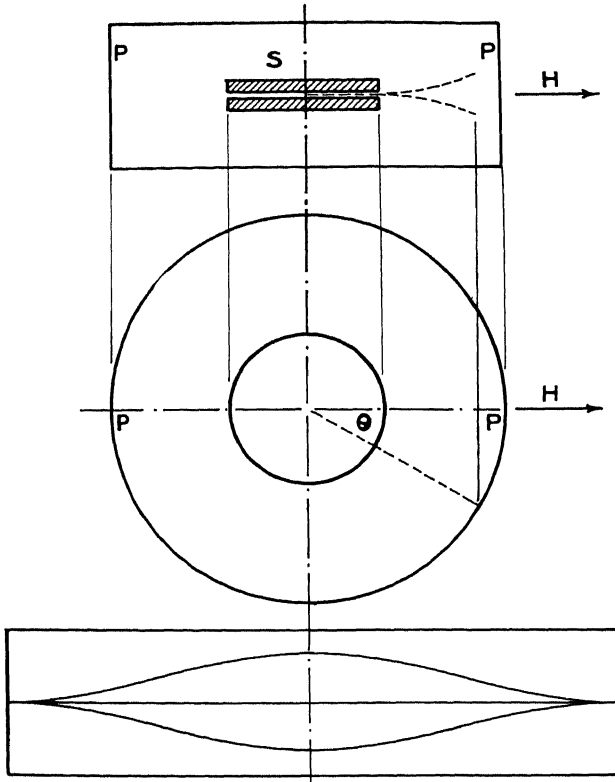


Figure 5-6. Schematic views of Bucherer's apparatus for measuring e/m for electrons of different speeds. The uppermost drawing is the elevation view of the apparatus with the plan view just below it. The entire apparatus is placed in a homogeneous magnetic field indicated by the vector, \mathbf{H} . A photographic film wrapped around the inner cylindrical surface of the evacuated pill-box shaped container receives electrons of different speeds which have emerged in different azimuths from between the two closely spaced condenser plates. Their subsequent deflection by the magnetic field alone causes a curved line to be recorded on the film. An example of such traces on one of the films corresponding to half the circumference of the box is shown at the bottom of the figure. The two traces on the film are successively formed by reversing both electric and magnetic fields simultaneously.

magnetic deflection feature and adopted a method first used by Perry and Chaffee. This was a combination of Kirchner's method for measuring the speed with a precision measurement of the voltage used to accelerate the electrons to that speed. Voltages of 10 and 20 kv, considerably higher than those previously used, were employed. Values of e/m in rather good agreement with the present best accepted value were obtained by both these authors in this work, although the estimated accuracy, which was of the order of 100 ppm, was far inferior to that of our latest knowledge, the 1955 value being accurate to about 11 ppm.

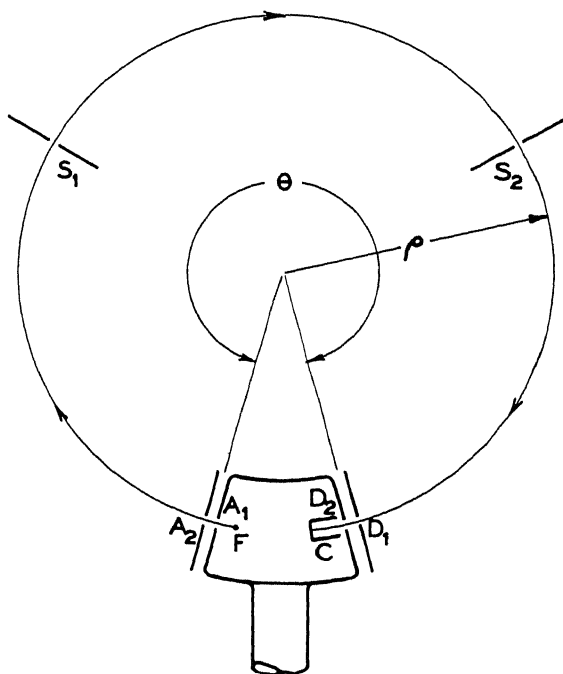


Figure 5-7. Schematic representation to illustrate Dunnington's method of measuring e/m . The entire apparatus is placed in an evacuated pill-box shaped metal enclosure, not shown, to which the metal slits, A_2 , S_1 , S_2 , and D_1 are electrically connected. The metal structure, provided with slits, A_1 and D_2 and containing the thermally emitting filament F and Faraday collector, C , is insulated from the box and connected to a source of high-frequency alternating voltage of accurately measured frequency. The entire apparatus is placed in a homogeneous magnetic field of known intensity normal to the plane of the figure.

Dunnington's method is illustrated schematically in Figure 5-7. Electrons leave a thermally emitting filament, F , and are accelerated by a high-frequency alternating field between plates A_1 and A_2 . Their speeds therefore depend on the phase of the alternating high-frequency voltage between A_1 and A_2 at which they are accelerated. The apparatus is in a homogeneous magnetic field, H , normal to the plane of the figure. Only one of the speeds, v , can execute the circular trajectory defined by the slits in A_1 , A_2 , S_1 , S_2 , D_1 , and D_2 , namely, that speed which satisfies the equation

$$Hev = mv^2/\rho \quad (5-43)$$

where ρ is the radius of curvature defined by the slits. What happens to the electron after it arrives at D_1 depends upon the length of time it required to execute the path of angular magnitude, θ . The same high-frequency potential in the same phase was applied between D_1 and D_2 as that applied between A_1 and A_2 . (A_2 and D_1 were in fact at the same potential as the evacuated cylindrical box in which the circular trajectory was executed while A_1 and D_2 were part of a common electrically conducting structure, insulated from the box, to which the high-frequency voltage was applied.) An electron which had required exactly one period of the alternating potential wave to travel from slits A_1 A_2 to slits D_1 D_2 would be decelerated completely in passing from D_1 to D_2 . For this critical condition, clearly the electrons must fail to reach the collector, C . Dunnington adjusted the magnetic field H until a sharply defined minimum of the current collected at C was observed. For this setting the electron speed, v , is

$$v = \rho\theta/T = \rho\theta f \quad (5-44)$$

where T is the period and f the frequency of the high-frequency voltage supplied to A_1 and D_2 and θ is measured in radians. Eliminating v between equations (5-43) and (5-44) gives

$$e/m = \theta f/H \quad (5-45)$$

Dunnington's first (1933) value, $e/m = (1.7571 \pm 0.0015) \times 10^7$ abs. emu g^{-1} was lower than the present accepted best value by only about one of his assigned probable errors. In later work in 1937 with some improvements he obtained a value $e/m = (1.7597 \pm 0.0004)$ slightly higher than the present accepted best value, his excess being about twice his estimated probable error.

In the meanwhile A. E. Shaw, using apparatus which we shall immediately describe, had made an important discovery also verified by R. L. Stewart (49). This revealed a source of previously unsuspected systematic error in all such work. It was shown that in vacuum there are formed, on or very close to the metal plates between which electric fields are established, polarization charges which effectively reduce the potential used to accelerate or deflect an electron beam. Furthermore, a charge seems to accumulate on a more or less permanent insulating layer which forms on metal surfaces in vacuum when these are bombarded with electrons. Such effects depend on the material of the metal plates, the residual gas pressure, the cleanliness of the vacuum pumping arrangements (freedom from organic materials), and the intensity of the electron bombardment. Residual gas such as oxygen adhering to the metal may account for the effect in part. It has been found that vaporizing a layer of gold on the interior of the entire vacuum chamber so as to cover the surfaces of all metal parts reduces these effects materially. However, the lesson from Shaw's work is one which every experimental physicist should remember: It is almost impossible to hope to define the potential of an evacuated region by means of electrically conducting metal walls, slits, or what-not with an uncertainty very much smaller than ± 1 volt. Many an otherwise well-planned experiment has ended in disappointment because of ignorance of this difficulty.

A. E. Shaw's method of measuring e/m , unlike the preceding methods, did not involve measurement of the electron speed. It depended on a focusing principle first conceived by Bartky and Dempster. Figure 5-8 shows the circular electrical condenser between whose plates a slightly divergent beam of electrons from the filament F executes a circular trajectory through an angle of $127^\circ 17'$, $(\pi/\sqrt{2})$, and is refocused at C . The beam is deflected by a magnetic field normal to the plane of the figure as well as by the electric field. The method permits sharp focusing in spite of a slight inhomogeneity in the speeds of the electrons from the thermal emitter. The basic idea of Bartky and Dempster was that for the particular angle $127^\circ 17'$ it was possible to obtain sharp focusing at C both for all electron speeds and also all directions over the small ranges of speed and divergence defined by the conditions and geometry of the instrument. Shaw obtained a value $e/m = (1.7571 \pm$

$0.0013) \times 10^7$ abs emu in close agreement with Dunnington's earlier 1933 value.

Two other methods not involving measurement of electron speed deserve mention, that of J. Classen (50) in 1908 and that of H. Busch (51) in 1922. In Classen's method electrons from a thermal emitter were simply accelerated through a known measured voltage; 1000- and 4000-volt electrons were studied. After passing through a slit the electrons were bent through a semicircle by a homogeneous magnetic field either to the right or to the left according to the

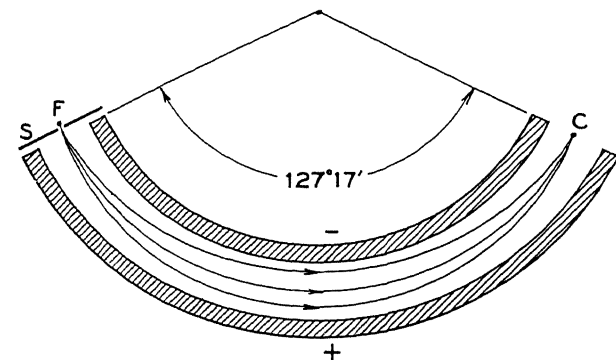


Figure 5-8. Schematic illustration of Shaw's apparatus for measuring e/m utilizing a principle of focusing by crossed electric and magnetic fields conceived by Bartky and Dempster. A homogeneous magnetic field is applied in a direction normal to the plane of the figure.

direction of the current in the Helmholtz coils furnishing the field. In this way two images were formed, one to the right and one to the left of the slit at the points where the beam impinged on a photographic emulsion. The distance between these images gave 4ρ , where ρ is the radius of curvature in the magnetic field, H . If V is the accelerating voltage and v the electron speed we can write two equations, the first equating the electron kinetic energy, $mv^2/2$, to the work, eV , done by the applied voltage, the second equating the magnetic deflecting force to the centrifugal force in the semi-circular trajectory of radius ρ . They are, neglecting relativistic corrections,

$$mv^2/2 = Ve \quad (5-46)$$

$$Hev = mv^2/\rho \quad (5-47)$$

From these two equations both e/m and v can be obtained but knowledge of v is clearly not necessary in order to obtain e/m .

$$e/m = 2V/(H^2\rho^2) \quad (5-48)$$

The results obtained at the two different voltages differed enough from the predictions of the nonrelativistic equations (5-46) and (5-47) to afford the first verification of H. A. Lorentz's theory of the variation of mass with velocity as distinguished from the theories of Abraham or of Bucherer. Extrapolation to zero velocity then yielded a value of e/m for the electron at rest. The value was about 1 per cent higher than the present accepted best value for reasons not entirely clear.

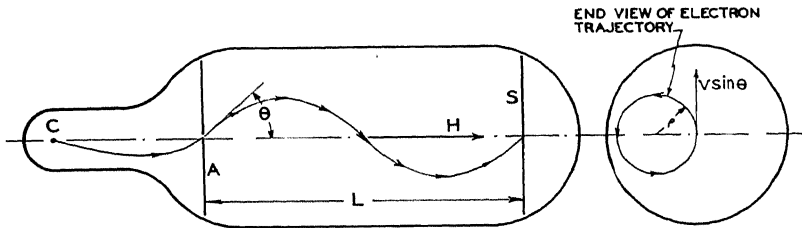


Figure 5-9. Busch's method of measuring e/m . The electrons emerging through the hole in partition, A , execute helical trajectories in the axially directed homogeneous magnetic field, H . If they have executed exactly one turn of the helix during their time of transit over the distance, L , they will refocus on the axis on the screen, S .

Busch in 1922 developed a method of focusing the electrons executing helical trajectories as they spiralled around the tubes of force of an axial magnetic field. Figure 5-9 illustrates the equipment. Electrons emitted by a filament, C , were accelerated through a measured voltage, V , to an anode A where they passed through a small hole. A solenoid was provided around the tube to give a homogeneous axial magnetic field of intensity, H , over the portion, AS . A localized magnetic field from permanent magnets served to deflect the beam in the region, CA , so that it passed through the hole in A at a small angle, θ , with the axis of the tube and the direction of the homogeneous field, H . Once in the region of homogeneous magnetic field the electrons spiraled around the tubes of force in helical trajectories which, viewed on end, appeared as circles as shown in the figure. Since electrons with high component speeds

perpendicular to H execute proportionately larger radius circles it is an easy matter to verify that the transit time, t , to execute one turn of the spiral is, at nonrelativistic speeds, independent of the speed of the electrons and given by

$$t = 2\pi/(H e/m) \quad (5-49)$$

If the field, H , was adjusted so that the electrons returned to the axis after exactly one turn of the spiral just at the detecting fluorescent screen, S , then the time, t , for one revolution could be equated to $L/(v \cos \theta)$, and for this condition one obtains using (5-49)

$$e/m = 2\pi v \cos \theta/(HL)$$

Combining this result with the equation, $Ve = mv^2/2$, which relates the initial accelerating voltage, V , to the speed, v , it imparts (for nonrelativistic speeds), one can eliminate v and obtain

$$e/m = 8\pi^2 V \cos^2 \theta/(H^2 L^2) \quad (5-50)$$

Busch and later Wolf (52) in 1927 used this method with considerable care, but both obtained results considerably higher than our present accepted best value.

5.10 J. A. BEARDEN'S MEASUREMENT OF THE REFRACTIVE INDEX OF X-RAYS IN DIAMOND

The theory of dispersion of Sellmeier when applied to the case of x-rays (53, 54) leads to the following formula for $\delta = 1 - \mu$, the amount (usually of order only a few parts per million) by which the index of refraction for x-rays in a given material is less than unity:

$$\delta = \lambda^2 N \rho / (2\pi c^2 M) [(e^2/m) \sum_s n_s (1 + A_s) + N(Ze)^2/M] \quad (5-51)$$

in which λ is the wavelength of the x-rays, N is Avogadro's number, ρ the density of the medium, M its molecular weight, n_s the effective number of electrons in the s^{th} level, and A_s a factor which takes into account the electronic binding and the x-ray absorption for the s^{th} level. The second term in the brackets is the contribution due to the nuclear scattering. The importance of this term was pointed out by Bethe and Longmire (54a); it represents an addition of 2.7 parts in 10^4 to the electronic scattering term. Since Bearden's wavelength, λ , was measured on the Siegbahn scale it must be

multiplied by the conversion constant Λ (see Section 5.6, *c*) to convert to the absolute cgs system. Let λ_s represent the wavelength in Siegbahn x-units. Then solving (5-51) so as to put all the experimentally measured quantities in the right-hand member we obtain

$$\frac{Ne^2}{mc^2} \Lambda^2 = \frac{2\pi\delta M}{\lambda_s^2 \rho} \left[\sum_s n_s (1 + A_s) + Z^2 \left(\frac{mN}{M} \right) \right]^{-1} \quad (5-52)$$

Although the ratio of the mass of the electron to the mass of the carbon atom appears in the right-hand side of this expression, only a very approximate value is needed here, so that this does not affect the accuracy of the calculation.

It will be noted that the peculiar combination of the atomic constants, N , e , m , Λ , and c , measured here is not strictly to be classified as a measurement of e/m . It is in fact in a class by itself. Since Ne equals F , the Faraday, we can regard this experiment as a way of measuring a function of F , e/m , c , and Λ so that, given reliable values of the other three constants, e/m can be computed.

Bearden measured the refractive index of a diamond crystal prism for Cu $K\beta$ x-rays and determined the density, ρ , of the diamond by adjusting a special solution so that the diamond would neither float nor sink in it (55). Diamond was chosen because of its low absorption for the x-rays and because, carbon having a low atomic number, the binding energies of the electrons and their critical absorption frequencies were very far removed from the quantum energy and frequency of the radiation. Because of this the quantities, n_s and A_s , can be evaluated with considerable accuracy. Bearden's measurements can then be interpreted to yield the result (56).

$$\Lambda^2 Ne^2/(mc^2) = (1.7052 \pm 0.0003) \times 10^{11} (\text{esu})^2 \text{erg}^{-1} \text{mole}^{-1} \quad (5-53)$$

5.11 EXPERIMENTS BEARING ON THE RATIO, h/e

We shall distinguish three types of closely related determinations which usually go by the name of determinations of h/e , although strictly they are determinations of the conversion constant between wavelength and quantum energy expressed in electron volts. If the experiment is in the domain of x-rays the wavelength will be expressed in Siegbahn x-units and the results must then be combined with a value of Λ to reduce them to the cgs system.

Listed in order of the accuracy obtainable the three types of determinations are: (1) Determinations of the short wavelength limit of the continuous x-ray spectrum from an x-ray tube operating under a precisely stabilized and accurately measured D. C. voltage. (2) Determinations of the retarding potential required to stop photoelectrons ejected by optical light of different precisely measured wavelengths. (3) Determinations of the voltage just requisite to excite certain x-ray or optical atomic levels whose wave numbers or wave number differences are known from spectroscopic measurements. For brevity we shall refer to these as (a) x-ray SWL (short wavelength limit) determinations, (b) photoelectric determinations, and (c) excitation potential determinations.

a. X-Ray SWL Determinations

When an x-ray tube is excited with an extremely stable D. C. high voltage, V_H , there is a well defined minimum wavelength, λ_m , of the continuous x-ray spectrum emitted by the tube. It has been shown (56-59) both by theoretical considerations and by internal experimental evidence that the quantum energy, $h\nu_m = hc/\lambda_m$, of the radiation at this limiting point corresponds ideally to the energy acquired by the thermally emitted cathode electrons falling through a potential difference, $V_A = V_H + V_W$, where V_H is the measured voltage difference between cathode and target, and V_W is the work function of the thermally emitting cathode. The reason for this is easily appreciated from the energy level diagram of Figure 5-10.

The voltage difference, V_H , between cathode and target, maintained by the high-tension source and in precision experiments always measured by a high-resistance potential divider connected between cathode and target, is in reality the difference in the energy levels of the uppermost conduction electrons of the respective "Fermi seas" in these two elements of the x-ray tube. The energy released for conversion into radiation of maximum photon energy in the continuous spectrum is, on the other hand, eV_A . This is the difference in the energy of an electron emitted from the cathode with zero velocity and an electron in the lowest empty level at the top of the conduction band in the target. The electron, in order to escape from the cathode, must have acquired, in the process of thermal emission, an energy at least equal to V_W in addition to the energy of the uppermost cathode conduction electrons in order to

overcome the "work function" of the cathode. Thus the energy which results in photons of maximum quantum energy comes from two sources, (1) the high-tension generator, (2) the electrical energy supplied to the cathode to keep it hot. It is well known that more energy is required to heat the cathode when an emission current is being drawn out of it by the applied high voltage than when the voltage is reduced so that no current flows. This is completely

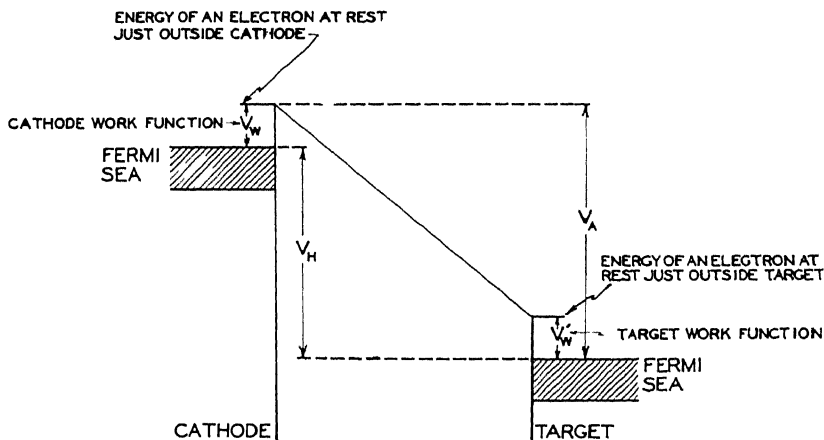


Figure 5-10. Energy level diagram for electrons emitted by the cathode of an x-ray tube and executing radiative transitions at the target resulting in continuous spectrum x-rays of maximum quantum energy, V_A . The energy V_A comes from two sources, V_H (the voltage difference between cathode and target (measured by a high-resistance divider and potentiometer) and the energy, V_W , supplied to heat the cathode and cause the electrons to surmount its work function barrier, V_W . The thermal kinetic energy of the electrons, after escaping over the barrier, is at ordinary emission temperatures only of order 0.2 eV and is here neglected.

analogous to the cooling of a liquid by evaporation. In fact the determination of the ratio of the additional power required to maintain constant cathode temperature to the emission current produced is one of the well-known ways of measuring the work function V_W .

The thermally emitted electrons have a Maxwellian distribution of kinetic energies characteristic of the filament temperature, but at ordinary operating temperatures this constitutes a negligible correction to the energy, $V_A = V_H + V_W$. The energy kT at 2000° K is only about 0.17 eV, whereas the x-ray measurements are usually made at tens of kilovolts.

The process of conversion of electron energy into photon energy, $h\nu$, is in general

$$eV_A/c = h\nu + T_F \quad (5-54)$$

where eV_A/c is the initially available electron energy and T_F is the kinetic energy of the electron *after* the radiative transition. As T_F approaches zero the value of $h\nu$ approaches $h\nu_m = hc/\lambda_m$, the value which obtains at the short wavelength limit of the spectrum. Thus we may express the conservation of energy for this limiting case by

$$eV_A/c = h\nu_m = (hc/\lambda_{m0})10^8 = (hc/\lambda_{ms})\Lambda^{-1} 10^8 \quad (5-55)$$

In equations (5-54) and (5-55) e is the electronic charge expressed in absolute electrostatic cgs units and e/c is the same charge in absolute electromagnetic cgs units, V_A is expressed in absolute electromagnetic units, λ_{ms} is the limiting continuous spectrum wavelength expressed in kilo-x-units (Siegbahn scale), and λ_{m0} , is the same wavelength in Angstrom units. Solving for the product of the two measured quantities, V_A and λ_{ms} , it is clear that this experiment yields a determination of the voltage-wavelength conversion constant, $V_A\lambda_{m0}$, divided by the conversion factor Λ between Siegbahn and Angstrom scales.

$$V_A\lambda_{ms} = (h/e) c^2\Lambda^{-1} 10^8 \quad (5-56)$$

Two methods of performing the experiment have been followed. In one of these the voltage applied to the x-ray tube is held constant and the x-ray intensity associated with a narrow band of the continuous spectrum (selected by an x-ray monochromator) is plotted as a function of the wavelength setting of the monochromator over the region in the neighborhood of the quantum limit. In the other and more usual method, known as the "method of isochromats," the wavelength setting of the monochromator is held constant and the voltage applied to the x-ray tube is varied in small steps. The intensity accepted by the pass-band of the monochromator is plotted as a function of the voltage applied to the x-ray tube and the curve so obtained is called an "isochromat."

The region in the neighborhood of the threshold which need be explored in either of these methods represents only a very small relative change (of order 0.1 per cent) in the independent variable,

wavelength or voltage as the case may be. Since the shape of the spectral distribution near the limit does not vary rapidly with applied voltage, it is easy to see that the isochromat curve is practically a scale replica of the spectral intensity curve.

The history of experiments of this type (56-66) goes back over a long period of years. The experimental results throughout the entire period have always tended to give a value of h/e which was *lower* (by as much as 0.4 per cent or more in the extreme cases) than the value required for consistency with the bulk of the data on the constants. This would imply that the maximum emitted photon energy, $h\nu$, is *greater* than the electron energy, eV_A , whose conversion into radiation produced it. As the experimental techniques have been improved the magnitude of the "discrepancy" has gradually diminished, although up to 1955 it had not been completely resolved.

In retrospect it is easy to understand the reasons for this discrepancy in the earlier measurements. As spectral resolving power in the x-ray region improved and as better methods of stabilizing and measuring the high voltage were developed, the shape of the thick target continuous x-ray spectrum in the regions adjacent to the quantum limit was defined with increasing fidelity of detail. (Only thick target spectra have been used for this precision measurement.) It is now known that near the SWL the thick target spectrum (or its counterpart, the isochromat curve) is composed of several approximately linear sections, each of which is steeper than its predecessor as we pass toward the limit. These "knees" or breaks in slope were successively revealed as technical improvements permitted the experiment to be performed with increasing energy resolution. In the earlier stages of progress, because of the much poorer spectral resolution, such details were obscured in the regions close to the quantum limit. Because of the finite resolving power of the instrumentation they were buried under a large fillet, such as the one shown in the region, *CD*, of the isochromat in Figure 5-11, which left the true position of the quantum limit of the spectrum ill defined. It was at first customary to estimate the true position of the limit by extrapolating a tangent (the dotted line in Figure 5-11) from that part of the spectrum (isochromat) just above this fillet down to the level of zero spectral intensity. However, because of the above-mentioned hidden structure, with segments of increasing steepness as we near the SWL, this asymptotic tangent

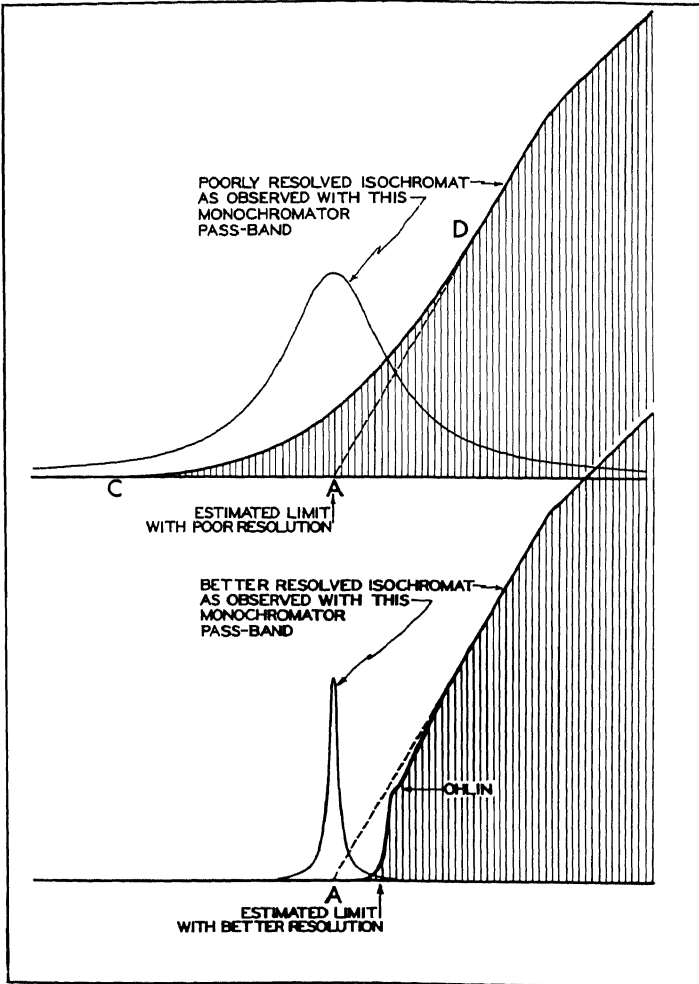


Figure 5-11. Sketch to illustrate one type of important early source of error in estimating the true position of the short wavelength limit of the continuous x-ray spectrum by the method of the extrapolated tangent. This type of error was caused by unsuspected "knees" and other irregularities in the isochromat such as the "Ohlin valleys," whose presence was obscured by the large "fillet" at the quantum limit arising because of the low resolving power of the x-ray monochromator.

line extrapolated to zero at a wavelength somewhat below the correct value in the way indicated at *A* in Figure 5-11.

When increased resolving power had revealed that breaks in slope existed quite close to the quantum limit, the following more subtle source of unreliability in the method of the projected tangent was recognized (56). For reasons fundamental to the dynamical theory of x-ray diffraction in crystal lattices, it can be shown that the band-pass curve of the two-crystal monochromator decays to zero at large spectral distances from its peak no faster than the inverse square of the distance. The product integral of this slow decay into a linearly rising continuous spectrum tends therefore to be logarithmically divergent and the fold of such a band-pass curve into a rectilinear spectral profile exhibits residual curvature which extends indefinitely far up the isochromat. It can be shown that as a result of this the method of the projected tangent will give the true quantum limit only if (1) the ideal spectral profile (i.e., the distribution for the case of infinite resolution) continues to be rectilinear indefinitely far from the quantum limit and (2) the point of tangency on the experimentally observed isochromat from which the tangent is projected can be chosen sufficiently far from the quantum limit to reduce the error introduced by the afore-mentioned curvature to negligible proportions. With these requirements to be met, the observed breaks in slope in the isochromat are demonstrably too close to the quantum limit for trustworthy applicability of the method of the projected tangent even when the highest resolution of the two-crystal spectrometer is available.

In an attempt to avoid this type of error an alternative method of locating the quantum limit was devised. It has been shown (56, 57) that if the "true" isochromat (the curve which would be measured with a monochromator of unlimited resolving power) can be assumed to have a sharp discontinuity in slope at the quantum limit, then a good approximation to the position of the true threshold will be given by the "point of maximum bending" (maximum of the second derivative) of the isochromat observed with finite resolution. This method has been adopted in all precision measurements (56-58, 65, 66) performed between 1937 and 1953.

In Section 6.7 we shall discuss in more detail the question of thin- and thick-target x-ray spectra and shall present evidence to show that when a precision of the order of a part in 10^4 or better is de-

sired in determining $V_A\lambda_{ms}$ of equation (5-56) (that is to say when a resolution of spectral details of the order of a few volts or less becomes important), even the method of the point of maximum bending may cause a small systematic error. At this point we shall only mention that theoretical considerations as well as the latest experimental evidence indicate that those determinations performed at the lowest voltages should have the smallest residual systematic error of this type. For this last statement to be true it is of course necessary that certain obvious sources of systematic error peculiar to low-voltage determinations shall have first been eliminated or corrected. Such matters as the proper correction for cathode work function and errors from electron retardation in low atomic number contamination on the target surface are of this variety.

Table 5-4 presents the results of continuous x-ray spectrum SWL

Table 5-4. Determinations of h/e and $V_A\lambda_{ms}$ Previous to World War II

Author and Reference	Value ^a of $h/e \times 10^{17}$ erg sec (esu) ⁻¹	Value of $V_A\lambda_{ms}$ kilovolt x-units
W. Duane, H. Palmer, and C. S. Yeh, <i>J. Opt. Soc. Am.</i> , 5 , 376 (1921)	1.3749	12330
H. Feder, <i>Ann. Physik</i> , 51 , 497 (1929)	1.3759	12340
P. Kirkpatrick and P. A. Ross, <i>Phys. Rev.</i> , 45 , 454 (1934)	1.3754	12335
G. Schaitberger, <i>Ann. Physik</i> , [5] 24 , 84 (1935)	1.3775	12354
J. W. M. DuMond and V. L. Bollman, <i>Phys. Rev.</i> , 51 , 400 (1937)	1.3765	12345
P. Ohlin, Dissertation, Uppsala (1941), <i>Arkiv Mat. Astron. Fysik</i> , 27B , No. 10 (1940)	1.3800	12376
R. T. Birge (indirect ^b) <i>Repts. Progr. Phys.</i> , 8 , 90 (1942)	1.3793	12370 ^c
W. K. H. Panofsky, A. Green, and J. W. M. DuMond, <i>Phys. Rev.</i> , 62 , 214 (1942)	1.3786	12364

^a The values of h/e were computed using $c = 2.99776 \text{ cm sec}^{-1}$ and $\Lambda = \lambda_g/\lambda_s = 1.00203$.

^b Birge computed h/e from the formula, $h/e = \{2\pi^2c^3F^2/[R_\infty N^2(e'/m)]\}^{1/2}$ with (e'/m) the electronic charge-to-mass ratio expressed in emu.

^c Birge's indirect value of h/e is here converted to kilovolt x-units using the same values of c and Λ .

determinations up to 1942 including for comparison an "indirect value" of h/e obtained by R. T. Birge. This material is taken from a paper (57) published in 1942 and the data were therefore reduced to calculate h/e using the values, $c = 2.99776 \times 10^{10}$ cm sec⁻¹ and $\Lambda = 1.00203$, then believed to be most nearly correct. We present therefore, in addition to the value of h/e so calculated and published at that time, the corresponding value of $V_A \lambda_{ms}$ in kilovolt x-units which represents the datum actually observed. We have omitted from this table a preliminary value given by Bearden and Schwarz in 1941 which they later corrected and which will be discussed in Section 6.7. The general upward trend of the h/e results with time because of improved techniques (and especially because of increased voltage resolution) can be clearly seen.

b. Photoelectric Determinations of h/e

It might at first sight be expected that photoelectric determinations would yield more reliable results than the x-ray method, in view of the statement just made that a serious systematic error is minimized by working at low voltages. Unfortunately this is not the case, because the dominant source of uncertainty is no longer the resolution with which the wavelength can be defined.

In the photoelectric measurements a monochromatic beam of radiation falls on a photoelectric surface. The current of ejected photoelectrons is measured as a function of a retarding potential, V , in an effort to find the kinetic energy of ejection by seeking that value, V_0 , of the retarding potential at which the current vanishes. If W is the work to extract the most loosely bound electrons from the photoelectric emitter then we should have

$$V_0 + W = h\nu \quad (5-56a)$$

Unfortunately the difficulty here is that V_0 is ill defined experimentally; the curve of photoelectric current versus retarding potential, V , does not present a sharp intercept with the zero axis but rather has an asymptotic transition to zero. This phenomenon, like the structures near the limit of the x-ray spectrum, is also connected with the detailed distribution over the energy levels of the solid-state structure electrons, in this case those in the photoelectric emitter. But because the energies, $h\nu$, in the optical region are only comparable to or a little larger than the work function energies, W , the asymptotic transition region of the photoemission curves in-

roduces a much greater obstacle to precision measurement than is encountered in the x-ray region. The difficulty is further enhanced by the fact that the effect is very sensitive to minute contamination of the photoelectric emitting surface so that reproducible results are hard to obtain. For these reasons, precision photoelectric determinations of h/e cannot compete in accuracy with the x-ray determinations.

c. Excitation Potentials

No measurements of excitation potentials have as yet attained the precision of the x-ray SWL method, although an experiment described by Dunnington (67) approaches it. In such experiments the energy necessary to ionize an atom or to excite a given level is determined in terms of wavelength, λ , by spectroscopy; this same energy is then measured by determining the voltage necessary to accelerate an electron so that it will just ionize or excite the same atom. The excitation potential in this experiment is the energy requisite to excite helium by electron bombardment from its ground state to the $2p^1P_1^0$ state. The loss in energy sustained by electrons which have done this work of excitation, about 21.2 volts, is measured, and this, combined with the spectroscopically measured wave number for the transition in question, supplies the data to compute c^2h/e . Dunnington and his co-workers used an apparatus with circular trajectories in a magnetic field somewhat like the one he devised for e/m which we have described in Section 5.9 (see Figure 5-7). His h/e apparatus had this difference, however, that at one point in their circular trajectories the electrons passed through a region of D. C. electric field wherein they could be accelerated by an adjustable and accurately measured voltage. In this same region a small amount of helium gas could also be continuously introduced and kept more or less concentrated by differential pumping so that inelastic collisions between electrons and gas atoms occurred almost exclusively in that region. When the applied D. C. voltage was practically zero, electrons which had made no collisions passed through the entire system and reached the collector. Actually a small D. C. voltage, V_0 , was necessary to correct for contact potentials and similar effects and a maximum in the electrons collected after one revolution was the criterion that this reference value was correctly adjusted. When the D. C. voltage was then raised by the amount ΔV corresponding to the chosen excitation potential for

the helium, a second maximum occurred corresponding to those electrons which had lost energy in one collision and regained an equal amount from the D. C. applied field so that they could complete their circular trajectories in the magnetic field. The value they obtained was

$$c^2h/e = 12393.7 \pm 1.8 \text{ volt } \text{\AA} \quad (5-57)$$

or assuming $\Lambda = 1.00202$ to facilitate comparison with the x-ray results, this is equivalent to

$$c^2h/(e\Lambda) = 12368.7 \pm 1.8 \text{ kv x-units} \quad (5-58)$$

The precision claimed by these experimenters (145 ppm) is only about half as satisfactory as that obtained from the postwar x-ray determinations. The excitation potential result disagrees with the 1955 least-squares adjusted value about twice as much as the x-ray result and in the same direction.

Earlier measurements of ionization or excitation potentials have been made by E. O. Lawrence on mercury vapor, by Van Atta and by Whiddington and Woodroffe on helium, neon, and argon using methods analogous to Dunnington's. These are insufficiently accurate to be of great interest at the present time (1957). They will be found listed with references in Table 5-6 and plotted to represent their consistency with other determinations on the chart of Figure 5-14.

A closely related type of precision determination falling in this same class of critical potential experiments has perhaps its best example in the work of Åke Nilsson (68). The intensity of K-series x-ray lines is measured as a function of the exciting voltage. Here the threshold voltage, V_{exc} , for excitation must be combined with the wavelength, λ_{abs} (measured in x-units), of the critical K-absorption discontinuity of the element whose K-series lines are to be excited. The difficulty here is associated with the structure of the excitation curve close to the threshold and the uncertainty involved in identifying features in the profile of the absorption edge with "corresponding" features in the profile of the excitation curve. The mean result obtained from the study of four different lines was

$$hc^2/(e\Lambda) = 12372 \pm 5 \quad (5-59)$$

Finally mention should be made of a critical-potential method proposed by Kai Siegbahn (69) involving the use of internally con-

verted β -rays ejected by a specified nuclear gamma-ray transition from different atomic energy levels, K , L_I , L_{II} , etc. He proposes to have the source material on a fine wire and to surround it with a cylindrical grounded metal shield provided with a slit. These are placed in a precision magnetic β -ray spectrometer and the magnetic field adjusted so as to focus a certain β -ray line from the K -shell of the radioactive source atom. With the magnetic field kept constant and with fixed geometry, a positive potential is then applied to the source wire such as to focus the conversion electrons from one of the L -shells. This potential, measured with high accuracy, and the wave number difference between the K and the L level (in reciprocal x-units, Siegbahn scale, obtained by x-ray spectroscopic means) constitute the data from which $hc^2/(\epsilon\Delta)$ is to be computed. Clearly the method is closely similar to the one exemplified by the experiment of Dunnington and co-workers save that it involves x-ray in place of optical spectroscopic data. Both these approaches have the advantage of working with *line peaks* and thus avoiding the difficulties of identifying the quantum limit of a continuous spectrum or the threshold point of an excitation curve. Kai Siegbahn shows how the x-ray energy level difference, $(K - L_I)$, may be accurately evaluated by spectroscopic measurements *on lines only*. In 1957 no results of this proposed method were yet available.

5.12 OTHER EXPERIMENTS BEARING ON PLANCK'S CONSTANT, h

We list under this heading five types of experiment which determine different functions of the atomic constants involving h . Only two of these, (b), Rymer and Wright's measurements by electron diffraction, and (e), the measurement of the wavelength of the annihilation radiation by Muller, Hoyt, Klein, and DuMond, approach in precision the postwar determinations by means of the SWL of the continuous x-ray spectrum. The other three are listed here for completeness only. References to the papers describing them will be found under Tables 5-6 and 5-7 and will therefore not be repeated here.

a. X-ray Photoelectric Effect

Photoelectrons ejected by x-rays of wavelength, λ (known in x-units), from atomic levels of known critical absorption wavelength, λ_c (also in x-units), are deflected in a magnetic field of

measured intensity, H , and their radius of curvature, ρ , is measured. This permits determination of the function $\Lambda e^2/(mh)$ from the relation

$$\Lambda e^2/(mh) = \frac{2c^3}{(H\rho)^2} \left(\frac{1}{\lambda} - \frac{1}{\lambda_q} \right) \quad (5-60)$$

G. G. Kretschmar has applied this method using values of λ_q from absorption edge measurements. H. R. Robinson in 1936 and Robinson and Clews in 1940 have applied the same method, but they eliminated the need for λ_q by taking measurements at two values of λ . Robinson's results are uncertain to about 500 ppm.

b. Electron Diffraction

The de Broglie wavelengths of electrons are measured by diffraction methods from crystals whose lattice constants are known on the Siegbahn scale in x-units. Since the de Broglie wavelength is given by the formula h/p , where p is the electron momentum, a determination either of electron velocity or electron kinetic energy is also needed. In the work of J. Gnan, the kinematic velocity of the electrons was directly measured by a method developed earlier by F. Kirchner. The method yields $h/(m\Lambda)$ but an accuracy of the order of only 0.1 per cent has been attained. A more precise method first applied by S. von Friesen and later much more accurately by Rymer and Wright (70) consists in measuring the voltage, V , which accelerates the electrons. This method yielded a numerical value for the function $h(c/em)^{\frac{1}{2}} \Lambda^{-1}$ as follows:

$$h(c/em)^{\frac{1}{2}} \Lambda^{-1} = (1.73065 \pm 0.00017) \times 10^8 \text{ x-unit (abvolts)}^{-\frac{1}{2}} \quad (5-61)$$

In comparison with this, the value computed from the 1955 data given in Table 8-7 yields the value $(1.73083 \pm 0.00002) \times 10^8$. Thus the measurement by Rymer and Wright agrees with our adjusted output value to within approximately one standard deviation of the difference. In view of the interpretive difficulties encountered in the short wavelength x-ray limit determinations (see Section 6.7) it would appear desirable to exploit further the possibilities of this method of electron diffraction.

c. Compton Wavelength Shift

The increase, $\Delta\lambda$, in wavelength experienced by initially monochromatic radiation after scattering by an initially stationary free

electron is given by the well-known formula

$$\Delta\lambda = (h/mc)(1 - \cos \theta) \quad (5-62)$$

where θ is the angle between the direction of incidence and the direction of scattering. In no real experiment is it possible to study scattering by anything but bound electrons, however, and this introduces two difficulties which render this method extremely inaccurate. (1) The randomly directed linear momenta of the bound electrons produce a considerable broadening of the shifted line which is so great as to make measurements of the shift quite inaccurate. (2) The atom from which the Compton effect ejects an electron shares to a slight extent in the momentum balance, the more so the more tightly bound the electron, and this introduces a systematic "defect" in the shift relative to the free electron value of equation (5-62) which is difficult to correct with high accuracy. In a remarkable experiment in 1934 Ross and Kirkpatrick have determined $h/(mc\lambda)$ by this difficult method to about 0.2 per cent.

d. Radiation Constants, c_2 and σ

The formula of Planck for the spectral distribution of the radiant energy from a black body is

$$J_\lambda = c_1\lambda^{-5} (e^{c_2/\lambda T} - 1)^{-1} \quad (5-63)$$

in which λ is the wavelength, $J_\lambda d\lambda$ is the power radiated per unit area in the spectral wavelength interval, $d\lambda$, and T is the absolute temperature. The two constants, c_1 and c_2 , are given by

$$c_1 = 2\pi c^2 h \quad \text{and} \quad c_2 = hc/k \quad (5-64)$$

where k is Boltzmann's constant. The Stefan-Boltzmann law giving the total power, σT^4 , emitted per unit area is derived directly by integration of equation (5-63) over the entire spectrum, while differentiation of that equation to find the wavelength, λ_m , at which the maximum of J_λ occurs yields Wien's displacement law according to which the product $\lambda_m T$ is a constant. The constants σ and $\lambda_m T$ are given by

$$\sigma = (\pi^2/60) k^4/(c^2 \hbar^3) \quad (5-65)$$

$$\lambda_m T = c_2/4.965 = hc/(4.965 k) \quad (5-66)$$

The number 4.965 is the root, to four significant figures, of the transcendental equation, $x = 5(1 - e^{-x})$. Since k equals R_0/N , the quotient of the gas constant by Avogadro's number, it is clear that, in principle at least, measurements of these radiation constants are capable of yielding information bearing on the constant, h . The situation has been reviewed by H. T. Wensel (71) in 1939 and by G. A. W. Rutgers (72) in 1949. The large uncertainties of more than 0.5 per cent in σ and of about 0.2 per cent in c_2 render these methods of no value for our purposes.

e. Wavelength of Annihilation Radiation

The radiation which results from the recombination of stationary pairs of positrons and electrons is emitted in each elementary process as two photons of equal energy propagating in opposite directions. The wavelength of this radiation under these ideal conditions is given by

$$\lambda_A = h/(mc) \quad (5-67)$$

DuMond, Lind, and Watson and later, after elimination of certain sources of systematic error, Muller, Hoyt, Klein, and DuMond (73a, b) have measured the wavelength of the radiation emitted when positrons from the unstable nucleus, ^{64}Cu , recombine with the structure electrons in a block of solid copper. The cross section for recombination is very small until the positron has slowed down to thermal velocity. Internal evidence from the Doppler broadening of the annihilation line indicated that the velocity distribution of the recombining pairs corresponded quite closely to the velocities to be expected for the conduction electrons in the copper. The potential energies of electron and positron must be equal in magnitude and opposite in sign when they collide and hence these cancel out. The energy of the radiation corresponds then to the rest mass energy of the particles plus a negligible correction for their kinetic energy. The final result of these measurements after all corrections was given as

$$\lambda_{A1} = h/(mc) = 24.262 \pm 0.0033 \text{ milliangstroms} \quad (5-68)$$

and since the value, $\Lambda = 1.00203$, was used in reducing the data this corresponds to

$$\lambda_{A1}/\Lambda = h/(mc\Lambda) = 24.213 \pm 0.0033 \text{ x-units} \quad (5-69)$$

The precision of this result (standard deviation, 137 ppm) could, it is believed, be bettered by improvements in the technique so as to make this method compete very favorably with the method of the continuous x-ray spectrum. The interpretive difficulties associated with locating an asymmetric spectral feature such as the short wavelength limit are completely avoided in the annihilation radiation measurement. The result is in excellent accord with the output value of the 1955 adjustment, Table 8-7.

5.13 NEED FOR CRITICAL EVALUATIONS OF DATA ON THE ATOMIC CONSTANTS

We have thus far reviewed in this chapter the various types of experiments leading to quantitative information about the atomic constants. As explained at the opening of the chapter, so many theoretical relationships exist between the different quantities measured that the results of this large mass of experimental evidence can be properly evaluated to find reliable and consistent values of the constants only by procedures which take account of all the data together. As the mass of experimental data on the atomic constants accumulated, the need for overall assessment of the situation became acute. Raymond T. Birge was the first to attempt such assessments, and his first paper in 1929 on this subject is a model of painstaking care to bring order out of what at that time was a very chaotic state of affairs. Much stimulus to undertake new and better measurements came from analyses such as this because of the various "discrepancies" which were thus brought into focus. We have spoken of three of these discrepancies. The first was the difference between oil-drop and x-ray values of N and e . This, as we have explained, was finally resolved but, with the accumulation of new types of measurements and the resulting increase in overdetermination and precision, new discrepancies inevitably made their appearance. The discrepancy between the "spectroscopic" and "deflection" values of e/m has been mentioned (Sections 3.6 and 5.9), as has also the discrepancy between "x-ray" and "indirect" values of h/e (Section 5.11). About two decades, starting in 1929 with Birge's first paper, may be regarded as the period of pioneer effort and refinement of method in the fields both of experiment and of overall assessment. Birge realized acutely the need for better statistical methods of evaluating the data and of estimating its

accuracy, and he made many original and valuable contributions to this subject, a few of which we shall now briefly describe.

5.14 BIRGE'S METHODS OF EVALUATING THE DATA ON THE ATOMIC CONSTANTS

Birge's earliest method (1929) of determining suitable numerical values to adopt for the atomic constants was the common-sense one of beginning with those constants least dependent on others and selecting a route at each stage of which a new constant was determined by utilizing constants and conversion factors already determined at earlier stages. Even with the data then available it frequently transpired, as might be expected, that there was more than one way of doing this. When a constant could be arrived at by many routes, Birge followed all those which appeared worthy of serious consideration, thus obtaining several values with different probable errors. He then took an average of these to obtain the "best" value for adoption. These averages were often strongly influenced by subjective evaluations of the reliability of the experimental data, in addition to the analytical evaluation based on the internal consistency of the data itself.

Specifically the route followed by Birge in his 1929 paper was this: (1) By a study of all available primary experimental sources he arrived at the best values to adopt for certain requisite "auxiliary constants," as he called them, such as the velocity of light, c , the atomic weights (chemical scale) of certain key atoms, the Rydberg constant, R_∞ , for a nucleus of infinite mass, the gas constant for ideal gases, R_0 , the electrochemically determined Faraday, F . (The auxiliary constants were those quantities whose values were so far beyond question for the purposes of his analysis that they could be treated as though known exactly.) (2) The best value of e was next determined by the two methods which then existed and which we have described in Sections 7 to 14. (3) Then Birge investigated the best value of the charge-to-mass ratio, e/m , for the electron, listing a considerable number of "deflection" and "spectroscopic" methods of measuring this constant (see Section 5.9). The spectroscopic methods, as we have seen, consisted essentially of (a) the measurement of the Zeeman splitting in a known magnetic field, and (b) the measurement of the reduced mass effect (mitbewegung des Kerns) for hydrogen. This latter in reality yields m_p/m , the ratio of

the masses of proton and electron. The Faraday, F , is then used along with the atomic mass, H^+ , of the proton to compute $e/m = (F/H^+)(m_p/m)$. (4) The next step was to compute m as a derived constant from e and e/m . (5) Finally Birge studied the results of six different methods of arriving at h , each of which depended in part on a knowledge of e . These were (a) the use of Bohr's formula for the Rydberg constant solved for h ,

$$h = [2\pi^2 e^5 R_\infty^{-1} c^{-2} (e/m)^{-1}]^{1/3}$$

together with his adopted values of e , c , and e/m ; (b) use in the manner explained in Section 5.11 of E. O. Lawrence's measurement (see Table 5-6) of the first ionization potential of mercury by electron bombardment to obtain h/e , from which the knowledge of e permitted calculation of h ; (c) use in a similar way of measurements of the short wavelength limit of the continuous x-ray spectrum from an x-ray tube operated under an accurately measured steady D. C. voltage; (d) use of the direct photoelectric effect in the ultraviolet and optical regions (this as explained in Section 5.11 is demonstrably less accurate than method (c), however); (e) use as explained in Section 5.12 of the measured value of the radiation constant, c_2 , occurring in Wien's displacement law and also in Planck's black body radiation law; $c_2 = hc^2F/(eR_0)$, in which R_0 is the gas constant; (f) use as explained in Section 5.12 of the measured value of the radiation constant, σ , in the Stefan-Boltzmann radiation law, $E = \sigma T^4$, in which σ is connected with h (using Planck's law) by the relation

$$h = [2\pi^5 R_0^4 / (15N^4 c^2\sigma)]^{1/3}$$

Methods (e) and (f) are the least accurate of the lot because of the poor accuracy with which c_2 and σ have been experimentally measured.

5.15 RESOLUTION OF DISCREPANCIES

In the decade from 1929 to 1949 progress in our knowledge of the atomic constants was reviewed and discussed in a series of papers by Birge (reference 12, Chapter 2; 74a-f) and others (75, 76, 77a-c). (a) The apparent discrepancy between the values of e/m as obtained by spectroscopic and deflection methods (reference 1, Chapter 1; reference 12, Chapter 2) was chiefly resolved during this period by better deflection measurements and partly also by the recognition

(77d-g) that the systematic error probably came from the electrochemically determined "silver" Faraday, F . (b) The "h/e discrepancy," though greatly reduced during this period by improved experimental techniques (especially higher spectral resolving power) and the discovery and application of appropriate corrections to the experiment on the short wavelength limit of the continuous x-ray spectrum, still remains in 1955 in a not entirely satisfactory state. This matter will be discussed in greater detail in Section 6.7.

An idea of the progress made during the decade under discussion and shortly thereafter can be obtained by comparing the consistency diagrams prepared to express the status of our information on the atomic constants at two different dates, 1939 and 1949.

a. The Birge-Bond Diagram

In order to get a clearer understanding of the complex situation regarding the interconsistency of the measured data bearing on various functions of the atomic constants, we shall now explain two types of consistency diagram devised for this purpose. The first of these, usually known as the Birge-Bond diagram, was first proposed by W. N. Bond (78). It has been very effectively and extensively used by R. T. Birge (79).

This diagram has been applied by Birge to the case of three unknowns, e , m , and h , the remaining primary quantities being treated as auxiliary constants. The diagram directs attention at one selected unknown, say, e . Each experimental determination of some function of the three unknowns, $f_i(e, m, h)$, by use of the Rydberg relationship, $R_\infty = 2\pi^2 m e^4 h^{-3} c^{-1}$, to eliminate one of the unknowns (m , for example) can be written as an equation between an experimentally determined number and a function of e and h , $\phi_i(e, h)$. A nominal value of h which we shall call h_0 , known not to differ greatly from the true value, is assumed. We shall refer to h_0 as the "origin" value of h . All the functions, $\phi_i(e, h)$, could always be so expressed as to take the form

$$\phi_i = h^{p_i} e = \text{an experimentally determined number}$$

Birge then plotted as ordinates on a Cartesian plot the value e_i' which each function, $\phi_i(e, h)$, equated to its experimental numeric, would yield as a solution for e if h_0 were substituted therein for h . As abscissa, the power, p_i , corresponding to the particular func-

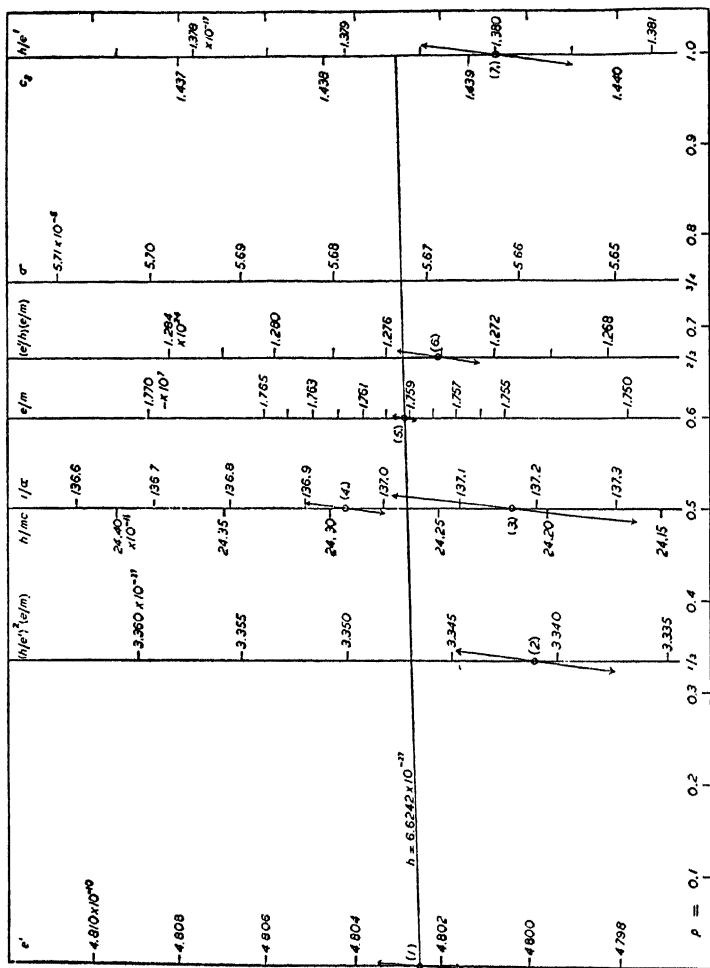


Figure 5-12. Birge-Bond diagram for depicting the consistency of the various methods of determining e , m , and h from various measured functions of these constants. The function is indicated near the top of its particular ordinate on the diagram. A specific value for the Rydberg constant, R_{∞} , is implicit in this diagram. Numerical values of the different functions of e , m , and h which are mutually consistent with R_{∞} and with each other will be colinear.

tion, ϕ_i , was plotted. It is easy to see from a Taylor's expansion that all functions, $\phi_i(e, h)$, whose numerical values are inconsistent should plot so as to lie on a straight line (save for the effect of terms in the Taylor's expansion of order $(h - h_0)^2/h_0^2$ which can easily be made negligible). The inconsistency of the various determinations could thus be judged by how well their points agreed in defining a straight line. Also if their rectilinearity was imperfect the chart afforded (1) an intuitive graphical method of effecting a compromise by drawing a straight line which came as near to the different points as could be managed and (2) an analytical method by the familiar process of least-squares fitting for finding the "best" straight line so as to allow for the different error measures of the various experimental determinations.

The extension of this straight line to intercept the ordinate at the abscissa value, $p = 0$, obviously gives the "best" value of e consistent with the compromise so effected. The slope of the line can also readily be interpreted to give the "best" compromise value of h . Birge constructed a convenient nomogram in this way by plotting scales on the ordinates corresponding to the different functions $\phi_i(e, h)$. Each scale read directly in terms of the value of the experimentally determined numeric, f_i (the function of e , m , and h before elimination of m with R_∞), so as to show just where to plot the results of any specified experimental determination. Such a plot reproduced from Birge's 1941 report is shown here as Figure 5-12. The probable error spreads are indicated by lines tipped with arrows and slightly inclined from the vertical. The value of h inferred from the slight slope of the straight line is indicated thereon.

b. The Isometric Consistency Chart

Another type of chart first suggested by R. A. Beth (80) has later become known as the "isometric consistency chart" for reasons which will soon become clear.

In preparing this consistency chart the constants e , m , and h have been selected as the primary unknowns. In addition, the Rydberg relationship

$$R_\infty = 2\pi^2 mc^4 h^{-3} e^{-1} = 109737.3 \text{ cm}^{-1} \quad (5-70)$$

between these unknowns and the experimentally very accurately measured value of R_∞ , is implicitly assumed to hold (R_∞ being re-

garded as a fixed auxiliary constant) so that the system really involves only two independent unknowns and can therefore suitably be displayed in two dimensions. The chart permits explicit display of any measured values of e , m , h and of any function of these variables subject, of course, to condition (5-70).

Unlike the Birge-Bond diagram the isometric consistency chart is not especially adapted to afford a graphical method of finding a compromise solution. Its chief purpose is to display the consistency of a large mass of data on the constants in such a clear way as to reveal not only the general state of agreement but also, if a few of the data depart markedly from the general consensus, to indicate these readily. We shall explain the isometric consistency chart here in order to be able to exhibit with it the state of consistency of our sources of knowledge on the atomic constants at two epochs, 1940 and 1947.

With the multiplication in the number of functions of the atomic constants which have been measured since 1950 and the increase in accuracy of the determinations, it has become necessary to include under the category of unknowns more and more of what could once be regarded as fixed auxiliary constants. Thus instead of involving two or three unknowns the situation has required the analytical consideration of four or even five. For this reason, consistency diagrams represented on a two-dimensional surface are unfortunately no longer very useful. They served a purpose only up to about 1950.

In order to construct a two-dimensional isometric consistency chart we consider first a three-dimensional rectangular Cartesian coordinate system in which the three primary variables are associated with the three orthogonal axes. A set of three values, e , m , h , will be represented by a point in this space and a function, $f_i(e, m, h)$ (such as e/m or e^2/mh), of the three primary variables equated to a number obtained by physical measurements of that function will be represented by a surface. Three such surfaces may, but need not necessarily, intersect in such a way as to locate a point in this space. (Three planes will fail to locate a point if any pair of them is parallel to a common plane, or if all three are parallel to a common line. In this latter case we shall describe them as "cozonal" planes; the three surfaces can then at most determine a line but not a point.)

The entire overdetermined situation regarding the various func-

tions of e , m , and h whose numerical values have been measured experimentally, can be represented as a set of variously oriented surfaces in this 3-space, all of which nearly pass through a common point, the nearer the more mutually consistent the determinations are. In general these surfaces are curved but we are interested only in a small domain of the space close to the region of quasi-intersection, since the incompatibility of the various equations, even in 1939, usually required no more than a 1 per cent change in any variable or function to establish consistency. At the time of the present evaluation (1955) matters are far better. In such a domain the tangent planes can be taken as good approximations to the actual curved surfaces.

To simplify matters then, we adopt a new origin close to the domain of quasi-intersection at a point, e_0, m_0, h_0 , so chosen that the coordinates e, m, h , of any intersection in which we are likely to be interested will differ from e_0, m_0, h_0 , by relative amounts $x_e = (e - e_0)/e_0$, $x_m = (m - m_0)/m_0$, and $x_h = (h - h_0)/h_0$ which are always smaller than say 0.001, and we then express the experimental measurements in terms of these dimensionless variables, x_e, x_m, x_h . To each type of experimental determination of a function of e, m , and h of the form

$$f_\mu(e, m, h) = e^{i_\mu} m^{j_\mu} h^{k_\mu} = A_\mu \quad (5-71)$$

there corresponds a plane

$$i_\mu x_e + j_\mu x_m + k_\mu x_h = a_\mu \quad (5-72)$$

which is tangent to the curved surface. Practically all experimentally determined functions are of the form of (5-71). The constant, a_μ , in (5-72) is given by

$$a_\mu = (A_\mu - A_{\mu_0})/A_{\mu_0} \quad (5-73)$$

in which $A_{\mu_0} = f_\mu(e_0, m_0, h_0)$ is the origin value of the function, $f_\mu(e, m, h)$. Clearly the *orientation* of the tangent plane (5-72) in the 3-space depends on the exponents, i_μ, j_μ, k_μ , which express the function determined, while the *origin distance* of the plane depends on the experimentally measured numeric, a_μ .

We may think of the estimated random errors attached to the different experimental determinations by conceiving the corresponding planes to have a certain diffuseness of localization to their sur-

faces so that each plane is blurred out into a lamina of cloudiness with a parameter σ_μ^2 describing the mean-square spread about the mean position.

The least-squares adjusted value is then represented by a point in this space such that the sum of the squares of its distances from the various planes, measured for each plane in units of the error spread, σ_μ , of that plane is a minimum. The theory of least squares, as we shall see, also allows us to find in this space a region of concentric isoprobability ellipsoids around the point corresponding to the least-squares adjusted "best" value, and there exists a "standard ellipsoid" in this set such that two planes tangent to it and normal to any coordinate axis in the space will be separated by just the spread expressing the "standard error" of the unknown associated with that axis. The location, size, and shape of the ellipsoid of error reflects the *state of our knowledge* at any given epoch. It therefore has no permanent or fundamental significance.

The ideas we have introduced so far can be taken over to the case of any number of unknowns by speaking of hyperplanes and of hyperellipsoids in hyperspace. It is only the application of these ideas to a practical two-dimensional nomogram for representing the consistency of the constants which breaks down when the number of unknowns is increased.

The representation of the interconsistency of determinations bearing on the constants by means of planes in a multidimensional space did not appear to offer any advantages until it was noticed (77a) in 1939 that a surprisingly large number of planes representing useful determinations available at that time happened to be *cozonal*; i.e., oriented parallel to a common axis, the space-diagonal of the x_e, x_m, x_h space. Planes parallel to this axis, but otherwise oriented quite arbitrarily, have the property that the algebraic sum of the coefficients i_μ, j_μ, k_μ of equation (5-72) vanishes. Table 5-5 shows that this condition was satisfied for five of the seven important types of data, functions of e, m , and h which had been accurately determined by various experimental methods in 1939. With the passage of time, other far more accurate determinations bearing on quite different functions of the atomic constants have been made so that the above-mentioned circumstance of cozonality is no longer of interest. It is instructive, however, to make clear the reason for its importance at that time.

Figure 5-13 shows in perspective the orientation of the five cozonal planes. Clearly if we look along the space-diagonal (the cozonal axis) the five cozonal planes seen on edge will be projected on our picture plane as five straight lines. In Figure 5-13 for better clarity all five planes pass through the arbitrarily chosen origin point (e_0, m_0, h_0) , although in the results of a set of physical measurements, the planes, while having these same orientations, may be

Table 5-5. Experimentally Determined Functions of e , m , and h (1939)

Function	i	j	k	$i+j+k$	Ref.	Method of Measurement
e/m	1	-1	0	0	g	Deflection and spectroscopic
h/m	0	-1	1	0	a	X-ray refractive index of diamond
h/m	0	-1	1	0	b	Electron wavelength and kinematic velocity
h/m	0	-1	1	0	c	X-ray fine structure evaluation of α
h/m	0	-1	1	0	d	Compton shift
h/e	-1	0	1	0	g	X-ray short wavelength limit
h^2/em	-1	-1	2	0	e	Electron wavelength, measured voltage
e^2/mh	2	-1	-1	0	f	H_p of x-ray photoelectrons
e	1	0	0	1	g	X-ray crystal density and λ_g/λ_x
me^4/h^3	4	1	-3	2	g	Spectroscopic; (Rydberg constant)

^a J. A. Bearden, *Phys. Rev.*, **54**, 698 (1938).

^b J. Gnan, *Ann. Physik*, [5] **20**, 361 (1934).

^c R. F. Christy and J. M. Keller, *Phys. Rev.*, **58**, 658 (1940).

^d P. Kirkpatrick and P. A. Ross, *Phys. Rev.*, **45**, 223 (1934).

^e S. von Friesen, *Proc. Roy. Soc. (London)*, **A160**, 424 (1937).

^f H. R. Robinson, *Phil. Mag.*, **22**, 1129 (1936).

^g A more complete set of references is given in Table 5-6.

at any distance from the origin (depending on how much that physical measurement differed from the origin values, e_0, m_0, h_0).

Clearly the first five types of determinations of Table 5-5 taken together are still insufficient to locate a point in the space of the constants e, m, h . Even if these five were mutually compatible so that their planes intersected in a single axis, we should still need at least one more plane intersecting that axis to locate a point. A heavy responsibility falls, therefore, on the two noncozonal determinations, R_∞ and e , of Table 5-5. This peculiarity of the matrix of linearized observational equations might well have escaped notice

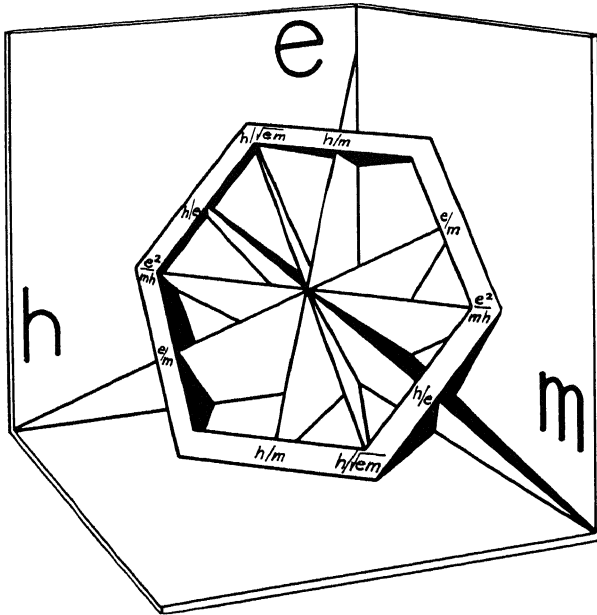


Figure 5-13. Perspective view of the intersection in three-dimensional e , m , h -space of the surfaces corresponding to various experimentally measured functions of e , m , and h . By a shift of the origin to a point e_0 , m_0 , h_0 close to that representing the true values of e , m , and h , the coordinates of the diagram can also (and preferably) be taken as representing the dimensionless variables $x_e = (e - e_0)/e_0$, $x_m = (m - m_0)/m_0$, $x_h = (h - h_0)/h_0$, and the surfaces over a small domain of relative deviation around e_0 , m_0 , h_0 , can be represented with sufficient accuracy as planes. The spatial orientation of these planes depends, as here shown, on the function determined. The experimentally measured value of the function determines the origin distance of the plane. Planes corresponding to determinations which are mutually consistent will have a common intersection. Of the seven most reliable types of determination in 1939 five are seen, when plotted thus, to be represented by planes which are parallel to a common axis, or normal to a common plane (the plane of the hexagon in the figure). These five therefore do not determine a point e , m , h in the space. At best they can determine only a line in that space. For simplicity in this diagram these five "cozonal planes" are here shown as though they were mutually exactly consistent so as to agree in determining one and only one line. Actually, however, the experimental values yielded planes which did not meet in a common axis as can be seen in Figures 5-14 and 5-15. The experimentally measured value of the Rydberg, $R_\infty = 2\pi^2me^4h^{-3}c^{-1}$, represents a function of e , m , and h , on the other hand, which is not cozonal with the five here shown. Millikan's direct oil-drop determination of e , here represented by a horizontal plane, is also not cozonal. On these two alone then in 1939 rested the entire responsibility of locating the point, along the cozonal axis determined by the other five, which determined the true values of e , m , and h . Not until such a three-dimensional plot as this had been made was this curious state of degeneracy in the input data realized.

if no attempt had been made at a spatial representation in this way. The existence of such a situation, however, is of no fundamental significance, but was a mere accident of the types of measurement which had been made at that epoch.

Figure 5-14 shows an example of the consistency diagram (77b) depicting the situation in 1940, and Table 5-6 lists all the data including the origin values used in preparing the chart. It is primarily a plot of (a) the cozonal planes viewed on edge and (b) noncozonal determinations, distinguished on the chart by the fact that their percentage deviation scales are ruled with double lines. Each line on the chart corresponds to the result of some individual experimenter or group in measuring a specific function of e , m , and h . Percentage deviation scales are provided at both ends of the line corresponding to each type of determination. These indicate the displaced position of each line for a determination whose result differs from the origin value of the function in question by a specified percentage difference.

Use is made of the Rydberg equation (5-70) (regarded as an exact relationship because of the extreme precision with which R_∞ is known) to depict the positions of those lines which correspond to noncozonal determinations. Any noncozonal function can always be expressed by appropriate transformation as a function of R_∞ and a cozonal function. Thus, for example, the noncozonal function, h , can be expressed as

$$h = (c/2\pi^2)^{\frac{1}{2}} R_\infty^{\frac{1}{2}} [h^5/(e^4m)]^{\frac{1}{2}} \quad (5-74)$$

where the right-hand member is seen to be cozonal since the sum of the exponents in the square brackets is zero. In geometrical language this corresponds to projecting onto the picture plane (which is normal to the cozonal axis) the line of intersection of the noncozonal plane and the R_∞ plane. The noncozonal planes for which scales are provided in Figure 5-14 are those corresponding to determinations of e , m , h , σ , and α . They are provided with double scales of percentage deviation; one of which gives the shift occasioned by specified percentage changes in the variable in question (holding R_∞ constant) and the other the shift occasioned by percentage changes in the numerical value of R_∞ (holding the other variable constant).

To use such a chart a straight line is plotted for each experi-

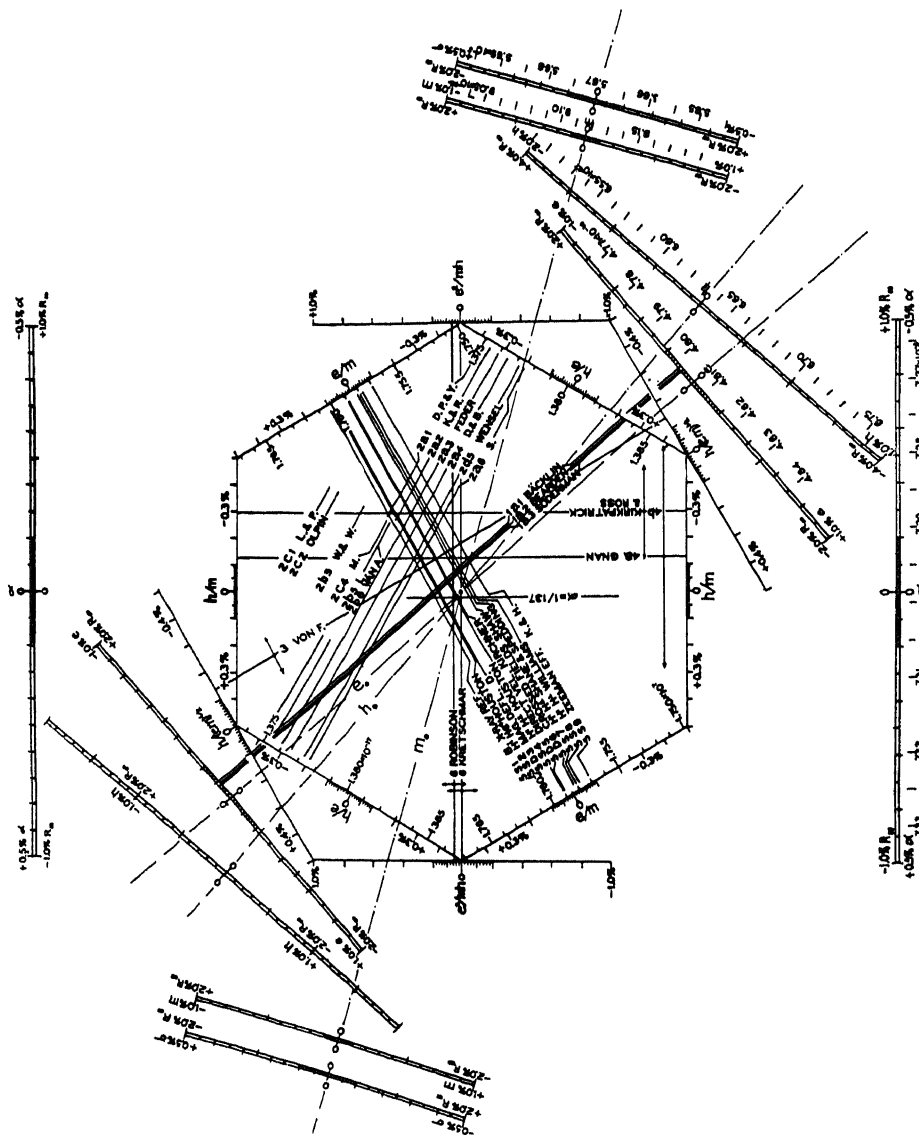


Figure 5-14.

mental determination of a function of e , m , and h ; this line runs between the two parallel percentage deviation scales for that function at the deviation from the origin value corresponding to the experimental value obtained. A scale reading directly the absolute value of each variable is also provided. Those traces which intersect in the same point represent mutually consistent determinations. Consistency with the Rydberg relationship, (5-69), is also implicit in the construction of the chart. The values of e , m , and h implied by any point on the diagram can be read off immediately on the scales of e , m , and h , either directly or in terms of per cent deviation from the origin values e_0 , m_0 , h_0 . To facilitate this operation the origin axes through the zeros of the percentage deviation scales of e , m , and h are also indicated with dot-and-dash lines. To find e , m , and h for any point in the diagram, one scales off the normal distance from that point to each of the dot-and-dash axes and transfers this distance to the appropriate scale of e , m , or h . The estimated probable errors of many of the more isolated determinations are indicated in Figure 5-14 by attaching arrows normal to the line. Any intersection point between two lines in Figure 5-14 represents one possible solution for e , m , and h (equation (5-70) for R_∞ always being implicitly understood in the construction of the diagram). The figure clearly shows the great number of possible solutions for e , m , and h which are implied by the complete array of data of Table 5-6. With data as discrepant as this diagram displays, one rightly hesitates to adopt any sort of least-squares method of compromise. The diagram also served very usefully as a

Figure 5-14. Isometric consistency chart exhibiting the consistency as of about 1940 of the various sources of information on the constants e , m , h and functions thereof. The scales at the ends of the value lines show the displacement in per cent deviation from a set of mutually consistent conventional origin values. These origin values and the experimental data are given in Table 5-6. Certain of the scales, it will be noted, are double scales—the position of the value line depends on two variables, one of which is R_∞ . These are the noncozonal functions. Each of the two scales in such a case shows the displacement for the value line if the variable of one scale alone is changed while the other variable is held at its origin value. The intersection of any two value lines gives a point to which corresponds a set of values for e , m , and h representing the simultaneous solution for those three constants which the two selected measurements combined with the value of R_∞ would yield. The huge number of possible just-determinate solutions implied by the data is obvious.

Table 5-6. Values Used in 1940 Isometric Consistency Chart, Figure 5-14

Conventional or origin values used in isometric chart.
 $e_0 = 4.80650 \times 10^{-10}$ esu, $m_0 = 9.11780 \times 10^{-28}$ g, $h_0 = 6.63428 \times 10^{-27}$ erg sec and in consequence:
 $e_0/m_0 = 1.75850 \times 10^7$ emu/gram, $h_0/e_0 = 1.38028 \times 10^{-17}$ esu, $h_0/m_0 = 7.27621$,
 $e_0^2/(h_0 m_0) = 3.81921 \times 10^4$, $h_0/(e_0 m_0)^{1/2} = 1.00216 \times 10^{-5}$, $R_\infty = 2\pi^2 e_0^2 c^{-3} (h_0/e)^{-3} (e/m) = 109,737$ cm $^{-1}$,
 $c = 2.99776 \times 10^{10}$ cm/sec, $a_0 = 7.29870 \times 10^{-3}$, $e_0 = 5.67122 \times 10^{-9}$ erg cm $^{-3}$ deg $^{-1}$ sec $^{-1}$

Experimental values used in isometric chart

Quantity Determined	Value	Symbols on Chart	Method	Observer	Reference	Recomputed by
e	4.8016×10^{-10}	1 a 1	Ruled grating and crystal x-ray diffraction	E. Bäcklin	<i>Z. Physik</i> , 93, 450 (1935)	Birge (1939 letter)
	4.8022	1 a 2		J. Bearden	<i>Phys. Rev.</i> , 37, 1210 (1931); 47, 883; 48, 385 (1935)	Birge (1939 letter)
	4.8026	1 a 3		M. Söderman	<i>Nature</i> , 135, 67 (1935)	Birge (1939 letter)
h/e	1.37494×10^{-17}	2 a 1	Continuous x-ray spectrum limit	Duane, Palmer, and Yeh	<i>J. Opt. Soc. Amer.</i> , 5, 376 (1921)	DuMond
	1.37541	2 a 2		P. Kirkpatrick and P. A. Ross	<i>Phys. Rev.</i> , 45, 454 (1934)	"
	1.37588	2 a 3		H. Feder	<i>Ann. Physik</i> , 51, 497 (1929)	"
	1.37646	2 a 4	Continuous x-ray spectrum limit	J. W. M. DuMond and V. Bollman	<i>Phys. Rev.</i> , 51, 400 (1937)	"
	1.3772	2 a 5	c_2 optical pyrometry	H. T. Wensel	<i>J. Research Natl. Bur. Standards</i> , 22, 386, 387 (1939)	Wensel
	1.3775	2 a 6		G. Schaitberger	<i>Ann. Physik</i> , 24, 84 (1935)	DuMond
	1.3715	2 c 1	Photoelectric effect	P. Lukitsky and S. Prilezav	<i>Z. Physik</i> , 49, 238 (1928)	"
	1.372	2 c 2	Photoelectric effect	A. R. Olpin	<i>Phys. Rev.</i> , 36, 251 (1930)	"
	1.3736	2 b 3	Critical potentials	R. Whiddington and E. G. Woodroffe	<i>Phil. Mag.</i> , 20, 1109 (1935)	"

1.375	2 c 4	Photoelectric effect	R. A. Millikan	Electrons (+ and -), Protons, Photons, Neutrons, and Cosmic Rays (U. of Chicago), p. 242 (1934)	"
1.3752	2 b 5	Critical potentials	E. O. Lawrence	<i>Phys. Rev.</i> , 28 , 947 (1926)	"
1.3752	2 b 6	Critical potentials	L. C. Van Atta	<i>Phys. Rev.</i> , 38 , 876 (1931); 39 , 1012 (1932)	"
$h'(\text{cm})^{\frac{1}{2}}$	3	Electron λ and voltage	S. von Friesen	<i>Proc. Roy. Soc. (London)</i> , A160 , 424 (1937) also Inaugural Diss., Uppsala, 1936	"
7.207	4 a	Electron λ and velocity	J. Gnan	<i>Ann. Physik</i> , [5] 20 , 361 (1934)	Kirchner
7.255	4 b	Compton shift	P. Kirkpatrick and P. A. Ross	<i>Phys. Rev.</i> , 45 , 223 (1934)	"
1.7602×10^7	5 s 1	X-ray refraction in diamond	J. A. Bearden	<i>Phys. Rev.</i> , 54 , 698 (1938)	Birge (1939 letter)
1.7600	5 s 2	Spectroscopic H α H ϵ^4	W. Houston	<i>Phys. Rev.</i> , 30 , 608 (1927)	"
1.7598	5 d 3	Magnetic deflection	F. Dunnington	<i>Phys. Rev.</i> , 52 , 498 (1937)	"
1.7590	5 s 4	Spectroscopic H α H ϵ^2	W. Houston	<i>Phys. Rev.</i> , 51 , 446 (1937); 55 , 423 (1939)	"
1.7590	5 d 5	Direct velocity	F. Kirchner	<i>Ann. Physik</i> , 8 , 975 (1931); 12 , 503 (1932)	"
1.7582	5 d 6	Crossed fields	A. E. Shaw	<i>Phys. Rev.</i> , 54 , 193 (1938)	"
1.7580	5 s 7	Spectroscopic H α H ϵ^2	C. D. Shane and F. H. Spedding	<i>Phys. Rev.</i> , 47 , 33 (1935)	"
1.7578	5 s 8	Spectroscopic H α H ϵ^2	R. C. Williams	<i>Phys. Rev.</i> , 54 , 568 (1938)	"
1.7570	5 s 9	Zeeman effect	L. E. Kinsler and W. V. Houston	<i>Phys. Rev.</i> , 45 , 104; 46 , 533 (1934)	"
3.82155×10^{21}	6	Magnetic deflection of x-ray photoelectrons	H. R. Robinson	<i>Phil. Mag.</i> , 22 , 1129 (1936)	Robinson
3.8194	6		G. G. Kretschmar	<i>Phys. Rev.</i> , 43 , 417 (1933)	Kretschmar

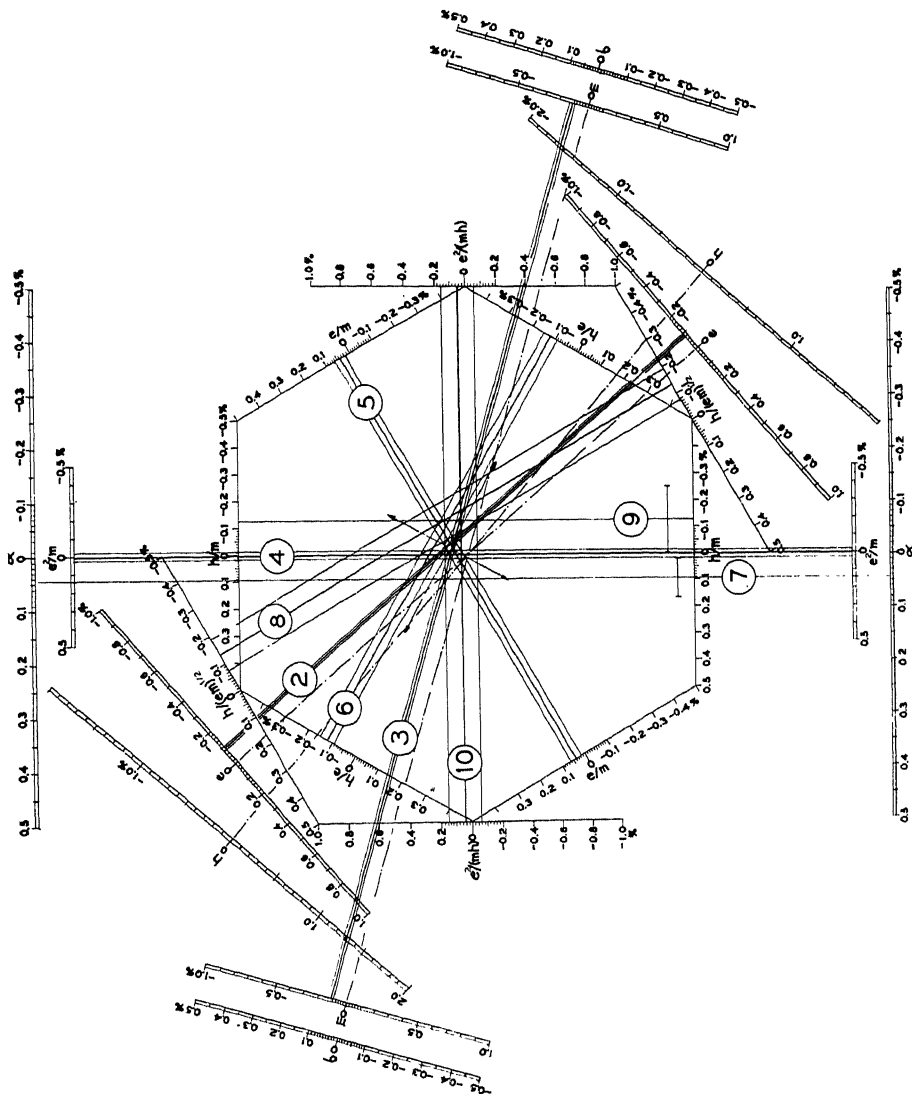


Figure 5-15.

guide in forming a judgment of the discrepancy situation which existed. The rather good consistency between the lines for e , $e^2/(mh)$, e/m , $\alpha^{-1} = 137$, and $h/(em)^{1/2}$ is striking, whereas the tendency of all the h/e determinations toward values lower than consistent with the region of intersection of the afore-mentioned lines throws suspicion on these. The sequel has shown that the trouble did indeed lie with the h/e determinations.

To illustrate the progress accomplished in the period under discussion, we reproduce in Figure 5-15 the consistency chart expressing the situation in 1947. Table 5-7 lists all the data employed in preparing the chart. This time the data were deemed sufficiently consistent to warrant making a least-squares adjustment. The small white ellipse in the region of most dense intersection of Figure 5-15 is the projection of the ellipsoid of error on this chart, and its center marks the point corresponding to the least-squares adjusted compromise values of e , m , and h . In this chart, separate determinations of the same function have not been plotted separately as in Figure 5-14 but have been averaged together and plotted as a single line. The error measures are shown in each case by lines on either side of the value line. The improvement in consistency over Figure 5-14 is striking; yet in the next few years, thanks to the advent of several new techniques, so much more improvement was made that it became necessary to change the scale of the diagram 100-fold in order to depict the inconsistencies adequately. By this time, however, several new types of information had become available, and the increased accuracy had made it necessary to include erstwhile "auxiliary constants" in the category of "unknowns" for least-squares adjustment so that much of the utility and significance of the isometric consistency chart disappeared. We shall not, therefore, reproduce this third chart here. Because of the need for a solution in terms of four or five unknowns we must be content with the

Figure 5-15. Isometric consistency chart exhibiting the data on the fundamental constants as of about 1947. The principle of construction is the same as already explained in the caption to Figure 5-14. The conventional origin values and the experimental data are given in Table 5-7. In this chart each value line is accompanied with side lines to indicate the estimated error measure. The small white ellipse of error for the least-squares adjusted point is also shown. The arrows indicate the orientation and relative magnitude of the principal axis of the error ellipse.

Table 5-7. Experimental Sources of Information in Least-Squares Adjustment for F , N , M , and h (1947) (Figure 5-15)

Description of Experiment	Numerical Value Determined	Location on Chart	Refs.
1. Spectroscopic determinations of Rydberg wave number	$R_{\infty} = 109737.3 \text{ cm}^{-1}$	(Implicit, not shown)	a, b
2. Direct determinations of Avogadro's number by ruled grating and crystal x-ray method	$N = (6023.38 \pm 0.43) \times 10^{20}$ (chem. scale)	(Not shown)	c, d
3. Direct determinations of the Faraday (silver and iodine voltameters)	$F = 9648.5 \pm 1.0 \text{ emu}$ (chem. scale) (Represented by $e = F/N$ using adjusted value of N)	②	e
4. Atomic weight of the electron by spectroscopy	$Nm = (5485.41 \pm 0.75) \times 10^{-7}$	③	f
5. $F(e/m)$ from Bearden's x-ray refractive index of diamond	$F(e/m) = (1698.24 \pm 0.35) \times 10^8 \text{ emu}$ (chem. scale)	④	g
6. Specific charge of the electron by deflection methods and Zeeman effect	$e/m = (1759.20 \pm 0.38) \times 10^4 \text{ emu}$	⑤	h
7. Measurements of quantum limit of continuous x-ray spectrum	$h/e = (1378.6 \pm 0.4) \times 10^{-20}$ erg sec esu ⁻¹	⑥	i
8. Determinations of fine-structure constant α	$\alpha^{-1} = 136.95 \pm 0.05$	⑦	j
9. Electron diffraction measurements of deBroglie wavelengths for electrons accelerated with a measured voltage	$h/(em)\ddagger = (1000.84 \pm 0.58) \times 10^{-11} \text{ esu}$	⑧	k
10. De Broglie wavelength by electron diffraction in which the speed of the electron is measured kinematically	$h/m = 7.267 \pm 0.009 \text{ cm}^2/\text{sec}$	⑨	l
11. X-ray photoelectrons ejected with known quantum energies, $h\nu$, and measured by magnetic deflection	$e^2/(mh) = (3819.7 \pm 4.5) \times 10^{21} \text{ esu}$	⑩	m

- ^a R. T. Birge, *Phys. Rev.*, **60**, 766 (1941).
- ^b R. T. Birge, *Repts. Progr. in Phys.*, **8**, 90 (1942).
- ^c J. A. Bearden, *J. Appl. Phys.*, **12**, 395 (1941).
- ^d R. T. Birge, *Am. J. Phys.*, **13**, 63 (1945).
- ^e G. W. Vinal, *Compt. rend., congr. intern. d'électricité, Paris*, **3**, 95 (1932).
- ^f R. T. Birge, *Phys. Rev.*, **60**, 766 (1941), Comparison of wavelengths of H_{α} and D_{α} lines and of R_H and R_{He} .
- ^g J. A. Bearden, *Phys. Rev.*, **54**, 698 (1938). Recomputed to give $F^2/(Nm)$.
- ^h R. T. Birge, ref. (b). In this reference the values from Birge's Table II numbered 6, 8, 9, 10, 11, and 12 are the pertinent ones for this datum.
- ⁱ W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, *Phys. Rev.*, **62**, 214 (1942).
- ^j R. F. Christy and J. M. Keller, *Phys. Rev.*, **58**, 658 (1940); R. T. Birge, *Phys. Rev.*, **58**, 658 (1940). The low value of α^{-1} obtained in these calculations from the L_{II} - L_{III} x-ray doublet separation has since been shown by Schawlow and Townes to have been chiefly the result of neglecting the effect of the finite size of the nuclear charge distribution.
- ^k The results are those of von Friesen, *Proc. Roy. Soc. (London)*, **A160**, 424 (1937); recomputed by F. C. Dunnington, *Revs. Mod. Phys.*, **11**, 68 (1939).
- ^l J. Gnan, *Ann. Physik*, [5] **20**, 361 (1934); recomputed by F. Kirchner, *Ergeb. exakt. Naturw.*, **18**, 66 (1939).
- ^m H. R. Robinson, *Phil. Mag.*, **22**, 1129 (1936); H. R. Robinson and C. J. B. Clews, *Proc. Roy. Soc. (London)*, **A176**, 28 (1940).
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less perspicuous device of listing the normalized residues of the least-squares analysis.

ADDENDUM

A downward revision of Λ was urged by M. Siegbahn in 1947 because of the results obtained by F. Tyrén and published in his thesis (Dissertation, Uppsala, 1940) (see Section 5.6, *c*). Tyrén used a concave grating vacuum spectrograph with which he compared the positions of certain x-ray lines (whose wavelengths in x-units on the crystal scale had already been established) with the positions of Lyman series spark lines from the one-electron ionized atoms, O^{VIII} , N^{VII} , C^{VI} , B^V , Be^{IV} . He computed the wavelengths of these spark lines in Angstrom units, using the very accurately known value of the Rydberg and theoretical formulae based on the Bohr-Sommerfeld-Dirac theory for the hydrogen-like atom. Using the spark lines as calibration lines it was then possible by interpolation to establish on the non-linear wavelength scale of the plates the wavelengths in Angstrom units of the x-ray lines. At the time Tyrén wrote his thesis the Bohr-Sommerfeld-Dirac theory was considered absolutely correct, but a few years later the advent of the Lamb shift and its explanation in terms of modern quantum electrodynamics called for a correction to the Bohr-Sommerfeld-Dirac theory which requires, in the case of Tyrén's Lyman α -line for O^{VIII} , a revision of the wavelength of 98.5 ppm upward. This is the worst case among Tyrén's reference wavelengths; the smallest correction is for the case of the δ -line of Be^{IV} , where a revision upward of 26.8 ppm is required. Unfortunately Tyrén's thesis does not specify just how the calibration lines were associated with the x-ray lines and since both sets of lines were recorded in many different orders one cannot conclude that x-ray lines and spark lines most closely adjacent in wavelength were necessarily those associated for the purpose of calibration.

This unfortunate flaw in Tyrén's thesis, otherwise probably the most accurate determination of Λ to date, was only noticed by the authors of this text shortly before it went to press. The hope of making a reliable correction to Tyrén's result in any short length of time seems tenuous. To the date of writing neither the original plates nor Tyrén's notes and calculations have been found although a search for these, which is still continuing, may eventually be suc-

cessful. At present we are able only to say with certainty that his result, $\Lambda = 1.00199$, must be raised by an amount between 26.8 ppm and 98.5 ppm, i.e., $1.002017 < \Lambda$ (Tyrén) < 1.002089 . A rough estimate based on the assumption that calibration and x-ray lines most nearly adjacent in wavelength were associated yields $\Lambda = 1.002026 \pm 0.000016$.

An upward revision in the directly measured value of Λ would have extremely far reaching effects on all the fundamental atomic constants in the present state of our knowledge. For each part per million change in the input value of Λ the change in ppm which eight important output quantities would sustain can easily be estimated from our variance-covariance matrix of Table 8-5 with the following results:

e	m	h	α	Λ	N	F	$hc^2/(e\Lambda)$
0.14	0.22	0.26	0.02	0.21	-0.21	-0.07	-0.08

See also, *Phys. Rev.*, **103**, 1583 (1956) for a more complete discussion of this situation.

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Postwar High-Precision Measurements

6.1 DEVELOPMENT OF NEW TECHNIQUES YIELDING INCREASED ACCURACY

Several closely related techniques which had been under development for some years prior to World War II were perfected to a high degree in the United States during the postwar period, partly through the stimulus of the increased financial support of pure research from government sources. These were the techniques of high-frequency and microwaves, microwave spectroscopy, atomic beams, nuclear magnetic resonance, and small-scale cyclotron resonance. In large part the high precision of most of the experiments based on these techniques is due to the high accuracy with which radio and microwave frequencies can be controlled and measured. The availability of these techniques has made possible since 1950 a series of remarkable precision experiments bearing on the atomic constants whose accuracy is so far superior to any of the earlier experiments as to constitute a veritable revolution in this field. Because of the relatively much greater error measures of the earlier data these would receive so little weight in a modern least-squares adjustment that, although the earlier results are not inconsistent with the later ones, they would make no significant contribution in fixing the least-squares adjusted values, and therefore might as well be ignored. We shall now briefly describe some of these high-precision experiments.

6.2 THE VELOCITY OF ELECTROMAGNETIC RADIATION

We have already described in Section 5.1 the methods used to measure the velocity of optical light. Of these the Kerr cell modulation method of Bergstrand using his "geodimeter" is the only one which qualifies for inclusion among high-precision postwar measurements. Since it has already been described, we shall confine dis-

cussion in the present section to high-precision postwar measurements of the velocity of electromagnetic radiation in the radio-frequency and microwave frequency ranges.

The high-precision radiofrequency measurements of c up to 1955 are those of Hansen and Bol (1) at Stanford University using microwave cavity resonance with a cavity of fixed length; Essen (2) at the National Physical Laboratory, Teddington, England, using cavity resonance in a cavity of variable length; Froome (3) also at NPL using a free-space microwave interferometer; Aslakson (4) using "Shoran," a radar method of measuring the distance of an airplane from a ground station; Plyler, Blaine, and Connor (5) using measurements of the molecular constants of carbon monoxide by infrared spectroscopy; Florman (6) using a large-scale radio interferometer at $172.8 \text{ Mc sec}^{-1}$ set up on a dry lake bed in Arizona.

All these methods indicate quite unequivocally that the earlier weighted average value arrived at by Birge, based chiefly on earlier measurements by Michelson, Pease, and Pearson (reference 2, Chapter 5) with the rotating mirror method in an evacuated tube, and by Anderson (reference 3, Chapter 5) using Kerr-cell modulation, namely, $299,776 \text{ km sec}^{-1}$, was low by about 16 or 17 km sec^{-1} . The newer values (those after 1948) are not all of equal reliability or accuracy nor are they all completely in agreement, and in particular the Hansen and Bol result disagrees with the others by about 3 km sec^{-1} —a disagreement which, though small judged by earlier standards, is uncomfortably large relative to the claimed probable errors.

The Hansen and Bol cavity resonance measurement consisted essentially of a determination of both the wavelength (in centimeters) and the frequency (in cycles per second) of an electromagnetic wave. The product of these two is then the velocity of light. The cavity was an accurately machined right circular cylinder with optically flat removable ends. In order to reduce losses and to insure a "high-Q" resonance, the cavity surfaces (which were machined from cast iron) were plated with silver. Three spacer rods (located in holes in the cylinder wall) were used to space the silver-plated surfaces of the cast iron optical flats which formed the ends of the microwave cavity. These spacer rods had convex ends which on each rod were zones of a common sphere. All three rods were carefully equalized so that, as long as contact was with the

ends, the distance between two parallel planes (one contacting each convex surface) was independent of the orientation of the rod axis. The rods themselves were intercompared in a temperature-controlled oil bath by an ingenious spring feeler multiplying gauge and lapped to uniform length. The distance between the cavity end faces was determined interferometrically by replacing the silver-plated cast iron flats with glass flats. Some uncertainty entered because of the possible difference in elastic or plastic yield at the points of contact between spacer rods and the two kinds of plates. A study of this effect was made by varying the loading. The diameter of the cylinder could not be measured accurately by direct means, but the ratio of length to diameter could be determined from the ratio of the resonant frequencies for two modes of electrical vibration (the TE_{012} and TE_{021} modes). One of these depends primarily on the length of the cylinder; the other depends primarily on the diameter. The ratio of length to diameter was so chosen as to put the frequencies of the two modes only a few megacycles apart out of 3000 Mc. A correction to the resonant frequencies was required because of the perturbations produced by the probe hole through which the electromagnetic energy is introduced into the cavity. The shift in resonant frequency produced by this hole was theoretically predicted to vary as the cube of the diameter, and this was experimentally verified. An insulating gap was purposely allowed between the plane ends and the cylindrical walls to suppress certain unwanted modes, and correction for this gap was small and easily made.

In this experiment the true electrical diameter of the cavity is greater than the mechanical diameter by an amount of the order of magnitude of the skin depth of the walls, a depth which depends of course on the frequency of the particular mode of oscillation which is being excited. The possible presence of a film of silver sulfides of unknown thickness with a conductivity and a dielectric constant differing from the values for bulk silver will affect the observed resonant frequency of the cavity. Correction for this should increase the Hansen and Bol value of the velocity slightly. It has been suggested in a private communication by E. S. Dayhoff that the mechanical effect of polishing the silver-plated surface may cold-work the metal and thus greatly decrease its conductivity in an extremely shallow layer. It is unfortunate that Hansen and Bol made

measurements at just enough frequencies to determine c in the absence of such anomalous skin effects. In any precision measurement it is always a better policy to overdetermine the measurements in an effort to uncover unsuspected systematic errors.

The four-horn Fraunhofer diffraction microwave interferometer of K. D. Froome is shown schematically in Figure 6-1. The source of microwaves is a Pound stabilized reflex Klystron oscillator with a frequency of $24,005 \text{ Mc sec}^{-1}$ corresponding to a wavelength of

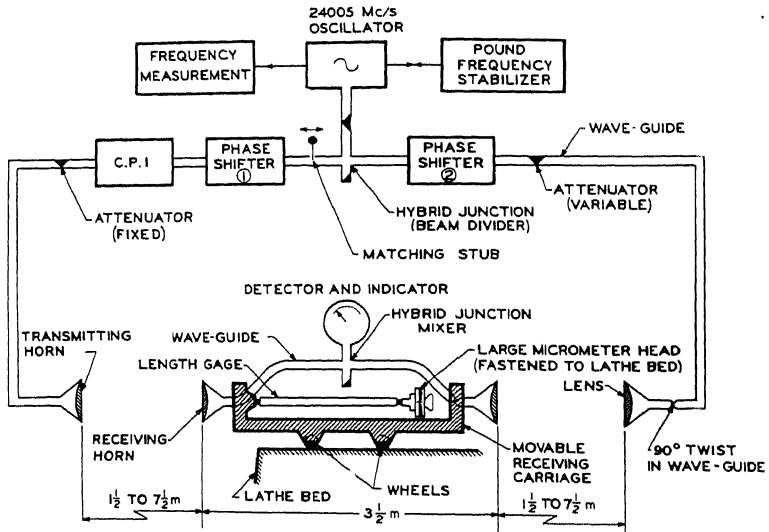


Figure 6-1. Four-horn microwave interferometer of K. D. Froome for precision measurement of the velocity of microwaves at $24005 \text{ Mc sec}^{-1}$.

about 1.25 cm. The accuracy of the frequency measurement is about 1 part in 10^8 . Energy from the oscillator passes to a hybrid junction ("magic T") which serves as a beam divider, from which it passes through two long wave guide arms to the pair of transmitting horns. The matching stub and phase shifter (1) to the left of the beam divider, together with a "constant phase auxiliary interferometer" (c.p.i.), constitute a device for altering the amplitude of the energy transmitted down this arm without producing a phase displacement. This ingenious device splits the input wave into two components of equal amplitude in two different paths. These components are subsequently recombined after a change of

phase brought about by an increase in the path length for one path, and an exactly corresponding decrease in the path length for the other. The two equal vectors representing the phases of the two components are thus rotated in opposite directions through the same angle so that the direction of their resultant is unchanged while its amplitude is reduced. The phase shifter (2) to the right of the beam divider, together with the variable attenuator, is required in order to adjust and balance the position of the first interference minimum.

The movable part of the interferometer situated between the transmitting horns consists of a pair of receiving horns mounted on a carriage constructed almost entirely of silica tubes (for thermal stability) and arranged to travel on ways through a path of about 1 meter. The two received signals are mixed to produce interference, and detected by means of a simple superheterodyne arrangement; the output is rectified and indicated on a milliammeter. An interference minimum is then detected as minimum current through the meter and the carriage can be set on a minimum to better than 1 micron.

To make a wavelength measurement the exact displacement of the carriage corresponding to 81 wavelengths (162 minima) is measured to $\frac{1}{4}$ micron by means of end-contact gauges.

Froome states that the 24005 Mc sec^{-1} equipment is merely a prototype for the investigation of sources of inherent error. The conditions were, therefore, deliberately chosen to cause errors, as, for example, the random effects arising from reflections in the rather small room. Nevertheless the apparatus was found to be capable of an accuracy of 1 part in 10^6 for the velocity measurements. Much better results are anticipated, therefore, with the final equipment, which is to operate at 70,000 Mc sec^{-1} ($\lambda = 4$ mm) over a path difference of 1000 minima in a much larger room. Ten observations with the present prototype have been reduced to yield a preliminary value for the free-space velocity of electromagnetic waves *in vacuo* of

$$c = 299793.0 \pm 0.3 \text{ km sec}^{-1} \quad (6-1)$$

Space limitations preclude description of many details and refinements to be found in the original papers (2, 3) and in particular the study of corrections for refractive index of the air and water vapor given in two papers by Essen and Froome (7).

We list in Table 6-1 the experimental values of the velocity of

Table 6-1. Recent Experimental Values of the Velocity of Electromagnetic Radiation in Vacuum

Author	Date of Publication	Reference	Method ^a	Velocity (km sec ⁻¹)
Aslakson	1949	4	Shoran	299792 ± 3.5
Hansen and Bol	1950	1	FLCR	299789.3 ± 1.2
Essen	1950	2	VLCR	299792.5 ± 1.0
Bergstrand ^b	1951	4 (Ch. 5)	Geodimeter	299793.1 ± 0.32
Froome	1952	3	FSMWI	299792.6 ± 0.7
Mackenzie ^b	1953	5 (Ch. 5)	Geodimeter	299792.4 ± 0.5
Froome	1954	3	FSMWI	299793.0 ± 0.3
Plyler, Blaine, and Connor	1955	5	Infrared spectr.	299792 ± 6
Florman	1955	6	FSMWI	299795.1 ± 1.9

^a FLCR = Fixed-length cavity resonance.

VLCR = Variable-length cavity resonance.

FSMWI = Free-space microwave interferometer.

^b The measurements of Bergstrand and Mackenzie are at optical frequencies; all the others are for radio waves.

light obtained since the advent of the new and highly improved microwave, radar, and Kerr-cell techniques. For convenience of comparison we have also included in this table the results of Bergstrand's and Mackenzie's optical determinations.

6.3 GYROMAGNETIC RATIO OF THE PROTON

The techniques developed at Stanford University (8) and at Harvard University (9) for the study of nuclear magnetic resonance have permitted extremely accurate determination of the gyromagnetic ratio of the proton, γ_p . It is well known that atomic nuclei exhibit the properties of angular momentum ("spin") and magnetic dipole moment, with the magnetic dipole axis along the axis of spin. When a proton is placed in a magnetic field, one may think, to use a classical picture, of a torque exerted on the proton dipoles which tends to align them with the field. In view of their spin, however, they respond to the externally applied torque by precessing around an axis parallel to the external field with a frequency of precession which is proportional to the applied external magnetic field. The experiments at Harvard and at Stanford have shown that

this "precession frequency" of the spinning protons can be measured very simply by placing a sample of water, sealed in a glass bulb, in a constant homogeneous magnetic field. A coil of wire with its axis perpendicular to the magnetic field supplied with radio-frequency current surrounds this sample. When the magnetic field of the applied radio-frequency resonates with the precession frequency of the protons, an exchange of energy occurs and the resulting perturbation of the precessing protons causes them to induce a detectable "signal" either in the applied radio-frequency coil itself (thereby changing its apparent impedance) or in a second detecting coil at right angles to the first. The Harvard method utilizes a single coil, the Stanford method two coils.

The ratio, γ_p , between the proton precession frequency, ω_p , and the magnetic field intensity, B , is an extremely important constant or conversion factor because the method of proton resonance has proved itself to be by far the most convenient and accurate absolute method of measuring magnetic field intensities when these are in the range above a few hundred gauss. Accordingly, the gyromagnetic ratio of the proton has been measured at the U. S. National Bureau of Standards by Thomas, Driscoll, and Hipple (10) with a precision of about 22 ppm. In this experiment the field distribution between the pole pieces of an electromagnet was first carefully explored by means of a small proton resonance detector. The field was then measured by weighing the force exerted on a rectangular current-carrying coil of exactly measured dimensions whose lower end was suspended between the pole pieces. The result was

$$\gamma_p = \omega_p/B = (2.67523 \pm 0.00006) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1} \quad (6-2)$$

6.4 RATIO OF THE CYCLOTRON FREQUENCY OF THE PROTON TO ITS MAGNETIC RESONANCE FREQUENCY

The term "cyclotron frequency of the proton" is related to the well-known underlying principle of the simple magnetic resonance particle accelerator of E. O. Lawrence, the constant-field, constant-frequency cyclotron. A particle with charge-to-mass ratio, e/m , in a magnetic field of constant intensity, B , executes circular orbits with an angular frequency of rotation which, at nonrelativistic speeds, is independent of the radius of the orbit. If the charge, e , is

expressed in esu, this frequency is given by

$$\omega = Be/(mc) \quad (6-3)$$

When the charged particle is a proton the angular resonance frequency so obtained is the "proton cyclotron frequency," ω_c , and if we measure B (as we can with high accuracy by the method of Section 6.3) in terms of ω_p we obtain an important measure of the charge-to-mass ratio e/m_p of the proton, a datum of great interest for our knowledge of the atomic constants. Combining equations (6-2) and (6-3) one sees that the ratio, ω_c/ω_p , the cyclotron frequency of the proton to the proton magnetic resonance frequency, is a universal constant

$$\omega_c/\omega_p = (e/m_p c) \gamma_p^{-1} \quad (6-4)$$

whose reciprocal is, in fact, the apparent magnetic moment of the proton, μ' (uncorrected for diamagnetism), expressed in nuclear magnetons, $\mu_n = eh/(4\pi m_p c)$, where e is expressed in absolute esu and m_p is expressed in grams. If one desires to know the absolute magnetic moment of the proton, μ , a small correction must be made for the fact that the magnetic field intensity at the proton is not exactly the same as the externally measured magnetic field, because of the diamagnetic effect of the proton-containing sample. The diamagnetic effect for hydrogen gas has been computed by N. F. Ramsey (11) and the small additional shifts, of the order of a part in 10^6 , when water or mineral oil are used have been measured by H. A. Thomas (12).

To determine ω_c , Hipple, Sommer, and Thomas (13) at the U. S. National Bureau of Standards built a miniature cyclotron which they called the "omegatron" because it determined the angular frequency ω_c . In the omegatron the maximum orbit radius was only 1 cm. The high vacuum (10^{-7} mm Hg) in this small apparatus, shown schematically in Figure 6-2, contained residual hydrogen, and ions (protons) were formed along an axis parallel to the magnetic field in the center of the device by impact from an axial beam of electrons. At right angles to the magnetic field a spatially uniform radio-frequency electric field (of variable frequency and of order 7 Mc per second) accelerated ions of a selected charge-to-mass ratio at their cyclotron resonance frequency in spiral orbits until they attained a radius of 1 cm, at which point they struck a collector.

The resulting current was measured with an electrometer tube amplifier. An ion having a particular charge-to-mass ratio could attain a radius sufficient to reach the collector only when the frequency

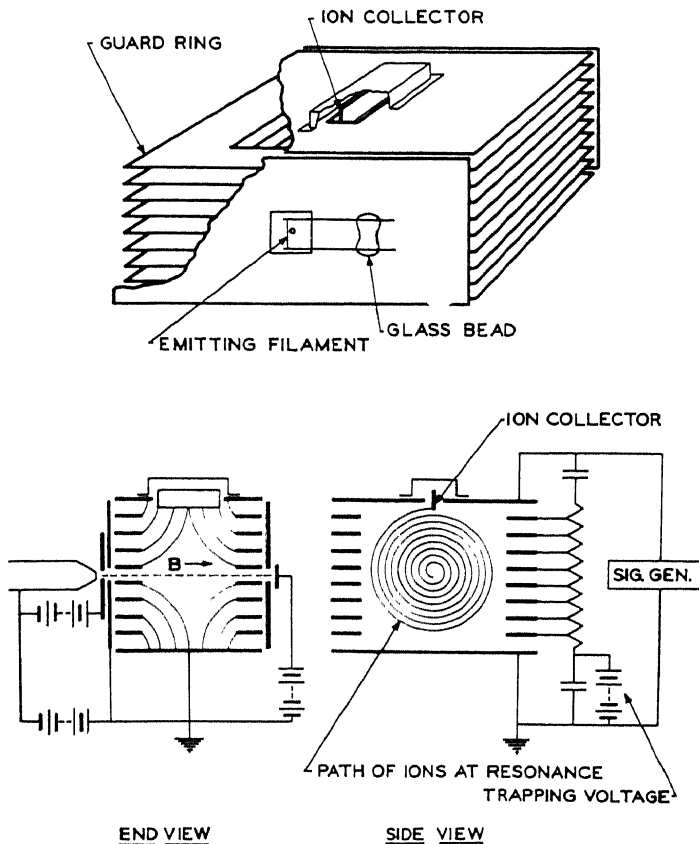


Figure 6-2. The "omegatron" of Sommer, Thomas, and Hipple. The guard rings which set up the D. C. trapping field are shown. This field is required to prevent the ions in their spiral orbits from drifting axially away from the central region.

was tuned for ions of this type. The frequency width of the resonance peak so established depends on the number of orbital revolutions which the proton makes while it is being accelerated from zero radius out to the radius of the collector. It was possible to make this

of the order of several thousand so that the resolution was extremely sharp. The magnet furnishing the field was the same one used in determining γ_p , and the cyclotron frequency of the proton was measured in relation to the nuclear resonance frequency of the proton. For this purpose the two resonance devices (cyclotron and nuclear) could be quickly interchanged while a third nuclear resonance probe, through a servo-system employing the probe signal, held the field constant.

A small source of systematic error was carefully studied. This came from the presence of a D. C. electric field (whose tubes of force are roughly indicated in Figure 6-2) which had to be provided to stabilize the proton orbits against axial drift. There must clearly be, in addition to the component of this D. C. field in the axial direction, a component in the radial direction and this latter must exert forces and (unlike the magnetic field) do work on the spiraling protons. The force from this D. C. field is much smaller than the magnetic force but it depends on the radius, ρ , in a way not very dissimilar from the latter. At the resonant frequency, $\omega_r = B(e/m_p c)$, the normal magnetic force on the proton is

$$F_{\text{mag}} = \frac{Be \omega_r}{c} \rho \quad (6-5)$$

while we may, to first approximation, express the radial component of the D. C. stabilizing field force as

$$F_{e1} = -k\rho \quad (6-6)$$

Thus the frequency, ω_r , would be slightly shifted by this additional force. This effect was carefully studied by varying the magnitude of the electric stabilizing field over a considerable range and plotting a curve showing the slight variation of the apparent proton cyclotron frequency as a function of the D. C. stabilizing field. This curve turned out to be linear as expected and could be extrapolated to zero electric field so as to correct for the latter. However, these experimenters found a still better way to make this correction. This depends on the fact that, whereas the resonance frequency, ω_r , is inversely proportional to the mass of the accelerated particle, the shift in frequency, $\Delta\omega$, due to the radial electric field, is independent of this mass. By determining in each case the resonant frequency for two different masses, e.g., H^+ and H_2^+ , and H^+ and D_2^+ , H^+

and H_2O^+ it was possible to evaluate the correction. After making this correction the average deviation from the mean was 1 part in 40,000—a result which gives considerable confidence in the reliability of the correction.

F. Bloch and C. D. Jeffries (14, 15) have also measured the cyclotron frequency of the proton by a method differing from that of the omegatron, in that the protons were injected at high speed (a kinetic energy of 20,000 ev) and were *decelerated* by cyclotron action. They therefore called their device an “inverse cyclotron.” It differed from the “omegatron” also in that “dees” were provided so that the region in which the protons encountered the high-frequency decelerating field constituted a very small fraction of a revolution. In consequence, it was possible to operate the device in “higher orders,” that is to say, at frequencies which were odd multiples of the frequency of revolution. Up to eleven half-cycles of the high frequency could occur during a half revolution of the particles, and much additional resolution was thus gained.

The respective results of the “inverse cyclotron” and the “omegatron,”

$$\mu' = 2.792365 \pm 0.000100 \text{ (36 ppm) (inverse cyclotron)} \quad (6-7)$$

$$\mu' = 2.792685 \pm 0.000030 \text{ (11 ppm) (omegatron)} \quad (6-8)$$

differ by only 115 ppm, but the difference is uncomfortably large relative to the standard deviations assigned to each experimental result. The difference is in fact three times its root-mean-square expectation value.

Work has since been published by Collington, Dellis, Sanders, and Turberfield (16), who repeated the inverse cyclotron experiment at the Clarendon Laboratory, Oxford. They used, instead of the conventional “dee” system, a central electrode with straight parallel sides to which the radio-frequency was applied while a grounded segmental electrode on either side completed the cylindrical box. With this arrangement the protons were decelerated to a radius at which they attained orbital stability without further gain or loss of energy. The value of μ' (uncorrected for diamagnetism) obtained by Collington, Dellis, Sanders, and Turberfield is

$$\mu' = 2.792730 \pm 0.000040 \text{ (14 ppm) (inverse cyclotron)} \quad (6-7a)$$

which is in good agreement with the omegatron measurement.

More recently still K. R. Trigger (15a) has made a careful theoretical analysis of the proton orbits in Bloch and Jeffries inverse cyclotron. This analysis yields a set of three coupled nonlinear equations which predict a frequency shift which is a function of the decelerating voltage on the dees. With this correction Trigger finds that the inverse cyclotron results of Bloch and Jeffries are in good agreement with both the omegatron value and that of Collington, Dellis, Sanders, and Turberfield. Trigger's corrected value is

$$\mu' = 2.79267 \pm 0.00010 \text{ (36 ppm)} \quad (6-7b)$$

6.5 THE FINE STRUCTURE SEPARATION IN DEUTERIUM

The energy separation, ΔE_D , of the $2^2P_{3/2}$ and $2^2P_{1/2}$ states of deuterium has been measured in frequency units with the astonishing accuracy of ± 9 ppm by E. S. Dayhoff, S. Triebwasser, and Willis E. Lamb, Jr., at Columbia University (17). This marked the culmination of the remarkable series of researches on the fine structure of the hydrogen and deuterium atoms by Willis Lamb, Jr., with his co-workers (18-21). Parts I and II of this series should be consulted (18, 19) for a basic description of the apparatus. It was through this series of researches that the existence of the "Lamb-Retherford shift," the energy difference between the $2^2S_{1/2}$ and $2^2P_{1/2}$ states, was established and its value accurately measured. From the point of view of fundamental physics the importance of the Lamb-Retherford shift greatly overshadows the precision measurements of the fine structure separation in deuterium. This latter is, however, of prime importance as a contribution to our knowledge of the atomic constants because of its relation to the Sommerfeld fine structure constant, α , and it is therefore the only result by these workers which we shall discuss here.

Lamb and his co-workers actually obtained the separation, $2^2P_{3/2} - 2^2P_{1/2}$, in deuterium by combining the results of two independent measurements. These were (1) the $2^2P_{3/2} - 2^2S_{1/2}$ and (2) the separation $\mathfrak{S}_D = 2^2S_{1/2} - 2^2P_{1/2}$, the famous "Lamb shift." Here we shall describe only the $2^2P_{3/2} - 2^2S_{1/2}$ measurement, referring the reader to the literature for the Lamb shift which was accomplished by similar methods.

Figure 6-3 is a cross section through the apparatus used by Lamb and his associates. The deuterium molecules pass through a tungsten

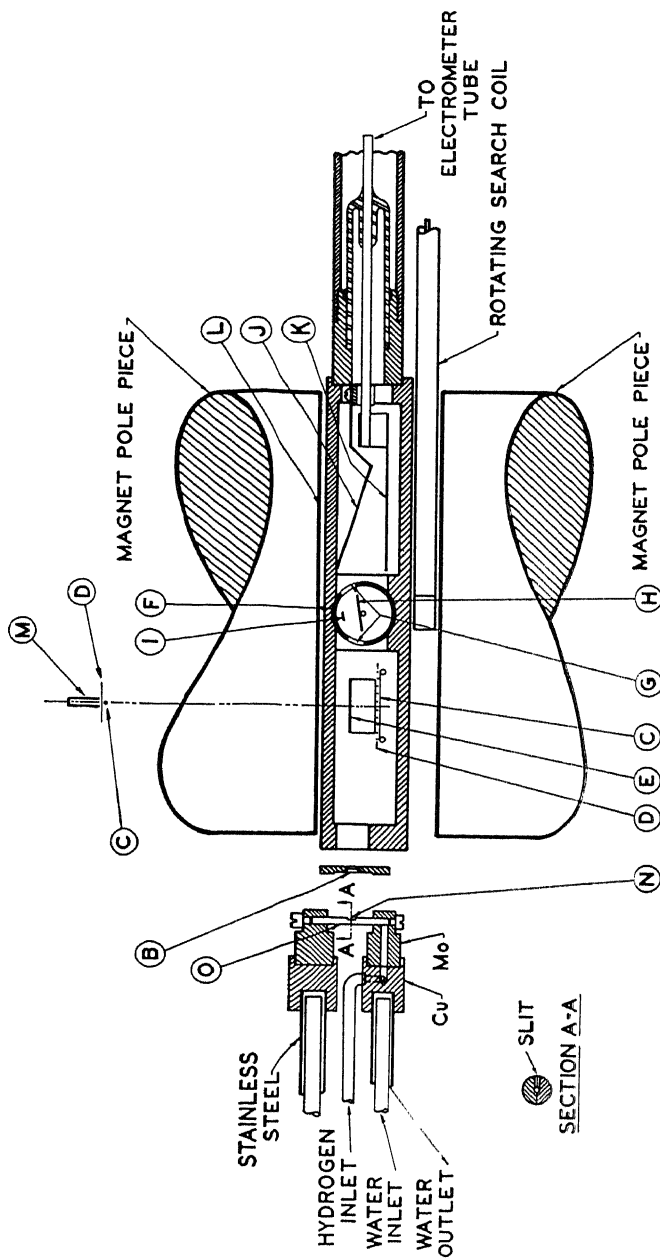


Figure 6-3. Atomic beam apparatus of W. Lamb, Jr., and associates. The hydrogen or deuterium dissociator is seen at the left. The tungsten tube, *O*, is heated to 2800° K by current supplied through water-cooled copper electrodes. In the experiment here described deuterium atoms issue through slit, *N*, of dimensions 0.010 x 0.050 inch and a collimated beam of them is selected by adjustable slit, *B*. Deuterium atoms passing through the U-shaped anode (shown at *E* and in cross section at *M*) are transversely bombarded with 10.8-volt electrons which are emitted from filament, *C*, and accelerated by grid, *D*. Deuterium atoms thus excited by bombardment to the metastable $2^2S_{1/2}$ state pass through an rf electric field between the slits, *G*, and then strike the target, *J*, where, if they are still in the metastable state, their energy of excitation ejects electrons from *J*. These electrons are collected by electrode, *K*. The transmission line, *F*, sets up an rf electric field between plate, *H*, and cylinder, *F*. At the resonance frequency the metastable atoms undergo transition to the nonmetastable excited states, $2^2P_{1/2}$ and $2^2P_{3/2}$, from which they decay to the ground state before they reach *J*, thus decreasing the electrometer tube current.

tube heated to about 2500° K by electrical conduction and are dissociated into monatomic deuterium. After passing through a slit they enter a box in an accurately controlled and measured magnetic field whose intensity may be varied from nearly zero to 4000 gauss. In this box the monatomic beam is bombarded with electrons of energy 10.8 volts so that excitation of the deuterium to its metastable $2^2S_{3/2}$ state occurs.* Their lifetime is sufficient to permit a beam of deuterium atoms to persist in this excited state over a distance of 7 or 8 cm or more. When the metastable atoms strike a metal target their energy of excitation is expended to eject electrons from it and these electrons are collected and measured with an "electrometer tube" (D. C. amplifier) as a means of detecting the metastable beam. Between the exciting bombarder and the detector, however, the beam of atoms is subjected to a radio-frequency electric field and, if this frequency is exactly right, the metastable atoms undergo transitions to the nonmetastable excited states $2^2P_{3/2}$ and $2^2P_{1/2}$, from which they decay with great rapidity† to the $1^2S_{1/2}$ ground state. In this state, no excitation energy being available, they are not detected. A decrease in the response at the detector is therefore the index of a resonance between the applied radio-frequency field and an atomic transition.

The purpose of the magnetic field, as originally planned, was to split the $2^2S_{3/2}$ and $2^2P_{3/2}$ states by the Zeeman effect in order to insure longer life to the $2^2S_{3/2}$ state. This was before the existence of the natural (Lamb-Retherford) splitting had been established or realized. The magnetic field was also deemed useful to keep charged particles away from the detector. The third, and actually most important, function of the magnetic field, however, turned out to be that of tuning the critical frequencies of the metastable atoms (through Zeeman effect) to the applied radio-frequency field, thus permitting the use of a rigorously constant, rather than a variable, applied radio-frequency which, for technical reasons, is preferable in a high-precision measurement of this sort.

* Even at this low bombarding energy the transverse recoil of the atoms is sufficient to introduce an angular spread in the beam of the order of three degrees. Lamb has therefore questioned the propriety of describing it as a "beam" in comparison with the beams of the better known technique developed by Rabi, Millman, Kusch, and Zacharias.

† The atoms are estimated to move only a few microns in this decay time.

The measurements of Dayhoff, Triebwasser, and Lamb yielded the value

$$\Delta E_D = 10971.59 \pm 0.10 \text{ Mc/sec} \quad (6-9)$$

for the fine structure separation in frequency units between the $2^2P_{3/2}$ and $2^2P_{1/2}$ states of deuterium. This, however, cannot be directly equated to the familiar expression $(\alpha^2/16)R_\infty c$, because this expression is not sufficiently accurate. Three corrections are required. In the first place R_∞ , the Rydberg constant for an infinitely heavy nucleus, must be replaced by the Rydberg constant for deuterium. This introduces the factor M_d/D , the ratio of the mass of the deuteron to the mass of the neutral deuterium atom. Secondly, higher order terms in the Dirac expression for the fine structure splitting must be included; this adds a correction term of relative amount $(5/8)\alpha^2$. These two corrections are both implicit in the Dirac theory, and their inclusion here is required by the increased accuracy of experimental techniques. The third correction represents a modification of the Dirac theory and is the result of the anomalous magnetic moment of the electron (22, 23). It is properly identified with the Lamb-Retherford shifts in the energy of the $2^2P_{1/2}$ and $2^2P_{3/2}$ levels (24, 25). The correct theoretical expression for the energy difference has been given by Lamb, accurate to terms of order $\alpha^6 mc^2$. This expression is

$$\Delta E_D = (1/16)\alpha^2 R_{DC} \left[1 + (5/8)\alpha^2 + \frac{\alpha}{\pi} \left(1 - 5.946 \frac{\alpha}{\pi} \right) \right] \quad (6-10)$$

6.6 RATIO OF ELECTRON MAGNETIC MOMENT TO PROTON MAGNETIC MOMENT

In Section 6.4 we described the measurement of the ratio of the proton cyclotron frequency to the proton nuclear magnetic resonance frequency. That measurement provided a value of the proton magnetic moment expressed in terms of the nuclear magneton. It is also possible to measure the magnetic moment in terms of the Bohr magneton by comparing the proton nuclear resonance frequency, ω_p , to the electron cyclotron frequency, ω_e . Such a measurement has been made by Gardner and Purcell (26, 27) at Harvard University. The magnetic field intensity, B , was such that ω_e was in the microwave region. The field intensity itself was measured

simultaneously in terms of the proton resonance frequency by the nuclear resonance absorption method.

The cyclotron frequency, ω_e , of a free electron in a magnetic field, B , is given by

$$\omega_e = eB/(mc) \quad (e \text{ expressed in esu}) \quad (6-11)$$

The proton precession frequency, ω_p , is given by

$$\omega_p = \gamma_p B = 2\mu_p B/\hbar \quad (6-12)$$

where γ_p is the gyromagnetic ratio of the proton, whose absolute determination was described in Section 6.3, and where μ_p is the proton magnetic moment. The ratio ω_p/ω_e is therefore

$$\omega_p/\omega_e = 2\mu_p mc/(e\hbar) = \mu_p/\mu_0 \quad (6-13)$$

This ratio is seen to be μ_p , the magnetic moment of the proton, expressed in Bohr magnetons, $\mu_0 = e\hbar/(2mc)$, a fundamental constant. If we combine the results of this experiment with a knowledge of γ_p , equations (6-11) and (6-12) show that we can calculate $e/(mc)$ the charge-to-mass ratio of the electron (expressed in emu) from the relation

$$e/(mc) = \omega_p/(\omega_e \gamma_p) \quad (6-14)$$

Furthermore if we combine ω_e/ω_p from the results of this experiment with ω_c/ω_p from the results of the Sommer, Thomas, and Hipple experiment described in Section 6.4, we can obtain ω_e/ω_c , the ratio of the respective cyclotron frequencies of electron and proton and this gives directly m_p/m , the ratio of the mass of the proton to the mass of the electron

$$\omega_e/\omega_c = (\omega_e/\omega_p)/(\omega_c/\omega_p) = m_p/m \quad (6-15)$$

The experiment was performed by providing slits, 2 mm \times 0.1 mm, on opposite sides of a rectangular shorted wave guide of 1 \times 0.5 inch internal cross section and supplied with microwaves of frequency 9400 Mc sec⁻¹ in the TE₁₀ mode so that a ribbon-shaped beam of slow electrons drifting across the 1-inch dimension of the guide from one slit to the other crossed in a region of voltage maximum of the microwaves. The electrons were supplied by an oxide-coated cathode in a copper cavity behind one of the slits and were collected by an electrode in a second copper cavity behind the other

slit. This equipment was placed in a magnetic field of 3300 gauss, between the poles of an electromagnet with the direction of the field parallel to the general direction of motion of the electrons from slit to slit across the wave guide. Closely adjacent to the wave guide between the magnet poles was placed the proton resonance head. This operated on a frequency of 14.24 Mc sec⁻¹. This frequency was multiplied 657 times for comparison with the electron cyclotron frequency in the wave guide. The positions of proton resonance head and wave guide between the magnet poles could be interchanged so that by averaging the results before and after such interchange the effect of any slight difference in magnetic field intensity at these two elements could be compensated.

The electrons drift in helical paths from one slit to the other across the wave guide executing the turns of their helices at the cyclotron frequency, $\omega_e = eB/(mc)$. If this frequency matches exactly the microwave frequency of the electric vector in the wave guide the electrons gain energy at each turn, and their helical trajectories will expand so that many of them will fail to pass through the second slit. It was thus anticipated that resonance would be recognized by a decrease in current to the collector. To make the resonance as sharply defined as possible it is desirable to have very slow electrons so that a maximum number of cyclotron cycles will be executed during the transit time from slit to slit in the region of the radio-frequency field.

The cathode was held more negative than the wave guide by a voltage, V_a , adjustable from 0 to 5 volts, and the collector was maintained approximately 20 volts positive relative to the guide so as to collect all the electrons passing through the second slit. When V_a was approximately 5 volts the expected dip in anode current (from approximately 0.4 microampere to 0.3 microampere) was observed at resonance. However, it was found that peaks instead of dips occurred at resonance, if V_a was less than about 3 volts. The peaks were considerably sharper than the dips, having a width of order 0.5 gauss contrasted with 5 gauss for the dips. The anode current under these circumstances was less than 0.0005 microampere when away from resonance. This unexpected behavior was attributed to space-charge limitation of the electron current through the guide save at resonance. The electrons having the slowest transverse velocity across the guide would be the ones most re-

sponsible for this space-charge limitation, and these are also the ones which at resonance are acted upon for the longest time by the microwaves. The resulting expansion of their orbits when resonance obtains would reduce the space-charge density and thus permit an increase in current across the guide on the part of other electrons (presumably those directed most nearly parallel to the magnetic field). Because of its superior sharpness, the peak attributed to the suppression of space-charge limitation was the one exclusively used for the measurements.

The authors reported a curious behavior of the position of this resonance peak. It shifted position with increase of V_a beyond 1 volt in a direction and to a degree depending on whether the small magnetic field from the cathode heating current was in a direction to oppose or to assist the main magnetic field. With the two fields opposing, a shift in the position of the resonance peak of 1 part in 10,000 was observed when V_a was increased from 1 to 1.2 volts. With the two fields aiding, a shift of about 1 part in 50,000 was observed in the opposite sense for the same range of values of V_a , while above $V_a = 1.2$ volts the peak shifted back to its original position.

The authors attributed this behavior to a combination of two effects. Quoting directly from Gardner's paper (27), these causes were: "the change from a Maxwellian velocity distribution to one for which a finite minimum velocity exists with a resultant shift of the region of the beam at which the most important contribution to the resonance takes place toward the cathode and hence further into the magnetic field of the heater current; and the accompanying increase in space charge density of this region with a resultant space charge shift in the resonance." Such uncertainties it seems might have been eliminated by heating the cathode intermittently and "gating" the measurement of anode current for the intervals when cathode heating current was zero.

The effect of the repulsive force on the spiraling electrons owing to the space charge inside their orbits should impose a small shift in the frequency at which cyclotron resonance occurs. There was no experimental way of knowing the actual space-charge density but under the assumption that equilibrium existed at the space-charge potential minimum an estimate based on the Boltzmann equation indicated that the shift in resonance from this effect would be of the order of 1 in 10^6 .

Magnetic contamination of the materials used in the magnetic field was avoided with great care. After the measurements were completed a hole was made in the wave guide to permit introducing the proton resonance sample into the region in which the electron cyclotron resonance had occurred. No effect was noticed even though a shift of 1 part in 200,000 could have been observed.

Great importance was attached to symmetry of the resonance peaks for both electron cyclotron and proton resonances on the oscilloscope in locating the true resonance position. The uncertainty in ω_e/ω_p claimed by the authors as the average of nine measurements is about 1.2 parts in 10^5 or about one-twelfth the width of the cyclotron resonance peak they used.

The final value assigned was

$$\mu_0/\mu_p' = \omega_e/\omega_p = 657.475 \pm 0.008 \quad (6-16)$$

without the diamagnetic correction to the field of the proton for the electrons in the hydrogen molecule. If we calculate ω_e/ω_c by equation (6-15) using (6-16) and the results of Sommer, Thomas, and Hipple (Section 6.4), we obtain for the ratio of the rest masses of proton and electron

$$\omega_e/\omega_c = m_p/m = 1836.12 \pm 0.03 \quad (6-17)$$

A quantity which is closely related to the one measured by Gardner and Purcell is the ratio, μ_e/μ_p' , of the electron magnetic moment to the proton magnetic moment (recall that we are using μ_p' for the apparent moment before correction for the diamagnetic effect; μ_p is the corrected moment). This ratio was measured by Koenig, Prodell, and Kusch (28) at Columbia University with such high accuracy (an error of ± 0.6 ppm) that it can be treated as a fixed auxiliary constant among the input data of a least-squares analysis. The well-known molecular beam method (29) for measuring nuclear magnetic moments was used in this measurement. An atomic beam passes successively through three magnetic fields; the first and last (the "A" and "B" fields) are inhomogeneous with gradients in opposite directions, while the intermediate field is uniform. Because of the interaction of the atomic dipole moment and the inhomogeneous magnetic field, an atom will suffer a deflection in passing through the "A" field. The "B" field then impresses on the atom a deflection in the opposite direction. Whatever the magnetic moment of the atom may be (as long as it is the same in both fields),

the two deflections will compensate each other and the atom will return to the instrument axis after passing through the two fields. If, however, during the time of transit through the intermediate "C" field, a transition is induced in the atom so that its magnetic dipole moment is altered, such atoms will not receive the correct compensating deflection in the "B" field and will fail to pass through the exit slit of the instrument. A magnetic field of frequency 3655 Mc sec⁻¹ perpendicular to the direction of the static field was used to induce the transitions between hyperfine structure levels in hydrogen in ²S_{1/2} state. The transition frequency of the line (1, 0 ↔ 1, -1) was measured, and from this and measurements of the proton nuclear magnetic resonance frequency in the same magnetic field (see Section 6.3), g_p/g_j could be calculated; g_p is the proton g -value while g_j , the g -value for the hydrogen atom in the ²S_{1/2} state, is closely related to the electron spin g -value, g_s . The experimental result obtained by Koenig, Prodell, and Kusch was (before the correction for diamagnetism in the proton resonance oil sample),

$$\begin{aligned} g_s/g_p &= [M_p/(Nm\mu')] (1 + \alpha/2\pi - 2.973 \alpha^2/\pi^2) \\ &= 658.2288 \pm 0.0004 \end{aligned} \quad (6-18)$$

in which M_p is the atomic weight of the proton, N is Avogadro's number, m the mass of the electron, μ' the magnetic moment of the proton (uncorrected for diamagnetism) expressed in nuclear magnetons, and the trinomial in the parenthesis is μ_e/μ_0 , the correction factor for the anomalous magnetic moment of the electron (22, 23). This can be computed from the value $\alpha^{-1} = 137.037$, with ample accuracy* to place μ_e/μ_0 in the category of auxiliary fixed constants. The result is

$$\mu_e/\mu_0 = (1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 1.00114536 \quad (6-19)$$

which gives us

$$\mu_0/\mu_p' = M_p/(Nm\mu') = 657.4758 \pm 0.0004 \quad (6-20)$$

Beringer and Heald (30) have measured the ratio of proton moment to electron moment using a microwave absorption technique.

* This value of α is practically beyond question. Our least-squares analysis yields $\alpha^{-1} = 127.0373 \pm 0.0006$. A change of 0.01 in α^{-1} produces a change of less than 10^{-7} in μ_e/μ_0 .

Since this method is basically distinct from the molecular beam method used by Koenig, Prodell, and Kusch, a comparison of the two results is useful. Hydrogen atoms are contained in a resonant cavity placed in a uniform magnetic field. This field produces a Zeeman splitting of the atomic energy levels, and the strength of this field is varied until the Zeeman splitting corresponds to the resonant frequency of the cavity. The absorption of energy by the atoms at this resonance reduces the energy transmitted through the cavity from a klystron oscillator to a detector. The magnetic field in the experiment is measured by a proton resonance probe. Thus the magnetic moment of the proton and the electron are directly compared. The result uncorrected for diamagnetism in a spherical sample of mineral oil is

$$\mu_e/\mu_p' = 658.2298 \pm 0.0003 \quad (6-21)$$

where the quoted error is a statistical standard deviation of the mean of 34 observations after 10 discordant data were rejected. This result is 1.5 ppm larger than Koenig, Prodell, and Kusch's measurement (6-18) and is twice as large as the standard error of that difference computed from the quoted errors.

In obtaining the result of equations (6-20) to compare with the measurement of Gardner and Purcell we made use of the theoretical value of the anomalous moment of the electron (equation (6-19)). We can also reverse the procedure and calculate the anomalous electron moment by combining Gardner and Purcell's results with the measurements of Koenig, Prodell, and Kusch or Beringer and Heald. In either case we obtain the result

$$\mu_e/\mu_0 = 1.001147 \pm 0.000008 \quad (6-22)$$

where the error is entirely due to the Gardner and Purcell value and masks the difference between the two values of μ_e/μ_p' . The agreement between this value of μ_e/μ_0 and the theoretical value 1.00114536 is excellent and serves as a verification of the validity of quantum electrodynamics. If the Gardner and Purcell experiment could be improved to an accuracy equal to that of KPK or BII a much sharper check on theory would be possible. Further work on this important experiment, in an effort to improve its accuracy and eliminate uncertainties of interpretation, is under way at Harvard University.

6.7 THE HYPERFINE STRUCTURE SHIFT IN HYDROGEN

One of the most accurately measured quantities in the field of atomic and nuclear physics is the hyperfine structure shift in the ground state of hydrogen. This quantity, $\Delta\nu_{\text{H}}$, would furnish an important observational equation connecting the quantities α , c , R_{∞} , and μ_e/μ_p , the ratio of the magnetic moments of proton and electron, were it not for the uncertainty regarding the correction terms which represent the effects of the finite extension of the proton's magnetic dipole. The theoretical relationship of this measurement to the atomic constants was originally given by Fermi (31). It is

$$\Delta\nu_{\text{H}} = (16\alpha^2/3)cR_{\infty}(\mu_p/\mu_e)(\mu_e/\mu_0)^2(1 + m/m_p)^{-3}(1 + \frac{3}{2}\alpha^2)\mathcal{E}\mathcal{I}\mathcal{R} \quad (6-23)$$

In this formula μ_p is the magnetic moment of the proton and μ_e that of the electron; μ_e/μ_0 is the magnetic moment of the electron (32) expressed in terms of the Bohr magneton, $\mu_0 = eh/(4\pi mc)$. The factor $(1 + m/m_p)^{-3}$ is the reduced mass correction term (33) and $(1 + 3\alpha^2)$ is Breit's additional relativistic correction (34). The importance of the factors \mathcal{E} and \mathcal{I} was first pointed out by Bethe and Longmire (35). They are introduced to correct for the finite extension of the electron and proton magnetic dipoles, respectively. The final factor \mathcal{R} is a proton recoil term and is simply an additional higher order relativistic reduced mass correction.

The shift $\Delta\nu_{\text{H}}$ was measured by the atomic beam magnetic resonance method with a precision of 6 ppm by Nafe and Nelson (36, 37) and with a standard deviation of only 0.2 ppm by the same method by Prodell and Kusch (38). More recently Wittke and Dicke (39) measured the zero field hyperfine splitting in hydrogen by means of a microwave absorption technique with a standard error which may be less than 0.1 ppm. These measurements are absolute in the sense that a microwave frequency which can be directly compared to a fundamental time standard is resonated with the frequency difference between atomic energy levels. The value of $\Delta\nu_{\text{H}}$ measured by Prodell and Kusch is

$$\Delta\nu_{\text{H}} = 1420,405.08 \pm 0.13 \text{ kc/sec} \quad (6-24)$$

if the standard error quoted is based entirely on the statistical distribution of the individual observations. It is therefore a measure

of precision and reproducibility rather than accuracy. To include a provision for residual systematic experimental error, the quoted error has been raised by Prodell and Kusch to ± 0.3 kc/sec.

Kusch has recently discovered a systematic error in this value which comes from the differences in phase of the radio-frequency current in the loop which furnishes the magnetic field to excite the transition. This difference in phase produces an apparent shift in the frequency of the magnetic field in the frame of the moving atom. The experiment has been repeated under improved conditions from this point of view and the revised value is

$$\Delta\nu_{\text{H}} = 1420,405.73 \pm 0.05 \text{ kc/sec} \quad (6-24a)$$

Wittke and Dicke, in order to reduce the width of the resonance in their microwave absorption technique, added molecular hydrogen, at a few tenths of a millimeter pressure, to the atomic hydrogen whose partial pressure was 5×10^{-4} mm. The reduction in width was obtained through the mechanism of collision reduction of the Doppler effect discovered by Dicke (39a).

The resonant frequency appeared to be shifted slightly with a change in the total pressure of the gas. If the observed data are extrapolated to zero pressure the resultant value is

$$\Delta\nu_{\text{H}} = 1420,405.80 \pm 0.08 \text{ kc/sec} \quad (6-25)$$

However, with observations made at only three pressures there are hardly enough data for an accurate determination of the pressure dependence, and the observed correlation in fact fails to pass the standard test for statistical significance. If the data are then analyzed on the assumption that no pressure dependence exists the result is

$$\Delta\nu_{\text{H}} = 1420,405.72 \pm 0.05 \text{ kc/sec} \quad (6-25a)$$

The standard errors quoted here include no allowance for systematic error but are based entirely on statistical precision. One such systematic error is the astronomical time correction to the nominal WWV frequencies; however, this is not expected to produce a change of more than ± 0.02 kc/sec.

Prodell and Kusch's revised value (6-24a) is in excellent agreement with the microwave absorption results, whether the pressure dependence is assumed or not.

In order to use these results to their fullest advantage in an eval-

uation of the atomic constants it is necessary to have a theoretical formula which has at least the same degree of accuracy as the experimental measurements. In this case it means that the theoretical expressions must be accurate to the order of 1 part in 10^7 . The anomalous magnetic moment of the electron is known only to second order in the fine structure constant; the unknown third-order terms could easily contribute a few tenths of a part per million. The factor $\mathfrak{C} = 1 - (\frac{5}{2} - \ln 2)\alpha^2 + \dots$ has been calculated by Karplus and Klein (40) and by Kroll and Pollock (41) and represents a correction of -95.6 ppm to the Fermi formula. The factor \mathfrak{R} is given by (42, 43)

$$\mathfrak{R} = 1 - \frac{\alpha m}{\pi m_p \mu} \cdot \left[3 \ln \frac{m_p}{m} - \left(\frac{\mu - 1}{2} \right)^2 \left\{ 3 \ln \frac{m_p}{m} + \frac{1}{2} - 9 \ln \frac{2k_0}{m_p} \right\} \right] \quad (6-26)$$

where μ is the proton magnetic moment in nuclear magnetons and k_0 is a cut-off constant inserted into the theory to prevent a logarithmic singularity. The cut-off constant k_0 has the dimensions of a mass and is presumably somewhere between the meson mass and the proton mass. There is an almost complete cancellation of terms which is probably fortuitous and the entire correction lies between -4.0 ppm if we use the proton mass and $+2.2$ ppm if we use the pi-meson mass. The magnitude of \mathfrak{F} is much less certain. Estimates of the size of the proton from other information would lead one to expect that $\mathfrak{F} - 1$ should be of the order of -2×10^{-5} , but it could conceivably turn out to be much smaller. By comparing the measurements of Prodell and Kusch or Wittke and Dicke with the value calculated from the least-squares adjusted constants an estimate of $\mathfrak{F} - 1$ may be found (44, 45). This comparison indicates that the correction for the finite spatial extension of the proton dipole is actually of the order of only a few parts per million, although the accuracy of these estimates is poor.

Thus, although the latest results of Prodell and Kusch and those of Wittke and Dicke may be said to be in excellent agreement on the basis of statistical accuracy, both these measurements have far outstripped the ability of the theory of the magnetic moment of the proton to utilize them.

6.8 PRECISION DETERMINATIONS OF THE QUANTUM LIMIT OF THE CONTINUOUS X-RAY SPECTRUM

In Sections 5.11 and 5.12 we have described the experiments which, in conjunction with a knowledge of other constants, can be made to yield information on Planck's constant, h . Of these, as we have seen, the one which has given the most accurate results to date is the measurement of the short wavelength limit (SWL) of the continuous x-ray spectrum which yields the voltage-wavelength conversion constant $V_A\lambda_s = hc^2/(e\Lambda)$. The elementary theory of this experiment has been explained in Section 5.11 and in order to discuss the results of the most recent high-precision measurements of this type, we shall confine our attention in this section to certain more advanced considerations required when systematic errors in the measured quantity $V_A\lambda_s$ of the order of a part in 10^4 become important. It was explained in Section 5.11 that the finite resolving power of the x-ray monochromator used in this experiment introduces a fillet at the SWL which obscures its true position and necessitates adopting some procedure to circumvent this difficulty (see Figure 5-11). The method of taking the "point of maximum bending" of the isochromat curve in the region of the fillet as a criterion of the SWL position, the method which has been generally used in precision measurements of this kind since 1937, was asserted to be valid provided the true spectral profile at the limit could be assumed to consist of a sharp second-order discontinuity—an abrupt change from zero intensity to a linearly rising profile of intensity. (The reason for this assumption will be explained presently.) When we become interested in a more finely detailed description (when accuracy of the order of 1 volt is important in the location of the true quantum limit), it appears, from the most recent data, that we cannot ignore the possibility that a small first-order, as well as a second-order, discontinuity may be present at the quantum limit. The evidence for this is indirect and appears as a systematic trend in the measured values of $V_A\lambda_s$ depending on the voltage at which the measurements are performed. A few words of explanation to clarify ideas regarding the continuous x-ray spectrum from thick targets will first be in order.

The quantum theory of the bremsstrahlung (46) predicts, and experiment has confirmed, that the profile of the "thin-target" continuous x-ray spectrum, the intensity per unit frequency in-

terval, is practically a flat plateau if the target is so thin that the relative energy loss sustained on the average by electrons traversing it is negligible. Such a thin-target profile is shown in Figure 6-4. At the low-frequency end there is an unimportant rise which would be logarithmically divergent with vanishing frequency if it were not for the screening effect on the nuclear Coulomb field produced by the presence of the atomic electrons. This need not concern us. At the voltages used in these experiments the nearly flat plateau of the thin-target spectrum extends to a first-order discontinuity at ν_m , the quantum limit, where it falls off abruptly to zero.

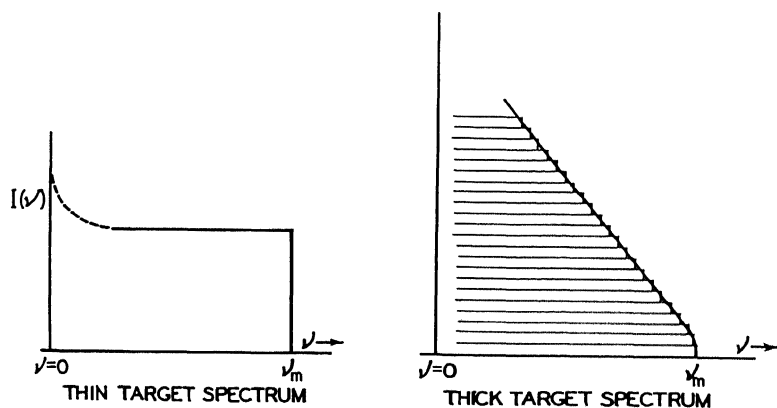


Figure 6-4. To illustrate certain elementary notions concerning thin- and thick-target continuous x-ray spectra.

Thick-target spectra, on the other hand, as Wagner and Kulenkampff were the first to show (47a, b) yield a continuous spectrum (see Figure 6-4) whose profile, save for minute details close to the quantum limit, is essentially a straight line of negative slope ending at the limit in what has till recently been inferred to be probably a second-order discontinuity. The precise behavior very close to the quantum limit, as we have already stated, is obscured by limited instrumental resolving power so that the possibility of a small abrupt precipice at the limit cannot be ruled out.

The explanation usually given for the thick target profile is that it may be conceived as consisting of a superposition of infinitely many plateau-like thin-target profiles in the way indicated in Figure 6-4. As the impinging electrons penetrate into the thick target they

are decelerated by a multitude of small energy losses communicated to the atomic electrons of the target material. This process is to be distinguished from the interactions with the strong fields in the neighborhood of nuclei which result in bremsstrahlung. At the voltages used in h/e experiments the deceleration by losses to target electrons accounts for more than 99 per cent of the energy input (released as heat in the target) and less than 1 per cent results in bremsstrahlung. The paths of the bombarding electrons in the target are not rectilinear but are to be described more nearly by a diffusion process. If, however, we may assume that the mean electron energy decreases monotonically with increasing length of path traversed, each successive element of path length will produce a thin-target spectrum of x-rays whose quantum limit is at lower energy than that of the preceding element. This had been supposed to account then for the sloping profile of the thick-target spectrum near the quantum limit, and no doubt it does so if we do not place ourselves on too high a level of energy resolution. It errs in the assumption that the energy losses sustained by the individual bombarding electrons can be regarded as a unique continuous function of the path length. Actually not only are the energy losses discrete but also they must be defined in terms of probability distributions rather than unique values. The resultant fluctuations in the energy loss as a function of path length may be expected to be most noticeable in the description of the first collision (i.e., at the quantum limit), since there the homogeneity of the bombarding electrons has not yet been disturbed by the straggling in energy.

Details of spectral profile within a few volts of the quantum limit must undoubtedly be closely connected with the banded character of the filled and empty energy levels of the structure electrons in the material of the x-ray target. It is probable that the banded structure actually enters in two ways: (1) by directly influencing the probability of radiative transition of the bombarding electron to different final energy states in the target structure and (2) by imposing a banded structure on the energy losses to structure electrons sustained by the bombarding electrons *before* they undergo the radiative interaction resulting in bremsstrahlung. This has been discussed theoretically by Nijboer (48) in an effort to account for certain irregularities of the spectral profile which were first observed by Ohlin (reference 64, Chapter 5). The Ohlin irregularities or

“valleys” in the profile of the continuous spectrum near its limit differ in shape with different target materials, and they have been observed at distances from the SWL varying from a few volts to a

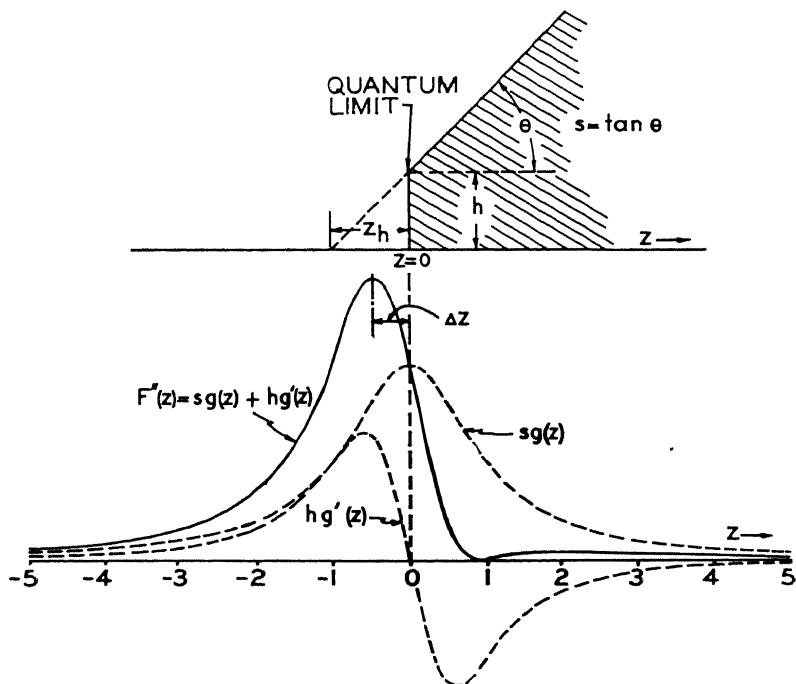


Figure 6-5. The upper diagram shows the postulated precipice in the profile of the continuous x-ray spectrum at its quantum limit. This feature has not been directly observed, presumably for lack of sufficient spectral resolution. It is postulated as an explanation of the systematic deviation of the position of the “point of maximum bending” for experiments performed at different voltages. The distance, z_h , from the quantum limit discontinuity to the intercept of the extrapolated tangent is herein referred to as the “overshoot.” The band-pass characteristic of the x-ray spectrometer or monochromator is here assumed to be a “witch” (or Cauchy distribution) and this latter, folded into the postulated profile of the upper diagram, yields an isochromat, $F(z)$, whose second derivative, $F''(z)$, is shown in the lower diagram. The two contributions, $sg(z)$ and $hg'(z)$, to this second derivative curve are also shown. The contribution, $sg(z)$, is generated as the result of the second-order discontinuity, of slope, $s = \tan \theta$. The contribution $hg'(z)$ is generated as the result of the first-order discontinuity of height, h . The shift, Δz , in the maximum of the second derivative curve by reason of the presence of the contribution, $hg'(z)$, is clearly evident.

few tens of volts. Their location relative to the limit has been observed to depend on the applied voltage (reference 58, Chapter 5). Unfortunately no solid-state theory covering the mechanism of generation of continuous x-rays in thick targets has been developed to predict in detail the shape either of the Ohlin irregularities or of the profile still closer to the quantum limit of the spectrum. In order to explain the afore-mentioned systematic downward trend in the apparent measured value of $V_A\lambda_s = hc^2/(eA)$ with decreasing voltage when V_A is established by the criterion of maximum bending of the isochromat, we shall postulate the existence of a precipice (or something closely approximating this) situated at the SWL in the manner shown in Figure 6-5. This postulated precipice has not been experimentally observed. The "overshoot," i.e., the distance from the precipice to the point on the axis of abscissas where the sloping part of the profile, if projected, would intercept that axis, must therefore be assumed to be sufficiently small in comparison to the instrumental resolving power as to render this entire feature unobservable. It is here proposed merely as a plausible *ad hoc* explanation, the simplest one we have been able to construct, of the systematic trends which we shall now describe.

Table 6-2 lists in column 4 the results of a series of measurements (references 58, 65, and 66, Chapter 5) of $V_A\lambda_s = hc^2/(eA)$, listed in the order of increasing voltage at which each measurement was made. In each case the point of maximum bending of the isochromat was taken as the quantum limit position. These results exhibit a fairly definite systematic variation from the constancy to be expected, the higher voltage experiments tending to exhibit the larger absolute "discrepancies" in volts. "Discrepancy" here is understood to mean the difference between each of the above measured values and a fixed reference value,

$$hc^2/(eA) = 12372.2 \text{ kv x-units} \quad (6-27)$$

which is the least-squares adjusted value of this constant published in 1953 (49). Column 6 of Table 6-2 shows the "discrepancy" expressed in volts, that is to say, the amount by which the observed point of maximum bending of the isochromat in each experiment must be displaced to agree with the predicted position assuming the constant value of equation (6-27). In Figure 6-6 we show these "discrepancies" in volts plotted as a function of the voltage at

Table 6-2. Recent Precision X-ray Quantum Limit Determinations

Experimenter	Nominal Voltage	a (volts)	$hc^2/(eA)$	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-fl.
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-fl.

The column labeled " a (volts)" gives the half-width at half maximum height of the spectrometer "window" curve.

The column labeled " $hc^2/(eA)$ " 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 labeled "discrepancy" give the relative and absolute deviations of each experimentally determined voltage threshold from the value required to give the D C 53 least-squares adjusted value for $hc^2/(eA) = 12372.2$ kv x-units.

^a J. A. Bearden, F. T. Johnson, and H. M. Watts, *Phys. Rev.*, **81**, 70 (1951).

^b J. A. Bearden and Guenter Schwarz, *Phys. Rev.*, **79**, 674 (1950).

^c G. L. Felt, J. N. Harris, and J. W. M. DuMond, *Phys. Rev.*, **92**, 1160 (1953).

which they were obtained, and in Figure 6-7 they are plotted as a function of the width in volts of the spectral pass band of the monochromator used. (Although the same pair of calcite crystals

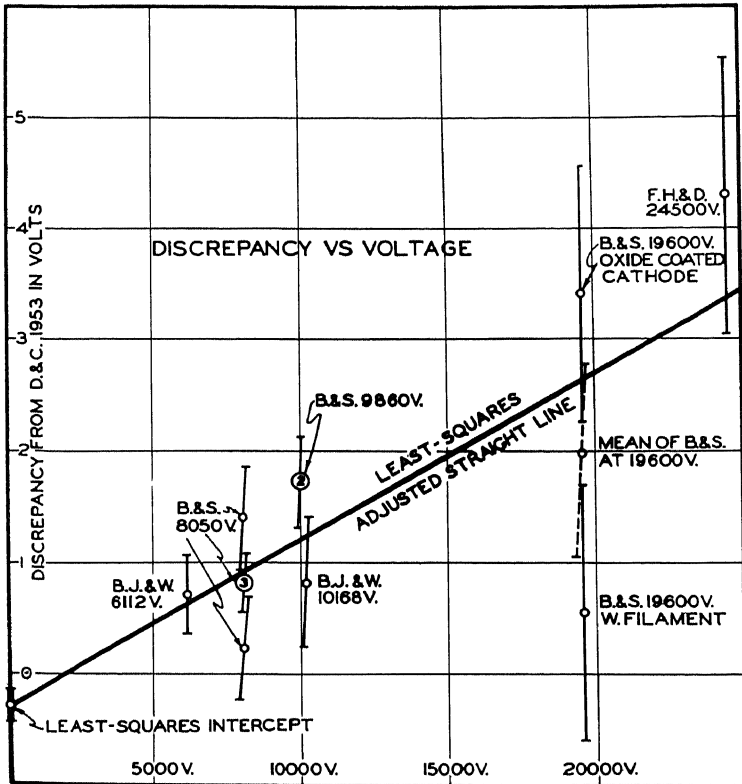


Figure 6-6. The "discrepancies" given in column 6 of Table 6-2 expressed in volts are here plotted as a function of the voltage at which each experiment was performed. By "discrepancy" is meant the amount by which the observed point of maximum bending of the isochromat in each experiment must be displaced to agree with the predicted position of the SWL assuming a constant value of $hc^2/(eA) = 12372.2$ kv x-units in accord with the D C 53 least-squares adjustment. When a point is shown with an encircled number this indicates the number of identical results which fell there, and the error range graphically indicated at such a point is the standard error of the weighted mean of the several observations. The "least-squares adjusted straight line" has been calculated after assigning weights to the ordinates inversely proportional to the squares of their standard deviations. The point marked "least-squares intercept" is not one of the experimental observations.

was used for the two-crystal monochromator in all the experiments by Bearden and his co-workers, it should be recalled that the width of the monochromator pass band expressed in volts diminishes with decrease in the voltage at which the experiment is performed.)

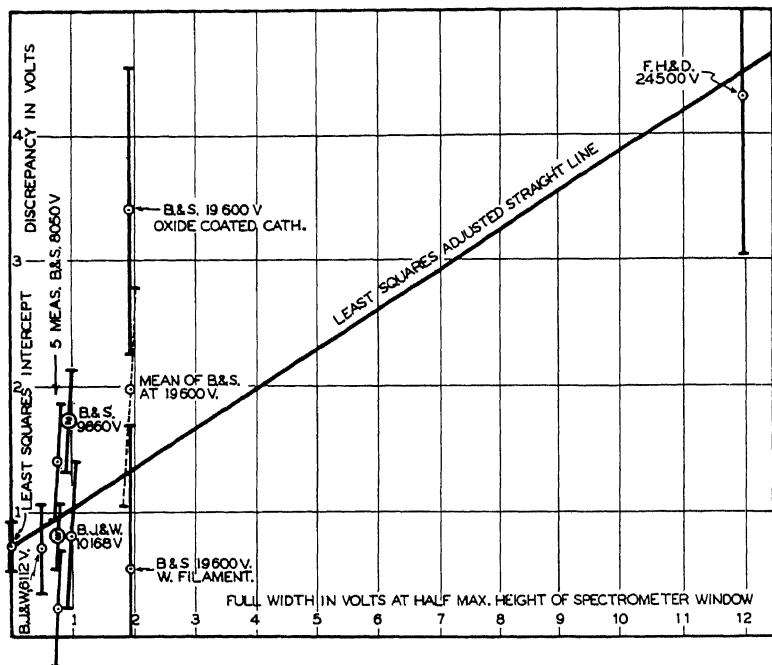


Figure 6-7. The "discrepancies" given in column 6 of Table 6-2 expressed in volts are here plotted as a function of the width in volts of the spectral pass band of the crystal monochromator used. With the same crystal monochromator the width of the pass band expressed in volts diminishes with decrease in the voltage at which the experiment is performed. The same explanatory remarks apply as in Figure 6-6.

Figure 6-8 shows one of the isochromats obtained in the FHD experiment (reference 66, Chapter 5) performed at the highest voltage listed in Table 6-2. The point marked *A* is the point of maximum bending of the isochromat. The point *B*, however, is the required position of the quantum limit for consistency with the bulk of the data on the atomic constants (adjusted value of 1953) given in equation (6-27). Figure 6-9 shows how the point of maximum

bending (A in Figure 6-8) was determined; by plotting the third derivative of the isochromat and locating its zero point. The third derivative was obtained by a numerical interpolation method using for each value of F''' an array of points at equidistant abscissa spacings on the smoothed curve of Figure 6-8. The point at which F''' was to be evaluated was always at the center of this array. The method yields the third derivative of a high-order polynomial

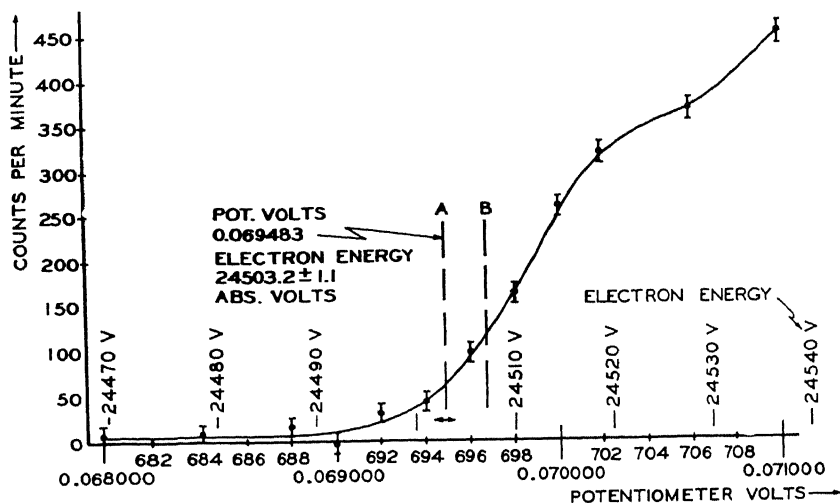


Figure 6-8. One of the isochromats obtained in the experiment (FHD) performed at the highest voltage listed in Table 6-2. The point, A , was adopted as the quantum limit on the criterion of maximum bending of the isochromat. The point B , however, is the quantum limit position for consistency with the bulk of the data on the atomic constants (D C 53). The method of assigning the uncertainty to the position, A , is explained in the caption to Figure 6-9.

fitted to the points, but is of course no more precise than the smoothing of the curve is reliable. The assigned uncertainty (indicated by the arrows in Figures 6-8 and 6-9) was therefore based on variations in the location of the point $F''' = 0$ when the curve was smoothed in different trials and by different people.

Let $F(z)$ be the observed intensity curve or isochromat. Here z stands for a variable, linear with the voltage, V_A , if the curve is an isochromat. Let $f(z)$ be the curve expressing the ideal shape of the continuous x-ray spectrum or isochromat for the case of indefi-

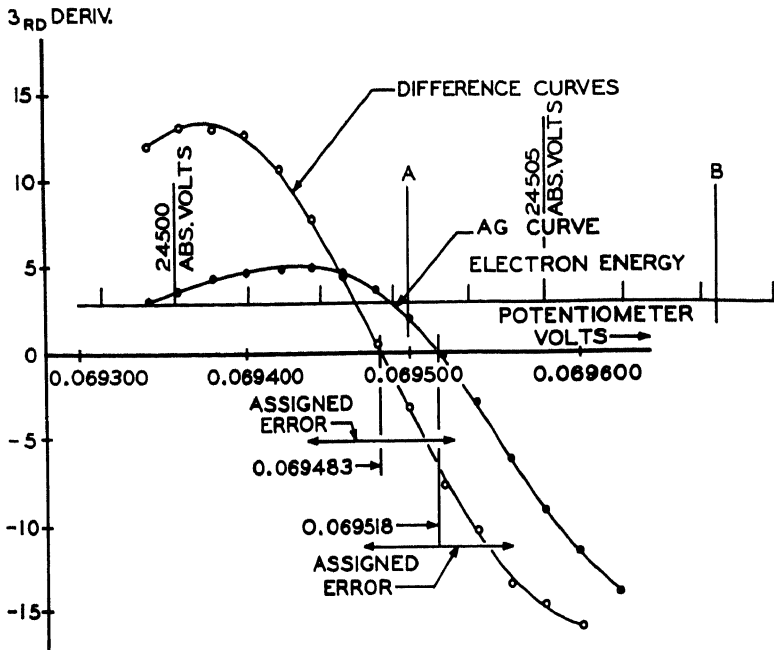


Figure 6-9. Showing how the point of maximum bending (*A* in Figure 6-8) was determined: by plotting the third derivative of the isochromat and locating its zero point. The major uncertainty comes from the way in which the isochromat is smoothed through the observed points. The assigned uncertainty, indicated by the arrows both here and in Figure 6-8, was estimated from variations in the location of the point, $F''' = 0$, when the isochromat curve of Figure 6-8 was smoothed in different trials and by different people. The "difference curve" gives the difference in the continuous spectrum intensities observed through "balanced" silver and palladium filters (Ross balanced filter technique). The "Ag curve" is the intensity with the silver filter alone.

nitely high resolving power. It has been shown (reference 57, Chapter 5) that the fold,

$$F(z) = \int_{x=-\infty}^{x=z} g(x)f(z-x) dx \quad (6-28)$$

expresses the relationship between F , f , and $g(x)$, the monochromator band-pass characteristic. In (6-28) we choose $z = 0$ to be the quantum limit of the ideal spectrum so that $f(z) = 0$ for $z < 0$; hence the upper limit of the integral can be set at $x = z$ since the

ideal spectrum vanishes beyond that point. If we differentiate (6-28) 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., if we let

$$f'(x) = a_i, \quad x_{i-1} < x < x_i, \quad i = 1, 2 \dots \quad (6-29)$$

we obtain

$$F''(z) = g(z)f'(0) + \sum_{i=1}^{\infty} g(z - x_i)(a_{i+1} - a_i) \quad (6-30)$$

This means that the second derivative, $F''(z)$, of the observed intensity curve will consist of a series of images of the monochromator band-pass 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 break with which it is associated. The leading term $g(z)f'(0)$ is consistent with this rule since in deriving (6-30) the slope of $f(z)$ is assumed to change abruptly from zero to $f'(0)$ at $z = 0$. This second-order discontinuity in the true spectrum will therefore generate, at the same abscissa point in the second derivative of the isochromat, a replica of the g -curve of the monochromator.

It should be clear then that the point of maximum bending will fail to give the correct threshold position if there are adjacent strong breaks in slope in the true spectrum which lie too close to the threshold break. This is because the corresponding images of the monochromator band-pass curve will then lie so closely adjacent as to be incompletely resolved. Such blending of adjacent g -curves with the one at the quantum limit may produce a shifting of the peak of the blend and may thus introduce an error. It can be shown, however, that the Ohlin structure, clearly visible in Figure 6-8 as the sinuosity near the upper part of the isochromat, can, on no reasonable assumptions regarding its true shape, have any such shifting effect as would be required to explain the difference in positions A and B .

The systematic trend indicated by the shifts of Table 6-2 and Figures 6-6 and 6-7 might be explicable, however, if, as already suggested, the ideal structure of the quantum limit consists of a superposition of a first- and a second-order discontinuity as shown in the upper diagram of Figure 6-5. Referring to the lower part of

that figure, if h is the height of the precipice, if $s = \tan \theta$ is the slope above it, and if $z_h = h/s$ is what we have called the "overshoot," it is easy to show that

$$F''(z) = sg(z) + hg'(z) = s[g(z) + z_h g'(z)] \quad (6-31)$$

Clearly, 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. (This follows because the first-order discontinuity or step function, considered by itself, is the limiting case of two equal breaks in slope of opposite sign which have approached indefinitely close to each other and have become indefinitely large.) The superposition of these two curves, the primitive g -curve 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. Such a superposition resulting in the shift, Δz , is illustrated in the lower curves of Figure 6-5.

The quantitative plausibility of this hypothesis has been tested on the assumption that the g -curve of the monochromator is a "witch" (Cauchy distribution),

$$g(x) = A(1 + x^2/a^2)^{-1} \quad (6-32)$$

where a is the half-width at half maximum height. This is the simplest curve which approximates roughly the pass band of the monochromator. In particular it has the same inverse square behavior at large distances which is expected (on the dynamical theory of x-ray reflection in perfect crystals) in the pass-band characteristic of a two-crystal x-ray monochromator used in the "antiparallel" position. It turns out (50) that if we assume the postulated overshoot, z_h , expressed in volts to be independent of the voltage at which the experiment is performed, then to explain the large shift (of order 4 or 5 volts) observed at 24,500 volts we must assume z_h so large that a vestige of the precipice would almost certainly start to manifest itself in the isochromats taken at the lowest voltages. At these lowest voltages the monochromator pass-band widths are narrow enough so that one should see a rounded hump (convex upward) on the isochromat corresponding to the brink of the precipice in the true spectrum. Nothing like this, however, has been reported.

If then we are to explain the observed systematic trend of the

results by the postulated precipice, it is necessary to assume that the overshoot, z_h , expressed in volts *decreases with decreasing voltage*. This is, however, not at all implausible, since another feature, the position of the Ohlin irregularities, is known to be voltage-dependent; its distance expressed in volts from the quantum limit decreases with decreasing voltage. The available data of Table 6-2 and Figures 6-6 and 6-7 are insufficiently precise to yield information on the overshoot, Δz , as a function of voltage, which

Table 6-3. Nine X-ray Short Wavelength Limit Determinations Made between 6112 and 10168 Volts

Experi- menters	Nominal Voltage	$hc^2/(e\Delta)$ (kv x-units)	No. of Observations
BJW	6112	12370 .8	1
BS	8050	12371 .9	1
BS	8050	12371 .0	3
BS	8050	12370 .1	1
BS	9860	12370 .1	2
BJW	10168	12371 .2	1
	Weighted mean value ^a	12370 .8 \pm 0.2	(Std. deviation by external consistency)
	D C 53 Adjusted value	12372 .2 \pm 0.4	kv x-units

^a The weight assigned to each datum is taken as equal to the number of observations. The standard deviation of the weighted mean reflects only the experimental "spread" of the nine determinations and makes no allowance for the possible interpretational error of using the point of maximum bending of the isochromat as the criterion for the threshold position. This latter error in $hc^2/(e\Delta)$ could well be as large as 1.4 kv x-units or 110 ppm.

can be safely used to correct the experimental data. A more complete analysis of the theory of the continuous x-ray spectrum from thick targets is much needed.

Unfortunately there is little hope of improving the spectral resolving power in this experiment greatly beyond what has been attained in the experiments listed in Table 6-2, since they are already close to the theoretically attainable limit with perfect crystals according to the "dynamical theory" of selective x-ray reflection.

The conclusions to be drawn seem to be:

1). The most important residual source of systematic error in the short wavelength limit experiment comes from uncertainties, be-

cause of limited resolving power, as to how the true limit position should be estimated from the isochromat profile.

2). The x-ray isochromats obtained at the lowest voltages seem more likely to yield the most reliable results.

Table 6-2 shows that the nine determinations which were made at the lowest voltages (between 6000 volts and 11,000 volts) form a cluster which is rather widely separated from the results obtained at the two higher voltages. Also the results of these measurements are rather consistent as regards the numerical values of $hc^2/(e\Delta)$. In view of our ignorance of how best to correct for the above-described systematic trend we shall adopt the weighted mean of this group of nine results made at the lowest voltages. Table 6-3 presents these data.

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The Method of Least Squares

7.1 THE BASIC THEORY OF LEAST-SQUARES ADJUSTMENT

If we examine all the different experiments described in the preceding chapter we find that they measure various combinations of the atomic constants. All these quantities can, however, be expressed in terms of h , e , m , N , α , c , and a few other auxiliary quantities whose numerical values are accurately known. Some of the combinations of quantities, such as the Rydberg constant which is a function of h , e , m , and c , are much more accurately measured than any of their component factors. It is therefore convenient to consider the Rydberg constant as an exact numerical quantity and to use it to express the electron mass as a known function of the other variables. In addition, to the accuracy required in the discussion to follow, it is convenient to treat the velocity of light, c , as an exactly known quantity. Furthermore, because of the fact that the fine structure constant, α , is more accurately determined by direct observation of fine structure in hydrogen than it can be computed by combining, say measurements of c , h/e , and e , it is also convenient to use α as a variable in place of h . Thus we shall choose to express all the experimental results in terms of the quantities α , e , N , and Λ , which we may call the primary unknowns of our analysis. The result of any experiment can then be described as measuring (except for quantities which can be considered as accurately calculable correction factors) some product of powers of the primary variables of the form:

$$\alpha^{i_{\mu}} e^{j_{\mu}} N^{k_{\mu}} \dots = A_{\mu} (1 - r_{\mu}), \mu = 1, 2, 3, \dots, n \quad (7-1)$$

where A_{μ} is the numeric which results from the measurement, and α , e , N , etc., are the primary variables. If we were to put true values of these variables (which we do not know) into the left-hand side

of equation (7-1) we would in general not obtain the number A_μ , since it is the result of measurement and therefore subject to error. We must include the factor $1 - r_\mu$ in order that equation (7-1) shall be a valid equation. The quantity r_μ is the relative fractional error in the measured numeric, A_μ . Since we do not know the true values of the primary variables, we cannot compute r_μ from equation (7-1). We know only an estimate of some of the parameters of its probability distribution. The most probable value of the error is zero, since the numeric quoted as the result of an experiment is, to the best of our knowledge, the number which is most likely to be the correct value of the quantity being measured. Furthermore, we have an estimate of σ , the root-mean-square deviation of the relative error, and we shall restrict ourselves momentarily to a Gaussian distribution for the errors such that the probability of the error r_μ lying between the values r and $r + dr$ is

$$P_\mu(r < r_\mu < r + dr) = \frac{1}{(2\pi)^{1/2}\sigma_\mu} \exp(-r^2/2\sigma_\mu^2) dr \quad (7-2)$$

The Gaussian distribution is not uniquely implied by the two parameters, A_μ and σ_μ , and the least-squares procedure can, as we shall show, be justified without recourse to any presumed probability distribution of errors. However, the introduction of such a distribution is convenient and makes possible a more direct development.

When we omit the factors $1 - r_\mu$ from equation (7-1) the system is, in general, overdetermined; we have n equations and only q variables ($q < n$), so that a solution is impossible (except for the very improbable situation in which all the experimental data are exactly compatible). When we introduce the quantities r_μ , we increase the number of unknowns to $q + n$, there being one residual for each observational equation, and we are able to satisfy the equations in infinitely many ways. It is now necessary to find some additional conditions which will allow us to choose that one solution, from the infinitely many which are available to us, which represents the "best" choice. This "best" choice can be based on the Axiom of Maximum Likelihood:

"Of all the possible choices for the set of residuals (r_μ), the best choice is that whose probability of occurrence is maximum."

The probability of obtaining simultaneously the set of values, $r_1, r_2, r_3, \dots, r_n$ is the product of the probabilities of obtaining each

value separately, provided these errors are all independent. (The importance of this proviso will soon become evident.) Therefore

$$P(r_1, r_2, r_3 \cdots) = [(2\pi)^n \sigma_1^2 \sigma_2^2 \sigma_3^2 \cdots \sigma_n^2]^{-\frac{1}{2}} \cdot \exp \left\{ -\frac{1}{2} \left(\frac{r_1^2}{\sigma_1^2} + \frac{r_2^2}{\sigma_2^2} + \cdots + \frac{r_n^2}{\sigma_n^2} \right) \right\} \quad (7-3)$$

This probability will be a maximum when the sum in the exponent is a minimum. This then is the "least-squares" condition: The n equations (7-1) are solved for the residuals r_μ written as functions of the unknown variables $\alpha, e, N \cdots$ and we seek that set of values for the variables which minimizes the sum of the squares of the quotient of each residual divided by its standard deviation.

The specific analytic procedure implied by the condition of Maximum Likelihood depends on the form of the error distribution assumed and no general procedure can be formulated. However, it has been shown (1-7) that, independent of any assumptions about the exact distribution of the errors of the A_μ save that the σ_μ exist (i.e., are finite) in each case, this least-squares condition is equivalent to the condition that the resultant solution shall be that set which has minimum root-mean-square deviations. This generalized theory is here briefly developed in Section 7.3.

For convenience in effecting the least-squares adjustment, the system of equations (7-1) is "linearized." We adopt origin values α_0, e_0, N_0 , etc., which have been chosen sufficiently close to our expected solution that any set of values α, e, N , in which we are likely to be interested will differ from these individual origin values only by small relative amounts: that is, $\alpha_0, e_0, N_0, \cdots$ are so chosen that $x_\alpha = (\alpha - \alpha_0)/\alpha_0, x_e = (e - e_0)/e_0, x_N = (N - N_0)/N_0 \cdots$ are always small, and we then express the experimental measurements in terms of these dimensionless variables $x_\alpha, x_e, x_N, \cdots$. To each type of experimental determination of a function of the type (7-1) there corresponds a hyperplane

$$i_\mu x_\alpha + j_\mu x_e + k_\mu x_N + \cdots = a_\mu - r_\mu \quad (7-4)$$

which is tangent to the curved surface (7-1). The constant a_μ is given by $a_\mu = (A_\mu - A_{\mu_0})/A_{\mu_0}$, in which A_{μ_0} is the value of the function when the origin values $\alpha_0, e_0, N_0, \cdots$ are inserted. The orientation of this plane in the hyperspace depends on the ex-

ponents $i_\mu, j_\mu, k_\mu \dots$ of (7-1), i.e., the coefficients $i_\mu, j_\mu, k_\mu, \dots$ of (7-4), while the origin distance of the plane depends on a_μ . The entire status of our knowledge regarding the "best" values of α, e, N , 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 standard error, σ_μ . The function $Q = \sum (r_\mu^2 / \sigma_\mu^2)$ which is to be minimized is therefore an expression of the second degree in the variables, x_α, x_e, x_N , 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 equations (7-4) omitting the residue r_μ in each case. Assign to each equation a weight

$$p_\mu = C / \sigma_\mu^2 \quad (7-5)$$

where the constant C may have any convenient numerical value. To obtain the normal equation associated with 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 coefficient of the variable in question in that equation and by the weight assigned to that equation. These individual expressions are then added 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_e, x_N , etc.

The solution is completed by inserting the values obtained for the x 's into the original set of observational equations (7-4) 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 variables x_α, x_e, \dots . The minimum value of the quadratic expression, Q , is usually denoted by the symbol χ^2

$$\chi^2 = \sum (R_\mu^2 / \sigma_\mu^2) \quad (7-6)$$

An important measure of the consistency of the entire set of equations is given by χ^2 divided by the difference between the number of the equations, n , and the number of the unknowns, q .

The expectation value of $\chi^2/(n - q)$ is unity; the square root of this quantity is the generalization to multidimensional space of R. T. Birge's (8) ratio of the measures of external and internal consistency. The difference, $n - q$, is known as the "number of degrees of freedom" of the system.

A word of caution about the actual method of formulating the equations of least squares from the data as applied to the atomic constants is desirable at this point. The general form of the primitive equations of observation is given in equations (7-1) above. In each such equation A_μ is a number with an estimated relative standard error σ_μ , the result of some particular experimental observations, combined perhaps with auxiliary constants, which, if care to avoid it has not been exercised, may be correlated observationally with some of the other A_μ by reason of the fact that one and the same error-contributing component may have been used in reducing the data to arrive at both A_μ 's.

Now it is an important point that the observational equations must be observationally independent, if the above classical procedure of effecting least-squares adjustment is to be followed. This is because one cannot otherwise assign simple independent weights to the different equations. If, on the contrary, the equations are observationally correlated, the standard errors of the a 's can be measured only by an error matrix involving correlation coefficients corresponding to all possible pairs of a 's as well as individual standard errors for each a , and the weights must be replaced by a "weight matrix," the inverse of the error matrix, to express the situation fully. The process of least-squares adjustment can then be formulated (9-13) in matrix algebra in a manner quite analogous to the simpler case of independent a 's but with considerable increase in labor.

The easy and obvious way out of this difficulty is to recast the entire system of equations in such a way as to remove the observational correlations between the a 's. This amounts to finding a transformation which diagonalizes the error and weight matrices. A linear transformation of the variables can always be found which diagonalizes these matrices, but such a transformation will in general yield awkward variables of obscure physical significance. What we desire is to find a transformation which diagonalizes the error matrix and which also yields convenient, physically significant

variables. It may be impossible to do this, however, without transferring some of the quantities with larger standard errors from the category of the known a 's to the category of the unknown x 's and also write for each of these an extra observational equation in which the new unknown, x , is equated to its appropriate input datum, a , the numerical result of direct measurements. This, of course, complicates the problem by increasing the number of unknowns to be adjusted, but it in no way affects the original overdetermination ($n - q$) of the set, since an additional observational equation is added for each new unknown introduced.

7.2 CALCULATION OF STANDARD ERRORS AND CORRELATION COEFFICIENTS

The statistical errors to be assigned to the output values of any least-squares adjustment must, in general, be described not only by stating the standard deviation for each numerical result but also by specifying the correlations which exist between each pair of results. The numerical output values of α , e , N , etc., are of little use unless functions of these quantities can be combined to compute other derived values. The standard deviations of such derived values must be computed by formulas which involve not only the standard deviations of the values entering into the function but also the correlation coefficients, r_{ij} , connecting all possible pairs of those values. This is because the output values of a least-squares adjustment are not in general statistically independent quantities but are "statistically correlated"—a concept which we shall now explain.

Each quantity subject to random or accidental error (frequently known as a "random variable") may conveniently be thought of as a sample taken at random from a "universe" of values which group themselves around a mean value according to some frequency law. This frequency law we shall usually assume to be the normal or Gaussian law. For each such random variable x_i , one is to think then of the implied universe of values from which the variable is selected. This universe may be described by giving some of its parameters. Thus, if the universe is known to be Gaussian, for example, then prescription of its first and second moments, i.e., its mean value, μ_i , and its variance, σ_i^2 , are sufficient.

Two such random quantities are observationally independent if the random selection of a sample value from one universe in no wise

affects or biases the free selection of a sample from the other universe. If, for example, two variables are connected by a strict functional relationship so that the value of either one is uniquely determined by the other, the variables are completely correlated and the correlation coefficient connecting them has the absolute value unity. Random samples can no longer be selected freely and independently from the two universes because of the functional condition which ties the selections rigidly together. Having selected a sample value from one universe at random, the second selection is now completely specified. On the other hand, if one of the two random variables is a function of the other and also of still other completely independent random variables, then these two will be partially but not completely correlated, and the correlation coefficient connecting them will have a value somewhere between -1 and $+1$. In general if we have a set of statistically independent random variables, x_i , then a second set of variables, y_j , obtained by linear transformation on the x_i

$$y_j = \sum_i a_{ji}x_i \quad (7-7)$$

will not be statistically independent. We shall illustrate this with the following two-dimensional example.

a. Bivariate Normal Distribution; the "Probability Hill"

Let x_1 and x_2 be statistically independent random variables obeying the Gaussian distribution law with mean values, \bar{x}_1 and \bar{x}_2 , and standard deviations σ_{x_1} and σ_{x_2} . In Figure 7-1 these distributions and their mean values are plotted on a Cartesian coordinate system. The chance of observing the first variable at the value x_1 in the range dx_1 and simultaneously observing the second variable at the value x_2 in the range dx_2 , that is to say, the chance that the observations will fall in the small shaded area of the graph, is simply the product of the individual chances because x_1 and x_2 are statistically independent. This chance is

$$\begin{aligned} P(x_1, x_2)dx_1dx_2 \\ = (2\pi\sigma_{x_1}\sigma_{x_2})^{-1} \exp[-\frac{1}{2}(\Delta x_1^2/\sigma_{x_1}^2 + \Delta x_2^2/\sigma_{x_2}^2)]dx_1dx_2 \end{aligned} \quad (7-8)$$

wherein for brevity we have abbreviated the deviations from the mean,

$$x_1 - \bar{x}_1 \text{ as } \Delta x_1; \quad x_2 - \bar{x}_2 \text{ as } \Delta x_2$$

Clearly the lines of constant probability in the (x_1, x_2) -space form a system of similar ellipses with major and minor axes parallel to the axes of x_1 and x_2 . In the (x_1, x_2) -space the “probability hill” has elliptical contours for its horizontal sections and Gaussian distribution curves for its vertical sections. The particular ellipse plotted in Figure 7-1 is the ellipse of standard deviation. Tangents

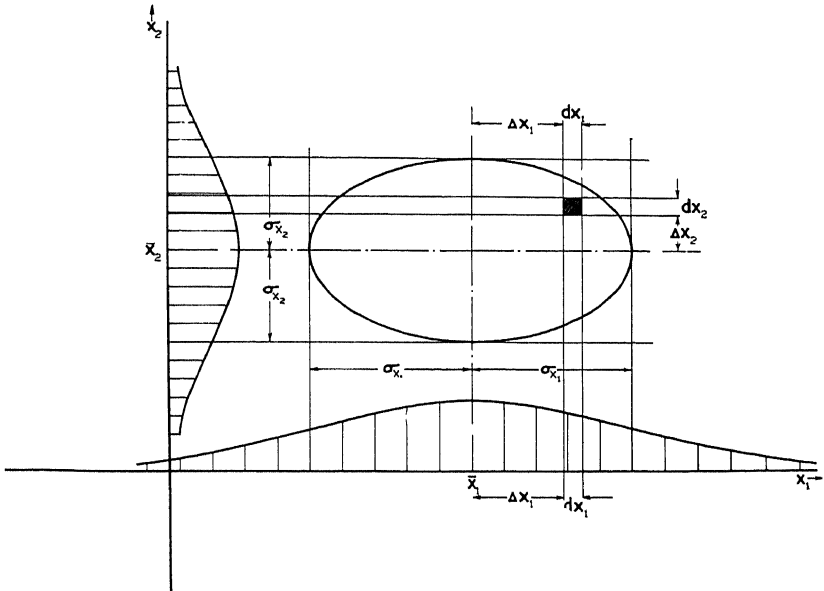


Figure 7-1. The elliptical isoproability contour at standard deviation of the “probability hill” for two statistically independent normally distributed random variables, x_1 and x_2 . The standard deviations, σ_{x_1} and σ_{x_2} , of x_1 and x_2 are shown.

to this ellipse projected normally upon the x_1 -axis define thereon the ranges of standard deviation extending from $x_1 = \bar{x}_1 - \sigma_{x_1}$ to $x_1 = \bar{x}_1 + \sigma_{x_1}$ with a similar statement for the variable x_2 .

b. Correlation as the Result of a Linear Transformation

Now let us consider certain new variables, y_1 and y_2 , derived from x_1 and x_2 by a linear transformation

$$\begin{aligned}
 y_1 &= a_{11}x_1 + a_{12}x_2 \\
 y_2 &= a_{21}x_1 + a_{22}x_2
 \end{aligned}
 \tag{7-9}$$

For the simple case of a rigid rotation of the axes through angle θ the coefficients a take the values

$$\begin{aligned} a_{11} &= \cos \theta; & a_{12} &= -\sin \theta \\ a_{21} &= \sin \theta; & a_{22} &= \cos \theta \end{aligned} \tag{7-10}$$

Figure 7-2 shows the standard deviation contour of the elliptical probability hill plotted in the new Cartesian system, (y_1, y_2) for the case of such a rigid rotation. The old axes (x_1, x_2) are also indicated with dotted lines. In the new system the principal axes of the ellipse of standard deviation (and of all the other contours) are now oblique to the coordinate axis. This implies correlation between y_1 and y_2 from the following consideration. The cross section of the hill along the line AA , a Gaussian profile with maximum at M , is called the *conditional probability distribution* of y_2 relative to the hypothesis $y_1 = y_1'$. With variation of y_1' and lateral displacement of AA , the maximum point M of the cross section moves along the oblique locus RR (called a "regression line"). This line is constructed so as to pass through the points of contact of the ellipse with the two tangents normal to y_1 , since the ellipse is one of the level contours of the hill and such a point of tangency is therefore also a maximum point of a vertical section. Clearly, then, the most probable value, Y_2 , of y_2 (defined by the point M in Figure 7-2) varies (along RR) when we vary y_1' . A similar statement can be made regarding the most probable value, Y_1 , of y_1 for a specific value, y_2' . In this case the locus of the maximum point is the other regression line $R'R'$.

If we make no specification regarding either variable, then the projected shape of the hill, on the axes of y_1 and y_2 , respectively, gives the probability distributions which describe our knowledge of each variable. These are called the *marginal probability distributions*. The projected widths of the oblique ellipse, as defined by the horizontal and vertical tangent lines, define on the two axes the respective ranges of standard deviation of the two variables, y_1 and y_2 . These marginal standard deviation ranges of y_1 and y_2 are

$$\begin{aligned} -\sigma_{y_1} &< \Delta y_1 < +\sigma_{y_1} \\ -\sigma_{y_2} &< \Delta y_2 < +\sigma_{y_2} \end{aligned}$$

The standard deviations σ_{y_1} and σ_{y_2} can be evaluated in terms of the standard deviations of the original variables σ_{x_1} and σ_{x_2} . We solve equation (7-9) for the Δx 's in terms of the Δy 's.

$$\begin{aligned} \Delta x_1 &= \frac{a_{22}}{D} \Delta y_1 - \frac{a_{12}}{D} \Delta y_2 \\ \Delta x_2 &= -\frac{a_{21}}{D} \Delta y_1 + \frac{a_{11}}{D} \Delta y_2 \end{aligned} \tag{7-11}$$

where $D = a_{11}a_{22} - a_{12}a_{21}$ ($D = 1$ for the simple case of rigid rotation through an angle θ).

These expressions for x_1 and x_2 may now be inserted into equation (7-8) in order to express the distribution in terms of the transformed variables. The exponent then becomes:

$$\begin{aligned} -\frac{1}{2D^2} &\left[\left(\frac{a_{22}^2}{\sigma_{x_1}^2} + \frac{a_{21}^2}{\sigma_{x_2}^2} \right) (\Delta y_1)^2 - 2 \left(\frac{a_{22}a_{12}}{\sigma_{x_1}^2} + \frac{a_{21}a_{11}}{\sigma_{x_2}^2} \right) (\Delta y_1 \Delta y_2) \right. \\ &\left. + \left(\frac{a_{12}^2}{\sigma_{x_1}^2} + \frac{a_{11}^2}{\sigma_{x_2}^2} \right) (\Delta y_2)^2 \right] \\ &= -\frac{1}{2} [A (\Delta y_1)^2 - 2B (\Delta y_1 \Delta y_2) + C (\Delta y_2)^2] \end{aligned} \tag{7-12}$$

When this expression is equated to $-\frac{1}{2}$ it gives the equation of the ellipse of standard deviation in the new coordinates. From this quadratic expression in Δy_1 and Δy_2 it is easy to find the extreme values of these two variables. They are found to be given by

$$\begin{aligned} \sigma_{y_1}^2 &= \frac{C}{AC - B^2} \\ &= a_{11}^2 \sigma_{x_1}^2 + a_{12}^2 \sigma_{x_2}^2 = \cos^2 \theta \sigma_{x_1}^2 + \sin^2 \theta \sigma_{x_2}^2 \\ \sigma_{y_2}^2 &= \frac{A}{AC - B^2} \\ &= a_{21}^2 \sigma_{x_1}^2 + a_{22}^2 \sigma_{x_2}^2 = \sin^2 \theta \sigma_{x_1}^2 + \cos^2 \theta \sigma_{x_2}^2 \end{aligned} \tag{7-13}$$

These expressions are identical with the simple law of propagation of independent errors. The exponent, equation (7-12), can be cast into the type-form

$$-\frac{1}{2(1-r^2)} \left[\frac{(\Delta y_1)^2}{\sigma_{y_1}^2} - 2r \frac{\Delta y_1 \Delta y_2}{\sigma_{y_1} \sigma_{y_2}} + \frac{(\Delta y_2)^2}{\sigma_{y_2}^2} \right] \tag{7-14}$$

in which

$$1 - r^2 = 1 - \frac{B^2}{AC} = \frac{(a_{22}a_{11} - a_{21}a_{12})^2 \sigma_{x_1}^2 \sigma_{x_2}^2}{(a_{12}^2 \sigma_{x_2}^2 + a_{11}^2 \sigma_{x_1}^2) (a_{22}^2 \sigma_{x_2}^2 + a_{21}^2 \sigma_{x_1}^2)} \tag{7-15}$$

For the case of a rigid rotation of axes through angle θ this reduces to

$$1 - r^2 = \frac{\sigma_{x_1}^2 \sigma_{x_2}^2}{(\sigma_{x_2}^2 \sin^2 \theta + \sigma_{x_1}^2 \cos^2 \theta) (\sigma_{x_2}^2 \cos^2 \theta + \sigma_{x_1}^2 \sin^2 \theta)} \quad (7-16)$$

c. Geometrical Interpretation of the Correlation Coefficient

In type-form (7-15), r is the correlation coefficient. To obtain a clearer geometrical idea of its significance consider the probability

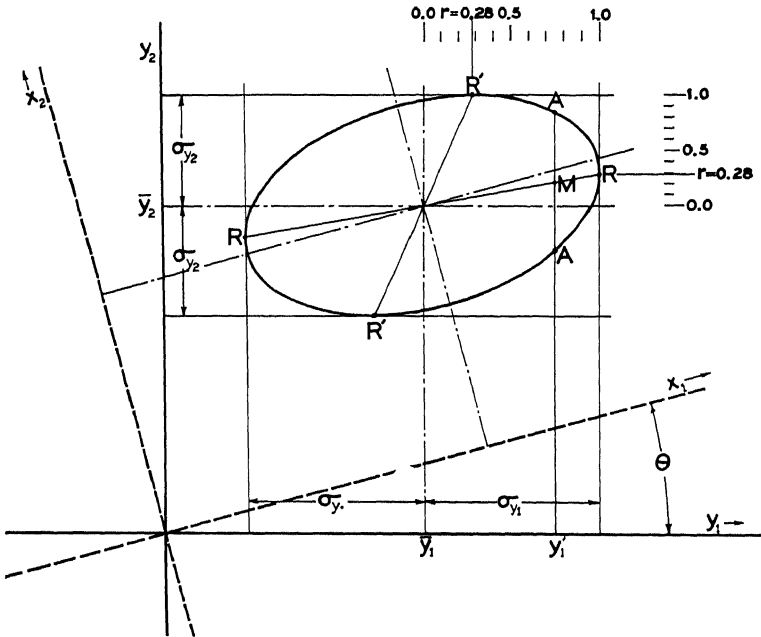


Figure 7-2. The standard deviation contour of the same "probability hill" as in Figure 7-1 expressed in terms of new variables, y_1 and y_2 , related to x_1 and x_2 by a linear transformation. The elliptical contour is skewed to the axes of y_1 and y_2 , and these new random variables are in consequence no longer statistically independent as were x_1 and x_2 . The vertical cross section of the hill along the line, $A-A$, is a normal distribution with maximum at M on the "regression line" RR . This cross section, called the conditional probability distribution of y_2 relative to the hypothesis, $y_1 = y_1'$, clearly shifts position with variation of y_1' . The fractional part of its standard deviation by which the conditional distribution of one variable shifts in response to one whole hypothetical standard deviation of the other variable is called the correlation coefficient, r , and is the same for either variable of any given pair. In the case illustrated, $r = 0.28$.

distribution of the error hill whose standard deviation contour is shown in Figure 7-2. The mean value of the cross-product moment, $\Delta x_1 \Delta x_2$, integrated over the distribution is called the *covariance* v_{12} of the probability distribution and for this two-dimensional Gaussian distribution it can be shown to be given by the formula $v_{12} = \sigma_{x_1} \sigma_{x_2} r$. Whereas the mean value of the cross-product moment, $\Delta x_1 \Delta x_2$, of the distribution of Figure 7-1 can be seen to be zero from symmetry, this is not true for the mean value of the product, $\Delta y_1 \Delta y_2$, as Figure 7-2 shows, since on the same probability contour this product is clearly greater in the first and third quadrants (of the $\Delta y_1, \Delta y_2$ coordinate system) than it is in the second and fourth quadrants (which contribute with opposite sign). By direct substitution in the standard deviation contour equation, obtained by equating (7-14) to $-\frac{1}{2}$, it is easy to verify that, on that ellipse, when Δy_2 equals σ_{y_2} , i.e., at the points $R'R'$ of Figure 7-2, we have $\Delta Y_1 = r\sigma_{y_1}$; and also when $\Delta y_1 = \sigma_{y_1}$, i.e., at the points RR , we have $\Delta Y_2 = r\sigma_{y_2}$.

The correlation coefficient, r , is thus seen to be a measure of the sensitivity of the conditional mean, ΔY_i , of either one of the random variables to a hypothetical deviation from the mean Δy_j on the part of the other.

$$r \frac{\Delta y_1'}{\sigma_{y_1}} = \frac{\Delta Y_2}{\sigma_{y_2}} \quad (7-17)$$

This relation conveys very simply and graphically the significance of r . The correlation coefficient, r , is seen to be a pure number which can have any value in the range, $-1 \leq r \leq 1$.

d. Generalized Law of Error Propagation for Correlated Variables

As y_1 and y_2 are statistically correlated variables we cannot compute the standard deviations of *functions* of y_1 and y_2 with the same simple law of independent error propagation which applied to functions of x_1 and x_2 , the law exemplified in (7-13). To illustrate this let us compute the standard deviations of two variables, ξ_1 , and ξ_2 , related to y_1 and y_2 by the same matrix of linear transformation coefficients as those of (7-11). We purposely choose these because, being the inverse of the transformation which led from the x 's to the y 's, this transformation should restore us to the x 's so as to make

$\xi_1 = x_1$ and $\xi_2 = x_2$. Our transformation will be

$$\Delta\xi_1 = a_{11}'\Delta y_1 + a_{12}'\Delta y_2 \quad \Delta y_1 = \frac{a_{22}'}{D'}\Delta\xi_1 - \frac{a_{12}'}{D'}\Delta\xi_2$$

or

$$\Delta\xi_2 = a_{21}'\Delta y_1 + a_{22}'\Delta y_2 \quad \Delta y_2 = -\frac{a_{21}'}{D'}\Delta\xi_1 + \frac{a_{11}'}{D'}\Delta\xi_2$$

in which, to duplicate the matrix of (7-11), we make

$$\begin{aligned} a_{11}' &= \frac{a_{22}}{D} & a_{12}' &= -\frac{a_{12}}{D} \\ a_{21}' &= -\frac{a_{21}}{D} & a_{22}' &= \frac{a_{11}}{D} \end{aligned} \quad (7-19)$$

(D and D' being determinants of inverse matrices, we have $DD' = 1$.)

Substituting transformation (7-18) into the equation of the ellipse of standard deviation of the y -coordinates (expression (7-14) equated to $-\frac{1}{2}$) we obtain a transformed equation for the ellipse in terms of the ξ 's of form

$$-\frac{1}{2} D^{-2} [A'\Delta\xi_1^2 - 2B'\Delta\xi_1\Delta\xi_2 + C'\Delta\xi_2^2] \quad (7-20)$$

in which A' , B' , and C' , unlike the A , B , C , of (7-12), are now trinomial quadratics in $1/\sigma_{y_1}$ and $1/\sigma_{y_2}$ instead of binomials as in (7-12). These trinomial coefficients involve r in their cross products. We follow the same procedure as before to find the extreme values σ_{ξ_1} and σ_{ξ_2} of $\Delta\xi_1$ and $\Delta\xi_2$ on the ellipse. These are found to be given by

$$\sigma_{\xi_1}^2 = a_{11}'^2\sigma_{y_1}^2 + 2a_{11}'a_{12}'r\sigma_{y_1}\sigma_{y_2} + a_{12}'^2\sigma_{y_2}^2 \quad (7-21)$$

$$\sigma_{\xi_2}^2 = a_{21}'^2\sigma_{y_1}^2 + 2a_{21}'a_{22}'r\sigma_{y_1}\sigma_{y_2} + a_{22}'^2\sigma_{y_2}^2 \quad (7-22)$$

Equations (7-21) and (7-22) are examples of the generalized law of error propagation for calculating the standard deviations of functions of correlated variables.

If now in these last two equations we substitute for σ_{y_1} , σ_{y_2} , and r their values in terms of σ_{x_1} and σ_{x_2} from equations (7-13) and (7-15) and also for the a' their values in terms of the original a 's (7-19), it can be verified that

$$\sigma_{\xi_1}^2 = \sigma_{x_1}^2 \quad \text{and} \quad \sigma_{\xi_2}^2 = \sigma_{x_2}^2$$

e. Application to Output Values of a Least-Squares Adjustment; the Error Matrix

In this computation the adjusted output values which result from a least-squares adjustment, such as the one we shall presently describe for the purpose of determining the "best" values of physical constants, in general constitute a set of correlated variables, x_i (the adjusted best values of the linearized x 's of equation (7-4)). To each such output value, x_i , there corresponds a standard deviation, σ_{x_i} ("variance" $v_{ii} = \sigma_{x_i}^2$), and to each pair (x_i, x_j) there corresponds a "covariance," $v_{ij} = r_{ij}\sigma_{x_i}\sigma_{x_j}$. The entire set of variances and covariances form a symmetric matrix called the error matrix. The elements of this matrix of values are required in order to compute the error measures of other quantities depending on the x_i . The variances $v_{ii} = \sigma_{x_i}^2$ and covariances $v_{ij} = r_{ij}\sigma_{x_i}\sigma_{x_j}$ can be used directly in the computation of errors of derived quantities by the generalized law of error propagation without any need for computing the correlation coefficients, r_{ij} . In this form equation (7-21) becomes

$$\sigma_{\xi_1}^2 = a_{11}'^2 v_{11} + 2a_{11}'a_{12}'v_{12} + a_{12}'^2 v_{22} \quad (7-23)$$

When we pass to situations which involve more than two variables, the elliptical contours must be replaced by surfaces or hypersurfaces of constant probability which are concentric ellipsoids or hyperellipsoids. There is then a covariance, v_{ij} , for each pair of variables. For each covariance there is a correlation coefficient

$$r_{ij} = v_{ij}/(\sigma_{x_i}\sigma_{x_j}) \quad (7-24)$$

Now it can easily be shown that, in general, the distribution in probability of the possible solutions of the set of equations (7-4), the linearized equations of observation which express the input data to be adjusted by the least-squares procedure, is represented by a hyperellipsoidal probability distribution in the constants space whose major axes are skew to the coordinate axes. The conditional probability distribution of a particular variable is dependent upon the specification of the values of all the other variables, the extent of such dependence being expressed by a square matrix of covariances or of correlation coefficients. The skew of the hyperellipsoid of error expressed by the elements of this matrix is a result which depends on the precision (and consequent weights) to be attached to the various input data.

As an example of the importance of the correlation coefficient,

let us consider now an extreme case. We can write the function $f(x) = x^{s+t}$ as $f(x) = x^s x^t$, and in this latter form, if we were to make the mistake of considering the two factors to be independent, we would calculate the relative standard error of f to be $(s^2 + t^2)^{\frac{1}{2}}$ times the relative standard error of x , whereas in the original form the relative error in f is $(s + t)$ times the relative error in x . However, we have neglected the effect of the correlation coefficient, which is in this case $r = +1$, so that the correct expression for the relative error in f , when written in the second form, is $(s^2 + t^2 + 2st)^{\frac{1}{2}}$, and *not* $(s^2 + t^2)^{\frac{1}{2}}$, times the relative error in x , and we have thereby resolved the paradox.

This method of computing errors will be called the method of the ellipsoid of error, because it is the analytical equivalent of constructing two parallel hyperplanes tangent to either side of the hyperellipsoid of error and normal to a given axis in the hyperspace of the unknowns (the axis for the linear function, f) to find the domain of standard deviation, $\pm\sigma_f$, cut off by those hyperplanes on that axis.

Example: What is the standard deviation of h , which is not one of the primary variables of the least-squares adjustment?

We used x_a and x_e as the primary variables of our solution. The fine structure constant α is given by $\alpha = 2\pi e^2/(hc)$ so that we have the relation

$$h = 2\pi e^2/(\alpha c)$$

and, since c is sufficiently accurate to be considered as an exact quantity, this leads to

$$x_h = 2x_e - x_a$$

We require not only the variances of x_e and x_a but also the covariance between x_e and x_a . The specific numerical values from Table 8-5 are

$$v_{ee} = 3.732; \quad v_{aa} = 0.215; \quad v_{ae} = 0.625$$

and hence from equation (7-21) we have

$$\begin{aligned} v_{hh} &= 4v_{ee} - 4v_{ae} + v_{aa} = 14.928 - 2.500 + 0.215 \\ &= 12.643 \end{aligned}$$

so that

$$\sigma_h = \sqrt{v_{hh}} = 3.56$$

We would also like to determine the correlation coefficient between h and all the other variables; we shall here compute only coefficients between h and α and between h and e . We can show, by means of arguments completely analogous to those that led to equations (7-21) and (7-22), that the covariance between a variable f and a variable x_i , where f is given as the linear combination

$$f = a_1x_1 + a_2x_2 + a_3x_3 + \dots$$

is

$$v_{fi} = a_iv_{1i} + a_2v_{2i} + a_3v_{3i} + \dots \tag{7-25}$$

The covariance between x_h and x_a is therefore

$$\begin{aligned} v_{ha} &= 2v_{ea} - v_{aa} = 1.035 \\ r_{ha} &= v_{ha}/(v_{hh}v_{aa})^{\frac{1}{2}} = v_{ha}/(\sigma_h\sigma_a) = 0.627 \end{aligned}$$

and similarly

$$\begin{aligned} v_{he} &= 2v_{ee} - v_{ae} = 6.839 \\ r_{he} &= v_{he}/(v_{hh}v_{ee})^{\frac{1}{2}} = v_{he}/(\sigma_h\sigma_e) = 0.994 \end{aligned}$$

7.3 THE GENERALIZED THEORY FOR NON-GAUSSIAN ERROR DISTRIBUTIONS

We assume as before that the equations to be adjusted can all be linearized so that the system is

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + \dots + a_{1q}x_q &= c_1 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + \dots + a_{2q}x_q &= c_2 \\ \dots & \dots \dots \dots \dots \dots \\ a_{n1}x_1 + a_{n2}x_2 + a_{n3}x_3 + \dots + a_{nq}x_q &= c_n \end{aligned} \tag{7-26}$$

We shall use Roman letters to indicate the indices which range from 1 to q and which refer to the unknowns, and Greek letters for those which range from 1 to n and refer to the observational equations.

Since the c_μ are assumed to be independent, the errors η_μ in c_μ are uncorrelated and

$$\begin{aligned} \langle \eta_\mu \eta_\nu \rangle &= \sigma_\mu^2 \quad \text{if } \nu = \mu \\ &= 0 \quad \text{if } \nu \neq \mu \end{aligned} \tag{7-27}$$

We wish to find x_i as a linear combination of the c_μ with appropriate coefficients, λ_μ^i , chosen so as to determine the x_i with maximum accuracy or minimum error. Thus we write

$$\begin{aligned} x_i &= \lambda_1^i c_1 + \lambda_2^i c_2 + \lambda_3^i c_3 + \cdots + \lambda_n^i c_n \\ &= \sum_\mu \lambda_\mu^i c_\mu = \sum_{\mu j} \lambda_\mu^i a_{\mu j} x_j \end{aligned} \quad (7-28)$$

This equation is to be understood as follows. Each of the n individual equations of observation (identified by the index, μ) is to be multiplied by a number, λ_μ^i , there being a set of n such numbers for each variable x_i . These numbers are to be chosen such that, when the n equations are then summed, the coefficient of each x , other than the specified x_i , is zero, while the coefficient of x_i is unity. This then implies that there are q conditions on each of the q sets of n multipliers;

$$\begin{aligned} \sum_\mu \lambda_\mu^i a_{\mu j} &= \delta_{ij}, & \delta_{ij} &= 1 \text{ if } i = j \\ & & &= 0 \text{ if } i \neq j \end{aligned} \quad (7-28')$$

The error in this value of x_i is given by

$$\epsilon_i = \sum_\mu \lambda_\mu^i \eta_\mu \quad (7-29)$$

Hence the mean-square error is

$$\begin{aligned} v_{ii} &= \langle \epsilon_i \epsilon_i \rangle = \sum_{\mu\nu} \lambda_\mu^i \lambda_\nu^i \langle \eta_\mu \eta_\nu \rangle = \sum_\mu (\lambda_\mu^i)^2 \sigma_\mu^2 \\ &= \sum_\mu (\lambda_\mu^i \sigma_\mu)^2 \end{aligned} \quad (7-30)$$

We now wish to minimize v_{ii} by proper choice of the λ_μ^i with the restriction of equation (7-28'). Hence we introduce Lagrangian multipliers L_j^i so that we may then take independent variations in λ_μ^i in the expression

$$W = \sum_\mu (\lambda_\mu^i \sigma_\mu)^2 - 2 \sum_j L_j^i (\sum_\mu \lambda_\mu^i a_{\mu j} - \delta_{ij}) \quad (7-31)$$

If we differentiate this expression with respect to λ_μ^i we obtain

$$\frac{\partial W}{\partial \lambda_\mu^i} = 2\lambda_\mu^i \sigma_\mu^2 - 2 \sum_j L_j^i a_{\mu j} \quad (7-32)$$

We now set $\partial W / \partial \lambda_\mu^i = 0$ in order to find the minimum condition. This gives us

$$\lambda_\mu^i = \frac{1}{\sigma_\mu^2} \sum_j L_j^i a_{\mu j} \quad (7-33)$$

We have thus defined λ_μ^i in terms of the L_j^i . If we now substitute equation (7-33) into equation (7-28') in order to evaluate the Lagrangian multipliers, we obtain

$$\begin{aligned} \sum_\mu \lambda_\mu^i a_{\mu k} &= \delta_{ik} = \sum_\mu \frac{1}{\sigma_\mu^2} \sum_j L_j^i a_{\mu j} a_{\mu k} \\ &= \sum_j L_j^i \left(\sum_\mu \frac{1}{\sigma_\mu^2} a_{\mu j} a_{\mu k} \right) \end{aligned} \quad (7-34)$$

We can solve equation (7-34) for L_j^i since L_j^i is a square matrix and $\sum_\mu (1/\sigma_\mu^2) a_{\mu j} a_{\mu k}$ is a (positive definite) square matrix. Since the product of these two matrices is the delta function, they are reciprocals. From equation (7-33) we also obtain, substituting it into equation (7-27)

$$\begin{aligned} x_i &= \sum_\mu \lambda_\mu^i c_\mu = \sum_\mu \frac{1}{\sigma_\mu^2} \sum_j L_j^i a_{\mu j} c_\mu \\ &= \sum_j L_j^i \left(\sum_\mu \frac{1}{\sigma_\mu^2} a_{\mu j} c_\mu \right) \end{aligned} \quad (7-35)$$

This solution is the best choice for the x_i in the sense that this value of x_i has the smallest assigned probable error of any possible weighting of the c_μ . Equation (7-35) is, however, the solution of the system of equations:

$$\sum_i \left(\sum_\mu \frac{1}{\sigma_\mu^2} a_{\mu i} a_{\mu j} \right) x_j = \sum_\nu \frac{1}{\sigma_\nu^2} a_{\nu i} c_\nu \quad (7-36)$$

and these are exactly the equations which one would deduce from the condition that the quadratic form

$$Q = \sum_\mu \left(\sum_i a_{\mu i} x_i - c_\mu \right)^2 \frac{1}{\sigma_\mu^2}$$

shall be a minimum, i.e., they are the "normal equations" alluded to in the preceding section. Hence the condition of Minimum Error is just the least-squares condition and is therefore equivalent to

the condition of Maximum Likelihood of the more restricted Gaussian case. It is, however, much more general than the latter. No restriction is put on the probability distributions of the input errors, η_μ , in the c_μ other than that these distributions must have finite second moments, i.e., the σ_μ must exist. Subject to this condition, they may have more than one "mode" or indeed any arbitrary shape. It is not even necessary that the distribution functions all have the same form.

This generality of the significance of the least-squares adjustment when stated in terms of the second moments of the error distribution is of great importance. It emphasizes also the desirability of adopting the root-mean-square deviation as a measure of error in preference to such error measures as the "probable error" or the "mean absolute error." For a Gaussian distribution, the three measures, root-mean-square error, mean absolute error, and probable error (that error which divides the distribution curve into equal areas, so that the probabilities of errors of absolute magnitude greater than or less than the probable error are equal) stand in the ratios 1 : 0.7980 : 0.6745. It is, however, a mistake to think of the different error measures as simply expressing the same error spread on different scales. When we do not limit ourselves to Gaussian distribution the root-mean-square error or standard error enjoys a position of far greater statistical significance and generality than do the others.

7.4 SPECIFIC CASE OF AN ADJUSTMENT IN FOUR UNKNOWNNS

The preceding proof is fairly involved; however, its results are relatively simple and straightforward: The usual least-squares formula has been shown to have a much wider applicability and to rest on a much firmer base than the usual dependence on Gaussian error forms would imply. We shall now carry out in somewhat more detail the solution of the least-squares condition. For definiteness we shall consider a system with four unknowns. Such a system is complex enough to show all the pertinent relationships and yet not so complex as to obscure them.

We shall write the (linearized) observationally independent equations in the form

$$a_{\mu 1}x_1 + a_{\mu 2}x_2 + a_{\mu 3}x_3 + a_{\mu 4}x_4 = c_\mu \quad \mu = 1, 2, 3, \dots, n \quad (7-37)$$

and to each of the n equations we assign a weight $p_\mu = C/\sigma_\mu^2$ (see equation (7-5)) in which σ_μ is the standard error of the constant term, c_μ . We construct the normal equations in accord with the instructions of Section 7.1; these equations can be written in the form

$$\begin{aligned} b_{11}x_1 + b_{12}x_2 + b_{13}x_3 + b_{14}x_4 &= k_1 \\ b_{21}x_1 + b_{22}x_2 + b_{23}x_3 + b_{24}x_4 &= k_2 \\ b_{31}x_1 + b_{32}x_2 + b_{33}x_3 + b_{34}x_4 &= k_3 \\ b_{41}x_1 + b_{42}x_2 + b_{43}x_3 + b_{44}x_4 &= k_4 \end{aligned} \tag{7-38}$$

The quantities b_{ij} are symmetric ($b_{ij} = b_{ji}$);

$$\begin{aligned} b_{11} &= \sum_{\mu} p_{\mu} a_{\mu 1}^2 & b_{22} &= \sum_{\mu} p_{\mu} a_{\mu 2}^2 \\ b_{12} = b_{21} &= \sum_{\mu} p_{\mu} a_{\mu 1} a_{\mu 2} \end{aligned} \tag{7-39}$$

and it should be apparent from the form of these four quantities exactly how the other twelve b_{ij} may be constructed. The constant terms of the normal equations, k_j , are calculated in a similar way:

$$k_1 = \sum_{\mu} p_{\mu} a_{\mu 1} c_{\mu} \quad k_2 = \sum_{\mu} p_{\mu} a_{\mu 2} c_{\mu} \text{ etc.} \tag{7-40}$$

It is well known that the solution of the set of equations (7-38) can be written in the form

$$\begin{aligned} x_1 &= d_{11}k_1 + d_{12}k_2 + d_{13}k_3 + d_{14}k_4 \\ x_2 &= d_{21}k_1 + d_{22}k_2 + d_{23}k_3 + d_{24}k_4 \\ x_3 &= d_{31}k_1 + d_{32}k_2 + d_{33}k_3 + d_{34}k_4 \\ x_4 &= d_{41}k_1 + d_{42}k_2 + d_{43}k_3 + d_{44}k_4 \end{aligned} \tag{7-41}$$

in which the sixteen numbers d_{ij} bear an inverse relationship to the set of numbers b_{ij} ; the element d_{ij} is equal to the minor of b_{ji} in the determinant of the b 's divided by the determinant itself. All the information required for the complete solution of the problem of least squares is contained in the sixteen b 's (or equivalently in the sixteen d 's) and the four k 's.

In addition to the "best" values of the x 's, we are equally interested in determining the precision measures which must be assigned to them. The x 's are not accurately determined quantities, since

they are computed from numbers which are the results of experiments and therefore are subject to error. Using our definition of the k 's from equation (7-40) in equation (7-41) allows us to express our solution in terms of the directly observed quantities, c_μ . Let E_μ be the error associated with each measured quantity c_μ . This error, E_μ , is unknown (if it were known we should remove the error by correcting the quantity c_μ). We know an estimate of the mean-square value of this error, however, and we can therefore make an estimate of the mean-square error in a function of the c_μ . The error ϵ_i in x_i which is produced by errors E_1 in c_1 , E_2 in c_2 , E_3 in c_3 , etc., can be calculated from the partial derivative of x_i taken with respect to c_μ :

$$\epsilon_i = \frac{\partial x_i}{\partial c_1} E_1 + \frac{\partial x_i}{\partial c_2} E_2 + \frac{\partial x_i}{\partial c_3} E_3 + \dots \quad (7-42)$$

The errors E_μ are to be considered as random variables; they may be positive or negative. Since the numeric c_μ is presumably the best estimate available for this quantity, we expect E_μ to be zero. On the other hand, the mean value of E_μ^2 is estimated to be σ_μ^2 , so that σ_μ is an estimate of the root-mean-square error in c_μ .

If we calculate the mean value of ϵ_i^2 (7-42) we find

$$\begin{aligned} \sigma_{x_i}^2 = \langle \epsilon_i^2 \rangle &= \left(\frac{\partial x_i}{\partial c_1} \right)^2 \sigma_1^2 + \left(\frac{\partial x_i}{\partial c_2} \right)^2 \sigma_2^2 + \left(\frac{\partial x_i}{\partial c_3} \right)^2 \sigma_3^2 + \dots \\ &+ 2 \left(\frac{\partial x_i}{\partial c_1} \frac{\partial x_i}{\partial c_2} \right) \langle E_1 E_2 \rangle + 2 \left(\frac{\partial x_i}{\partial c_1} \frac{\partial x_i}{\partial c_3} \right) \langle E_1 E_3 \rangle + \dots \end{aligned} \quad (7-43)$$

in which the sign $\langle \rangle$ about a quantity denotes the operation of taking the average value of that quantity. Since the c 's have been assumed to be observationally independent, the errors in two different c 's are in no way related to each other and the average value of the product of two different errors vanishes, since for any value of one error the other may be averaged out to zero. Thus in such a case, the cross-product terms in equation (7-43) disappear, and we have the law of propagation of independent errors

$$\sigma_{x_i}^2 = \langle \epsilon_i^2 \rangle = \sum_\mu \left(\frac{\partial x_i}{\partial c_\mu} \right)^2 \sigma_\mu^2 \quad (7-44)$$

When the differentiations of (7-44) are actually carried out (with the x 's given in terms of the k 's by equation (7-41) and the k 's in turn given in terms of the c 's by equation (7-40)) we find, after

straightforward but somewhat lengthy algebraic manipulation, that the mean-square error in x_i is given simply by Cd_{ii} . Thus the diagonal elements of the matrix (d_{ij}) of (7-41), the inverse to the matrix of the coefficients of the normal equations (7-38), are directly related to the standard errors of the solution. Furthermore, it may be shown that the off-diagonal elements of matrix (d_{ij}) are similarly related to the mean value of the product of the errors in two different variables. The variances and covariances, v_{ij} , of the adjusted x_i are in fact proportional to the elements of matrix (d_{ij}) with the common constant of proportionality C so that in general

$$\langle \epsilon_i \epsilon_j \rangle = C d_{ij} \quad (7-45)$$

and the matrix (d_{ij}) is called the "error matrix" of the solution. It is important to realize that the mean value of the product of the errors of two different x 's does not vanish. These quantities, being expressed ultimately in the least-squares procedure by some linear combination of the independent c_μ , are correlated quantities, for the same reason that y_1 and y_2 of equation (7-9) above were not independent. The ellipsoid of error is in general skew to the axes of the x 's.

The extent of this correlation is given by the correlation coefficient, r_{ij} , connecting the two variables x_i and x_j . This coefficient is given by

$$r_{ij} = d_{ij} / (d_{ii} d_{jj})^{1/2} \quad (7-46)$$

and it can be shown that r_{ij} , as before, lies between the limits $-1 \leq r_{ij} \leq 1$. If the two variables are uncorrelated, in the sense that an error in one is completely independent of an error in the other, $r_{ij} = 0$; at the other extreme, if the two variables are functionally related to the extent that an error in one completely determines the error in the other, then the equality, $r_{ij} = \pm 1$, holds, the sign depending on whether a positive error in one variable is associated with a positive or a negative error in the other. Once we have calculated the error matrix, it is no longer necessary to express a function of the x 's in terms of the independent quantities, c_μ , in order to calculate its standard error, as long as we realize that the errors in the x 's are correlated. If we have any function, $f(x_1, x_2, x_3, x_4)$, the error ϵ_f in the function arising from specified errors, $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$, in the x 's is

$$\epsilon_f = \alpha_1 \epsilon_1 + \alpha_2 \epsilon_2 + \alpha_3 \epsilon_3 + \alpha_4 \epsilon_4 \quad (7-47)$$

where $\alpha_i = \partial f / \partial x_i$, and the mean-square error (variance) of f is given by

$$\sigma_f^2 = \langle \epsilon_f^2 \rangle = \sum_{ij} \alpha_i \alpha_j \langle \epsilon_i \epsilon_j \rangle = C \sum_{ij} \alpha_i \alpha_j d_{ij} \quad (7-48)$$

The quantity C is the constant relating the "weight" of an observation to its variance; our a priori choice for this constant (its value by "internal consistency") is the value from equation (7-5)

$$C_I = p_\mu \sigma_\mu^2 \quad (\text{internal}) \quad (7-49)$$

(The adjective "internal" is used to designate that this value is an estimate based on information internal to each individual physical measurement, c_μ). It is possible also to make an a posteriori estimate of C (its value by "external consistency") based on a measure of the mutual compatibility of the input data. We expect the quantity, $\chi^2 / (n - q)$, to be equal to unity, as explained in Section 7.1; if this is not so, we make an a posteriori readjustment in the scale of our standard deviations and define

$$C_E = C_I \chi^2 / (n - q) = \sum_{\mu} p_\mu R_\mu^2 / (n - q) \quad (\text{external}) \quad (7-50)$$

If $\chi^2 / (n - q)$ exceeds unity by more than might be probable from statistical sources alone, this may be interpreted either as indicating that systematic errors were present in the measurements, c_μ , or that the estimates, σ_μ , of the statistical errors of the c_μ derived from information internal to the experiments were underestimated.

Equation (7-48) gives us the generalized law of the propagation of errors; written out in terms of the standard deviations and correlation coefficients of the four variables it becomes

$$\sigma_f^2 = \sum_{i=1}^4 (\alpha_i \sigma_{x_i})^2 + 2 \sum_{i < j} r_{ij} (\alpha_i \sigma_{x_i}) (\alpha_j \sigma_{x_j})$$

and this form must be used rather than an expression of the form (7-44), if we are dealing with correlated variables (i.e., if the correlation coefficients, r_{ij} , do not vanish).

7.5 THE STANDARD ERRORS OF THE RESIDUES OF A LEAST-SQUARES ADJUSTMENT

In any least-squares adjustment of data it is obviously important to be able to assign a standard deviation to the difference between

the adjusted output datum and the input datum from which it was obtained. Closely related to this question is the question of the value which would be obtained in a least-squares analysis if a specific input datum had been omitted. The input and output data may be strongly correlated, and it would certainly be incorrect to calculate the standard deviation of the difference without considering this correlation.

The measured input data consist of the numbers c_μ as in equation (7-37); after the least-squares solution has been performed and we have obtained the adjusted values for the x 's we can insert these values into equation (7-37) to obtain the adjusted value of c_μ which we shall designate by c_μ^* . The number c_μ^* is the best estimate which we can make of the correct value of c_μ based upon all the data available to us. The difference between c_μ and c_μ^* is thus a measure of the extent to which the observed value c_μ is consistent with all the other data. In order to evaluate this consistency we must have an estimate of the magnitude of the difference which might be expected on the basis of statistical fluctuations. It can be shown fairly easily that the variance of the difference, $c_\mu^* - c_\mu$, is given by $\sigma_\mu^2 - \sigma_\mu^{*2}$, where σ_μ^2 is the variance of the input datum and σ_μ^{*2} is the variance of the adjusted value (14). This is a surprisingly simple result, and it justifies the description of the adjusted value as being compounded of two terms; one is the direct input value c_μ while the other is an effective or indirect value which is determined by the combined action of all the other data.

This indirect value is the value of c_μ which would be deduced from a least-squares analysis from which the directly observed datum had been omitted.

The indirect value and its variance are given by

$$c_\mu^i = \frac{\sigma_\mu^2 c_\mu^* - \sigma_\mu^{*2} c_\mu}{\sigma_\mu^2 - \sigma_\mu^{*2}} = c_\mu^* + \frac{\sigma_\mu^{*2}}{\sigma_\mu^2 - \sigma_\mu^{*2}} (c_\mu^* - c_\mu) \quad (7-51)$$

$$\sigma_\mu^{i2} = \frac{\sigma_\mu^2 \sigma_\mu^{*2}}{\sigma_\mu^2 - \sigma_\mu^{*2}} \quad (7-52)$$

This expression for the variance implies that the statistical weights, which are proportional to the reciprocal of the variances, are related by the equation

$$p_\mu^* = p_\mu^i + p_\mu, \quad p = C/\sigma^2 \quad (7-53)$$

If we use weights rather than variances, equation (7-51) takes on the simple form

$$c_{\mu}^* = \frac{p_{\mu}c_{\mu} + p_{\mu}^i c_{\mu}^i}{p_{\mu} + p_{\mu}^i} \quad (7-54)$$

which is merely the statement that the least-squares adjusted value is the weighted mean of the direct input value and the indirect value. We shall make use of this in Section 8.2 of the following chapter when we discuss the results and implications of a specific least-squares analysis.

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Least-Squares Adjustment of the Atomic Constants

The major portion of this book has been devoted to a careful analysis of the various experimental determinations of certain fundamental atomic constants. The interrelatedness of all these experiments has been emphasized, and it has been pointed out how the numerical value of a specific atomic constant may be computed by following any one of several different "paths." Ideally, all these paths should lead to the same numerical value; however, because of experimental error, the various paths will, in general, each lead to different numerical values and hence will be inconsistent with each other. The choice as to which of these numerical values, if any, represents the correct answer should not be made subjectively. The method of least squares which is described in the preceding chapter represents an impartial analytic procedure to be applied to the data which have been surveyed in Chapters 4, 5, and 6.

One must be careful, however, not to apply the method of least squares blindly. It is not a substitute for careful selection of data; indeed lack of care in the selection of data may be more serious in a least-squares solution, since the error measures which can then be assigned to the output data will be unrealistically small. No provision exists in the method which can account for systematic error; the comparison of χ^2 with the theoretical probability table is useful in this regard but not definitive unless there are a great many more data than are usually present in an adjustment of the atomic constants. Thus, the selection of data becomes an important part of any analysis.

8.1 SELECTION OF DATA FOR A LEAST-SQUARES ANALYSIS

In a least-squares fitting each datum is to be assigned a weight which is inversely proportional to its variance. Such a weighting

is not arbitrary; it can be deduced directly from the form of the quadratic expression

$$Q = \Sigma (r_{\mu}/\sigma_{\mu})^2 \quad (8-1)$$

which we attempt to minimize. An observation with a large variance therefore carries little weight in determining the value of Q , and hence may be omitted without greatly affecting the result. There is, however, a more important reason for omitting data of low weight. When an experimenter designs his experiment he must carefully consider the possible presence of systematic error as well as the presence of random error. The random error of the final result can be reduced by duplication and repetition, since these errors are different in each repetition; the systematic errors, on the other hand, do not cancel out but remain. Now it is proper in an experiment to reduce any possible source of systematic error to a point where it may be of the order of one-tenth or one-third of the random error of a single observation. In this way the systematic error will be of the same order as, or smaller than, the random error of the final quoted result. However, it is neither feasible nor practical to do much better than this in the suppression of systematic error.

Thus an experiment with a quoted error which is large compared to another similar but more precise measurement may well be afflicted with a systematic error which is large compared to the accuracy of the second experiment. This systematic error would then a fortiori be large compared to the accuracy which might be claimed for the weighted mean of the two results. It would therefore be inappropriate to include the less precise observation in a weighted mean. A simple numerical example should demonstrate the situation. This is a completely artificial example which is not based on actual data.

Assume that we have two measurements of the velocity of electromagnetic radiation. Let these two results be

$$c_1 = 299788 \pm 5 \text{ km/sec}$$

$$c_2 = 299790.2 \pm 0.6 \text{ km/sec}$$

The weighted mean of these two measurements is 299790.17 ± 0.59 ; we have therefore gained very little in accuracy and have altered the value only slightly from the more precise result. Now consider

the situation which exists if c_1 actually suffers from a systematic error such that the result should be increased by 4.5 km/sec (such an error would not be unreasonable in view of the quoted standard error); the mean of the two should be increased to 299790.23 ± 0.59 . We therefore see that the inclusion of the imprecise datum has produced only a small shift in the value of c and that the shift it has made (relative to the more precise value) is actually in the wrong direction! In practice of course, we do not have as clear-cut a situation. For one thing we may not know that a systematic error exists, and for another the systematic error may indeed be in the precise value. In either case we gain very little from including an imprecise result in conjunction with data of much higher weight. We therefore base the selection of data upon the general principle that results of low estimated numerical precision shall be rejected if their assigned weights are such as to imply only a negligible influence on the entire solution.

It is also necessary to reject data which suffer from serious systematic error even if (and perhaps, especially if) the data are precisely measured. Grounds for the suspicion of such systematic error may arise either from experimental sources (such as a reevaluation of the conditions under which the experiment was performed under such circumstances that corrections for such systematic errors can not be made to the existing data) or from theoretical sources (in which, as in the case of the hyperfine structure splitting in hydrogen, the precision of the experiment is higher than the existing state of the theory of the experiment can handle).

a. Rejection of Low Weight Data

By the first criterion for rejection almost all the historically important early experiments, including many which were considered important as late as 1947, are excluded. Within their estimated precision ranges such measurements are not inconsistent with the later more precise results but they are relatively so much less accurate as to have quite negligible influence in the present (1955) least-squares adjustment. As a result of this criterion very few measurements published prior to 1950 remain. The exceptions, as we shall see, are Vinal and Bates' determination in 1914 of the Faraday constant with the iodine coulometer, the work on Λ by several researchers, notably by J. A. Bearden circa 1930 and by Tyrén, 1938,

and the precision determinations with various crystals of densities and x-ray lattice constants to obtain the product, $N\Lambda^3$, some of which date back to 1930.

b. Data Retained for Least-Squares Adjustment

We have surveyed in Chapters 5 and 6 the important experiments which have a bearing on the values of the atomic constants. We shall now collect here the results of those chapters which are to be used in an analysis of these constants.

1. The *conversion factor*, Λ , from the Siegbahn nominal scale of x-ray wavelengths (in x-units) to milliangstroms. We have used the value recommended by Sir Lawrence Bragg (see Section 5.3c), since it presumably superseded the earlier value quoted by R. T. Birge.*

$$\Lambda = 1.002020 \pm 0.000030 \quad (8-2)$$

2. The *Siegbahn-Avogadro number* N_s' . The data pertinent to this constant have been presented in Section 5.7. We use Birge's value converted to the physical scale

$$N_s' = N\Lambda^3 = 6.06179 \pm 0.00023 \times 10^{23} \text{ mole}^{-1} \quad (8-3)$$

3. The *fine structure separation in deuterium*, ΔE_D . The frequency separation between the levels $2^2P_{3/2}$ and $2^2P_{1/2}$ measured by Dayhoff, Triebwasser, and Lamb is discussed in Section 6.5; the result is

$$\begin{aligned} \Delta E_D &= \frac{1}{16} \alpha^2 \left(1 + \frac{5}{8} \alpha^2 \right) R_D c \left[1 + \frac{\alpha}{\pi} - 5.946 \frac{\alpha^2}{\pi^2} \right] \\ &= 10971.59 \pm 0.10 \text{ Mc/sec} \end{aligned} \quad (8-4)$$

4. The *gyromagnetic ratio of the proton*, γ_p , obtained at the National Bureau of Standards by Thomas, Driscoll, and Hipple before making the diamagnetic correction is (Section 6-3)

$$\gamma_p = \mu' N_e / M_p c = 26752.3 + 0.6 \text{ sec}^{-1} \text{ gauss}^{-1} \quad (8-5)$$

5. The determination of the *Faraday* by electrolysis is discussed in Section 3.6. Although more accurate values may soon be available, we are at the moment confronted with two somewhat discrepant measurements on silver and on iodine. The iodine value is

$$F = N_e / c = 9652.15 \pm 0.13 \text{ emu mole}^{-1} \text{ (physical)} \quad (8-6)$$

* In this regard, however, see the Addendum to Chapter 5.

and the silver is

$$F = Ne/c = 9651.29 \pm 0.19 \text{ emu mole}^{-1} \text{ (physical)} \quad (8-7)$$

6. The *magnetic moment of the proton* in terms of the nuclear magneton $\mu_n = eh/(4\pi m_p c)$ has been discussed in Section 6.4. Bloch and Jeffries obtain the value (uncorrected for diamagnetism)

$$\mu' = 2.79236 \pm 0.00010 \quad (8-8)$$

and Hipple, Sommer, and Thomas obtain for the same quantity

$$\mu' = 2.79268 \pm 0.00003 \quad (8-9)$$

7. There are three recent published results on the value of the *short wavelength limit* of the continuous x-ray spectrum as mentioned in Section 6.8. They are the measurement by Felt, Harris, and DuMond

$$hc^2/(\Delta e) = 12370.02 \pm 0.63 \text{ emu} \quad (8-10)$$

the value reported by Bearden, Johnson, and Watts

$$hc^2/(\Delta e) = 12371.03 \pm 0.48 \text{ emu} \quad (8-11)$$

and the value reported by Bearden and Schwarz

$$hc^2/(\Delta e) = 12370.77 \pm 1.03 \text{ emu} \quad (8-12)$$

In addition to these three results we shall also list here the value deduced in Section 6.8 (Table 6-3) based only on measurements carried out at voltages of less than 11000 volts. The error given in Table 6-3 is based solely on the consistency of the data with no allowance for possible interpretational error. The error in the position of the true end point could be as large as 1.4 kv x-units and hence with a realistic estimate of accuracy we adopt

$$hc^2/(\Delta e) = 12370.8 \pm 1.0 \text{ emu} \quad (8-13)$$

8. The *velocity of light* as measured by Bergstrand with Kerr-cell modulated light (the "geodimeter," see Section 5.1)

$$c = 299793.1 \pm 0.32 \text{ km sec}^{-1} \quad (8-14)$$

and as measured by K. D. Froome using microwave interferometry (Section 6.2)

$$c = 299792.6 \pm 0.7 \text{ km sec}^{-1} \quad (8-15)$$

In formulating the data (equations (8-2) to (8-15) inclusive) on which our input equations of observation are to be based, care has been taken to do so in such a way as to avoid hidden correlations between the equations of observation. For example, the measurements resulting from observed values of crystal densities and their x-ray grating constants are almost invariably quoted as measurements of Avogadro's number, N . To obtain N from these measurements, however, it is necessary to combine the results with the cube of the conversion constant, Λ . Consequently in equation (8-3) we have equated the numeric which was actually measured to the appropriate function, $N\Lambda^3$, of our primary unknowns. In other words we have been careful to see that no single measured quantity shall be involved as a substantial contributor to the error measures of two or more of the observational equations at once.

In addition to these data there are also certain auxiliary data which will not be subject to least-squares analysis. Such items fall into two classes. The first class is comprised of those quantities which are not overdetermined experimentally and can therefore be evaluated without recourse to least squares. The second class is comprised of those items which are of so much higher accuracy than those which are listed here for least-squares fitting that there is no need to use least squares to improve their accuracy since none of them is the major error contributor in any expression in which they appear combined with the "least-squares" variables; such quantities may be considered to be exactly determined quantities in the least-squares analysis.

9. An example of an item of the first class (and the only one which we shall use here) is the *universal gas constant*, R_0 . This constant is not part of the least-squares analysis, and it is utilized only to compute some of the derived constants of our final table of values. The numerical value, which has been computed in Section 3.3, is

$$R_0 = (8.31696 \pm 0.00034) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1} \quad (8-16)$$

10. In the second class of auxiliary data we have the *atomic masses* which were discussed in Chapter 4 and certain other accurately measured constants. The data from Chapter 4 which we will need are primarily the masses of hydrogen and deuterium, from which we calculate the masses of the proton and the deuteron using a value $Nm = 5.488 \times 10^{-4}$ for the atomic mass of the electron.

This value of Nm is sufficiently accurate in the present instance and is, to this accuracy, an essentially exact number.

$$H = 1.008142 \pm 0.000003 \quad (8-17)$$

$$M_p = 1.007593 \pm 0.000003 \quad (8-18)$$

$$H/M_p = 1.0005446 \quad (8-19)$$

$$D = 2.014735 \pm 0.000006 \quad (8-20)$$

$$M_d = 2.014186 \pm 0.000006 \quad (8-21)$$

$$D/M_d = 1.0002724 \quad (8-22)$$

11. The *Rydberg constant* for infinite mass, R_{∞} , is determined from observations of the spectrum of hydrogen and deuterium. The observed data must be interpreted in the light of the Lamb shift (Section 6.5), and the value which we shall adopt here is (1)

$$R_{\infty} = \alpha^3 \frac{mc^2}{4\pi e^2} = 109737.309 \pm 0.012 \text{ cm}^{-1} \quad (8-23)$$

We shall assume that this expression is exact. Hence it represents a constraint on the variables α , m , c , e and we may use equation (8-23) to eliminate one of the variables. It is most convenient to eliminate m rather than one of the other variables, since in this way we avoid fractional exponents; hence we write

$$m = 4\pi e^2 R_{\infty} / (\alpha^3 c^2) \quad (8-24)$$

12. The *anomalous magnetic moment of the electron* or, more correctly, the ratio of the electron moment to the Bohr magneton, μ_e/μ_0 , occurs in our analysis only as a correction factor. The experimental data on this constant were discussed in Section 6.6. Although the direct experimental evaluation of μ_e/μ_0 is not accurate enough to verify the theoretical formula, there is no reason at present to mistrust it, and hence we shall take

$$\mu_e/\mu_0 = 1 + \frac{\alpha}{2\pi} - 2.973 \frac{\alpha^2}{\pi^2} = 1.00114536 \quad (8-25)$$

13. The measurement of the *ratio of the electron magnetic moment* μ_e to the proton magnetic moment μ_p' (without diamagnetic correction) is so accurate as to warrant its inclusion in the category of fixed auxiliary constants. The disagreement between the results of

Koenig, Prodell, and Kusch (reference 28, Chapter 6) and Beringer and Heald (reference 30, Chapter 6) is small, and merely as a matter of convenience the former value has been adopted in preference to evaluating an appropriate weighted mean.

$$\mu_e/\mu_p' = M_p(\mu_e/\mu_0)/(Nm\mu') = 658.2288 \pm 0.0004 \quad (8-26)$$

14. There is one other constraint on the data which have been summarized in equations (8-2) to (8-26); this is the interrelation between the variables α , e , h , c . The variable h may therefore be eliminated by means of the relation

$$h = 2\pi e^2/(\alpha c) \quad (8-27)$$

8.2 PRELIMINARY LEAST-SQUARES ANALYSIS

The equations of observation for the least-squares analysis are formed from the data contained in equations (8-2) to (8-15). The auxiliary data, equations (8-16) to (8-27), are then used as exact relationships to reduce the number of variables in the solution. None of the error measures of equations (8-2) to (8-15) are appreciably influenced by this procedure so that the numerics of the observational equations remain uncorrelated, each having its error and hence its weight determined by one and only one of the data of equations (8-2) to (8-15). These observational equations together with the sources from which each arises and their relative standard errors are listed below. The numbers in parentheses on the left of each equation refer to the error-determining datum from which each numeric is derived. The numbers in square brackets refer to the auxiliary constants and equations which were used for eliminating variables in each observational equation. For brevity the physical units in which each numeric is expressed have been omitted. In each case these units are cgs units and e is the absolute value of the electronic charge in esu.

$$(8-2) \quad \Lambda = 1.002020 \quad (30 \text{ ppm}) \quad (8-28)$$

$$(8-3) \quad N\Lambda^3 = 0.606179 \times 10^{24} \quad (38 \text{ ppm}) \quad (8-29)$$

$$(8-4) \quad [8-20, 8-22, 8-23] \quad \alpha^2 c = 1.596412 \times 10^6 \quad (9 \text{ ppm}) \quad (8-30)$$

$$(8-5) \quad [8-23, 8-24, 8-25, 8-26] \quad \alpha^3 c/e = 2.425517 \times 10^{13} \quad (23 \text{ ppm}) \quad (8-31)$$

$$(8-6) \quad Ne/c = 9652.15 \quad (13 \text{ ppm}) \quad (8-32)$$

$$(8-7) \quad Ne/c = 9651.29 \quad (20 \text{ ppm}) \quad (8-33)$$

$$(8-8) \quad [8-23, 8-24, 8-25, 8-26] \quad Ne^2/(\alpha^3 c^2) = 3.979879 \times 10^{-10} \quad (36 \text{ ppm}) \quad (8-34)$$

$$(8-9) \quad [8-23, 8-24, 8-25, 8-26] \quad Ne^2/(\alpha^3 c^2) = 3.979423 \times 10^{-10} \quad (11 \text{ ppm}) \quad (8-35)$$

$$(8-10) \quad [8-27] \quad ec/(\Lambda\alpha) = 1968.750 \quad (51 \text{ ppm}) \quad (8-36)$$

$$(8-11) \quad [8-27] \quad ec/(\Lambda\alpha) = 1968.911 \quad (40 \text{ ppm}) \quad (8-37)$$

$$(8-12) \quad [8-27] \quad ec/(\Lambda\alpha) = 1968.869 \quad (83 \text{ ppm}) \quad (8-38)$$

$$(8-14) \quad c = 2.997926 \times 10^{10} \quad (2.3 \text{ ppm}) \quad (8-39)$$

$$(8-15) \quad c = 2.997931 \times 10^{10} \quad (1.1 \text{ ppm}) \quad (8-40)$$

In order to carry out the least-squares fitting these equations must be linearized as described in Section 7.1; we arbitrarily adopt the following origin values:

$$\alpha_0 = 0.007297000$$

$$c_0 = 4.802200 \times 10^{-10} \text{ esu}$$

$$N_0 = 0.6025000 \times 10^{24} \text{ mole}^{-1}$$

$$\Lambda_0 = 1.0020200$$

$$c_0 = 2.9979000 \times 10^{10} \text{ cm sec}^{-1}$$

and with these we define the linearized variables x_1, \dots, x_5 as follows:

$$\alpha = \alpha_0(1 + 10^{-5}x_1)$$

$$c = c_0(1 + 10^{-5}x_2)$$

$$N = N_0(1 + 10^{-5}x_3)$$

$$\Lambda = \Lambda_0(1 + 10^{-5}x_4)$$

$$c = c_0(1 + 10^{-5}x_5)$$

so that the x 's are the relative deviation of the primitive variables from the origin values expressed in parts per hundred thousand. These values are then substituted into equations (8-28) to (8-40) to give a set of thirteen linear equations in five unknowns. These equations will serve as the basis of a least-squares analysis; they are listed below in the same order in which the equations from which they came appear above. To indicate more clearly the relationship between the observational equations and the linearized set which is derived from them, the latter will bear the same equation number

as the equation from which they come with an added prime. The linearized equations are therefore

	x_4	=	0 ± 3.0	Weight	0.11	(8-28')
	$x_3 + 3x_4$	=	3.5 ± 3.8		0.07	(8-29')
$2x_1$	x_5	=	9.0 ± 0.9		1.23	(8-30')
$3x_1 - x_2$	x_5	=	-1.3 ± 2.3		0.19	(8-31')
	$x_2 + x_3$	-	$x_5 = 10.1 \pm 1.3$		0.58	(8-32')
	$x_2 + x_3$	-	$x_5 = 1.2 \pm 2.0$		0.25	(8-33')
$-3x_1 + 2x_2 + x_3$	$-2x_5$	=	22.9 ± 3.6		0.08	(8-34')
$-3x_1 + 2x_2 + x_3$	$-2x_5$	=	11.5 ± 1.1		0.83	(8-35')
$-x_1 + x_2$	$-x_4 + x_5$	=	-10.6 ± 5.1		0.04	(8-36')
$-x_1 + x_2$	$-x_4 + x_5$	=	-2.4 ± 4.0		0.06	(8-37')
$-x_1 + x_2$	$-x_4 + x_5$	=	-4.6 ± 8.3		0.015	(8-38')
	x_5	=	0.87 ± 0.23		19.8	(8-39')
	x_5	=	1.03 ± 0.11		83.0	(8-40')

The weight attached to each equation is the square of the reciprocal of the standard deviation of the numeric on the right-hand side of the equation.

Inconsistencies exist in this set. Thus, for example, it is apparent that (8-32') and (8-33') are not consistent, since the difference between them is 8.9 ± 2.4 ; and that (8-34') and (8-35') are not consistent, since their difference is 11.4 ± 3.8 ; and that (8-36'), (8-37'), and (8-38') exhibit a disagreement among themselves which is outside the error limits attached to these data. However, it will

Tabl 8-1. Least-Squares Adjusted Values

(Preliminary adjustment)

Linearized Unknowns	Primitive Variables
$x_1 = 3.61$	$\alpha = 0.007297264$
$x_2 = 14.21$	$e = 4.802882 \times 10^{-10}$ abs esu
$x_3 = -4.59$	$N = 0.6024723 \times 10^{24}$ (g mole) ⁻¹ (phys.)
$x_4 = 4.29$	$\Lambda = 1.002063$
$x_5 = 0.98$	$c = 2.9979294 \times 10^{10}$ cm sec ⁻¹

Table 8-2. Error Matrix

The elements are the variances and covariances in (parts per 10⁶)².

	α	e	N	Λ	c	m	h
α	0.198	0.556	-0.545	0.181	-0.005	0.529	0.920
e	0.556	3.041	-3.769	1.259	-0.006	4.426	5.533
N	-0.545	-3.769	5.479	-1.777	0.016	-5.936	-7.009
Λ	0.181	1.259	-1.777	1.751	-0.003	1.980	2.340
c	-0.005	-0.006	0.016	-0.003	0.010	-0.017	-0.008
m	0.529	4.426	-5.936	1.980	-0.017	7.298	8.340
h	0.920	5.533	-7.009	2.340	-0.008	8.340	10.163

be useful and instructive to carry out a least-squares analysis on this set as it stands without further screening to determine which of the equations should be omitted in a final analysis because they are suspected of being the victim of systematic error. We shall call this our preliminary analysis. The adjusted values, the error matrix, and the correlation coefficients of this least-squares adjustment are given in Tables 8-1, 8-2, and 8-3. The error matrix of Table 8-2 has been extended to include the variables m and h . These two variables were eliminated from the least-squares solution by the use of the auxiliary equation (8-24) and (8-27). It is, however, inconvenient to be forced to use these equations in order to express m and h in terms of our primary variables each time one needs to compute correlation coefficients between these variables and other variables. These variances and correlation coefficients can be cal-

Table 8-3. Correlation Coefficients and Standard Errors

(Internal, a priori, consistency)

	α	e	N	Λ	c	m	h
α	1.000	0.717	-0.523	0.308	-0.115	0.441	0.649
e	0.717	1.000	-0.923	0.546	-0.036	0.939	0.996
N	-0.523	-0.923	1.000	-0.574	0.070	-0.937	-0.940
Λ	0.308	0.546	-0.574	1.000	-0.021	0.554	0.555
c	-0.115	-0.036	0.070	-0.021	1.000	-0.063	0.025
m	0.441	0.939	-0.937	0.554	-0.063	1.000	0.969
h	0.649	0.996	-0.940	0.555	0.025	0.969	1.000

Standard Errors—parts per 10⁵

	α	e	N	Λ	c	m	h
	0.445	1.744	2.341	1.323	0.098	2.702	3.188

culated once and for all by the use of equations (7-20) and (7-24). Thus, although we have produced a matrix of seventh order, it is still only of the fifth rank since the last two rows (or columns) can be expressed as linear combinations of the other rows (or columns). The near equality of m and h columns of the matrix of correlation coefficients (Table 8-3) is a reflection of strong coupling between the adjusted values of these two variables. This is a result of the relationship

$$m = \frac{2R_{\infty}h}{c\alpha^2} \quad (8-41)$$

in which R_{∞} , the Rydberg constant, was assumed to have no error while c and α have relative standard errors which are much smaller than the error in either m or h .

8.3 ANALYSIS OF THE PRELIMINARY LEAST-SQUARES ADJUSTMENT

We have found the adjusted values of the primary variables as well as their standard errors and correlation coefficients as contained in the error (or variance) matrix. This does not complete the solu-

Table 8-4. Comparison of Input and Output Values of the Least-Squares Analysis

Equation Number	c_{μ} Input Numeric	c_{μ}^* Output Numeric	c_{μ}^i Indirect Value
8-28'	0.0 \pm 3.0	4.29 \pm 1.32	5.31 \pm 1.47
8-29'	3.5 \pm 3.8	8.26 \pm 3.25	21.86 \pm 6.38
8-30'	9.0 \pm 0.9	8.20 \pm 0.88	---
8-31'	-1.3 \pm 2.3	-2.40 \pm 1.20	-2.81 \pm 1.41
8-32'	10.1 \pm 1.3	8.96 \pm 0.98	15.37 \pm 2.24
8-33'	1.2 \pm 2.0		
8-34'	22.9 \pm 3.6	12.02 \pm 0.93	10.30 \pm 1.98
8-35'	11.5 \pm 1.1		
8-36'	-10.6 \pm 5.1		
8-37'	-2.4 \pm 4.0	7.29 \pm 1.31	10.48 \pm 1.47
8-38'	-4.6 \pm 8.3		
8-39'	0.87 \pm 0.23	0.98 \pm 0.10	-----
8-40'	1.03 \pm 0.11		

$$\chi^2 = \Sigma \left(\frac{c_{\mu} - c_{\mu}^*}{\sigma_{\mu}} \right)^2 = 52.1$$

tion; we must also compute the adjusted values of the input numerics and hence determine the correction to each experiment which is implied by the least-squares fitting. These values are shown in Table 8-4, in which we list the input numeric of our observational equations c_μ and the least-squares fitted value c_μ^* . From this we calculate the value of χ^2 which is the minimum value of the quadratic expression Q , equation (8-1); we have

$$r_\mu = c_\mu - c_\mu^*$$

and hence

$$\chi^2 = \sum_\mu \left(\frac{c_\mu - c_\mu^*}{\sigma_\mu} \right)^2 = 52.1 \quad (8-42)$$

This value of χ^2 is quite large, since with thirteen equations and five unknowns there are eight degrees of freedom, and hence we would expect $\chi^2 = 8$. A value of χ^2 as large as 52.1 is highly improbable; the probability is less than 0.001 that this statistic would exceed 26.1 entirely as a result of random error (2). It is therefore apparent that we may say, almost with certainty, either that there are systematic errors in the observational equations or else that the standard errors of these equations have been underestimated.

The most convenient method for investigating the existence of systematic error in a set of data such as the one at hand is the comparison of input and effective values. The effective or indirect values of each input numeric are defined in equations (7-51) and (7-52). In those cases in which there are two or three individual measurements of the same quantity (as, for example, the short wavelength limit of the continuous x-ray spectrum) it is convenient to combine all these data into one item by taking a weighted mean and then calculating the indirect value associated with this weighted datum. This has the effect of asking for the solution of the least-squares equations if *all* the data on a given experimental determination were excluded simultaneously. It is of course possible to ask for the indirect value based on the exclusion of one datum at a time; however, all the measurements of a given quantity may suffer from the same systematic error or we may be interested in whether one item or the other agrees best with all the remaining data; in such instances it is best to exclude the items together. The indirect values for equation (8-30') and the combination of equations (8-39') and

(8-40'), which represent, respectively, $\alpha^2 c$ and c , are omitted because the numerical accuracy with which the indirect values can be determined is so poor that the numbers would not be significant. The direct measurements are so accurate and hence have so much weight that the effect of the indirect value is of the same order as the rounding error of the numerical calculation.

The implications of Table 8-4 are direct and conclusive. If we look at equations (8-32') and (8-33') which represent the iodine and silver Faradays, respectively, it is apparent that the former is much more consistent with the indirect value than is the latter. The difference between the input numeric of (8-32') and the indirect value is 5.3 ± 2.6 , while the difference between that of (8-33') and the indirect value is 14.2 ± 3.0 . Thus it is quite probable that the value of the Faraday deduced from the silver coulometer is in error. The possible sources of error have been discussed in Section 3-6, and the physical interpretation then strengthens the significance of the statistical implication.

Similarly, equation (8-35'), which is Hipple, Sommer, and Thomas' measurement of the proton magnetic moment, differs from the indirect value by 1.2 ± 2.3 , whereas the Bloch and Jeffries result, equation (8-34'), differs by 12.6 ± 4.1 . Collington, Dellis, Sanders, and Turberfield (reference 16, Chapter 6) have indicated that there is indeed a possible source of systematic error in the Bloch and Jeffries result, and their improved apparatus yielded a value (Section 6.4, equation 6-7a) which would correspond to an input numeric, $c_\mu = 9.8 \pm 1.5$, in terms of the linearized variables of Table 8-4. Hence Collington, Dellis, Sanders, and Turberfield's result is in excellent agreement both with the omegatron value and with the indirect value implied by the combination of all the other data. There is thus adequate reason to suspect the Bloch and Jeffries result.*

The determination of the short wavelength limit of the continuous x-ray spectrum (equations 8-36', 8-37', 8-38') are all in disagreement with the indirect value. Hence we may tend to doubt the direct data. There are certainly valid experimental reasons to believe that

* The reanalysis of the Bloch and Jeffries experiment by K. R. Trigger (reference 15a, Chapter 6), which appeared after this section was written, confirms our statistical conclusions (see Section 6.4).

we should; these have been thoroughly discussed in Section 6.8. We are therefore tempted to reject all these data; the implications of such a move will be treated more fully below.

A word of caution is in order at this point. Of the thirteen items which were included in this preliminary analysis we have deduced reasons to reject five. This represents a rather drastic censoring and should be carried out with care. As soon as we eliminate one item the values of all of the other adjusted output values change. Hence strictly we should reevaluate the least-squares solution after each rejection in order to determine the basis for the subsequent rejections. Furthermore, the decision to reject a datum as discrepant may very well depend upon the order in which other data are rejected. It is quite possible, in general, that a particular experimental result is in disagreement with the indirectly determined value, not because of an error in the experiment itself, but because some other error-ridden experiment is strongly distorting the indirect value. If the latter experiment were rejected first, the former one might well be retained.

A completely different approach to the problem of determining which equations of the thirteen are likely to suffer from systematic error is afforded by an analysis of variance approach. Such an analysis has been performed (3) on the data represented by the set of equations (8-28) to (8-40); this analysis involves the calculation of χ^2 for every possible subset of the thirteen equations and the comparison of these values of χ^2 to determine whether the large value of $\chi^2 = 52.1$ can be ascribed to the effect of one or a few items or whether all the data contribute equally to this large value. In the first instance we would be willing to say that those items responsible for anomalously large contributions to χ^2 were, in fact, suffering from systematic error; in the second instance we would ascribe an increased standard error to all the data and admit that if systematic errors existed they were so widespread as to defy identification.

A complete and exhaustive survey would be prohibitively long and expensive, even with the use of modern high-speed electronic digital computers. Furthermore, the velocity of light, c , is determined so accurately by direct experiments and the correlation between c and the other variables is so small (see Table 8-3) that it was felt justifiable to eliminate c from the least-squares analysis and

consider it instead as an auxiliary fixed constant. From Table 8-3 it is clear that a shift in the value of c of ten of its standard errors would not shift the values of any of the other unknowns, with the exception of α , by one of their standard errors and in the case of α the shift would exceed σ_α by less than 20 per cent. Such a shift of ten standard errors in c is sufficient to include the result of Hansen and Bol's microwave cavity measurements at Stanford University, and there seems extremely little evidence that the true value is likely to differ from the weighted mean of equations (8-39) and (8-40) by more than this. The value of c and its standard error given in Tables 8-1 and 8-3 correspond to giving the linearized variable, x_5 , the value, $x_5 = 1 \pm 0.1$. Substituting this value for x_5 in the linearized equations (8-28') to (8-38') reduces the set to eleven input equations in four unknowns.

A program of calculation of χ^2 for various subsets of this system of eleven equations in four unknowns yielded 219 cases (which is far from exhaustive). The survey, although not complete, is adequate to confirm the implications of Table 8-4: that the silver coulometer value for the Faraday constant and Bloch and Jeffries' proton magnetic moment determination are in error and that all the short wavelength limit measurements are also suspect. Actually suspicion does not fall strongly on the Bearden and Schwarz value, but this is due more to its low weight than to its close agreement. Thus although the residue of equation (8-38') is in most comparisons as large or larger than the residues of equations (8-36') and (8-37'), its contribution to χ^2 is much smaller because of its much larger assigned standard error.

8.4 SELECTION OF "BEST" CURRENT VALUES

Because of the uncertainty associated with the interpretation of the short wavelength limit, the three equations (8-10), (8-11), and (8-12) were replaced by the single equation (8-13). Using this value for the short wavelength limit and omitting the silver Faraday and Bloch and Jeffries' proton magnetic moment measurements, we can repeat the least-squares calculation. We now have reduced the system to seven equations in four unknowns. We therefore have three degrees of freedom. The calculated value of χ^2 is 3.25, which is deceptively close to the expectation value, since the 90 per cent confidence interval is $0.352 < \chi^2 < 7.815$.

If the short wavelength limit measurements are dropped entirely (and a strict adherence to the conditions set down in Section 8.1 would require that we do so), the resulting system of six equations in four unknowns has a χ^2 equal to 0.44. This value of χ^2 may appear at first sight to be quite low compared to the expectation value $\chi^2 = 2$; however, a system of only two degrees of freedom is not very significant with regard to statistical discrimination, since the 90 per cent confidence interval is quite broad: $0.103 < \chi^2 < 5.99$. In fact, the probability that χ^2 would lie between 0 and 0.44 for a system with two degrees of freedom is almost 20 per cent. Furthermore, the actual solution is quite insensitive to whether or not the short wavelength limit data are retained. The maximum change in the best value of any of the variables is less than one-fourth of the assigned standard deviation.

The system of seven equations in four unknowns which is obtained when we exclude those data which appear to be discordant with the remainder of our data and consider the velocity of light as a fixed auxiliary, is given below. In each instance the number of the equation in Section 8.2 from which the present equation is derived is given in square brackets on the left.

			Weight	Description of Experimental Source	
[8-28]	$x_4 =$	0	0.11	$\Lambda = 1.002020$	(8-43)
[8-29]	$x_3 + 3x_4 =$	3.5	0.07	$N\Lambda^3$ (Birge's average)	(8-44)
[8-30]	$x_1 =$	4.0	4.92	Dayhoff Fine Structure Splitting in Deuterium	(8-45)
[8-31]	$3x_1 - x_2 =$	-2.3	0.19	Thomas, Driscoll, and Hipple gyromagnetic ratio of proton	(8-46)
[8-32]	$x_2 + x_3 =$	11.1	0.58	(Iodine) Faraday by elec- tro-chemistry	(8-47)
[8-35]	$-3x_1 + 2x_2 + x_3 =$	13.5	0.83	Sommer, Thomas, and Hipple (omegatron) mag. mom. of proton	(8-48)
[8-38]	$-x_1 + x_2 - x_4 =$	-5.6	0.015	Short wavelength limit of continuous x-ray spec- trum. Mean of low- volt- age values.	(8-49)

The normal equations are formed according to the rules given in Section 7.4; they are

$$(\alpha) \quad 14.115x_1 - 5.565x_2 - 2.490x_3 + 0.015x_4 = -15.162 \quad (8-50)$$

$$(e) \quad -5.565x_1 + 4.105x_2 + 2.240x_3 - 0.015x_4 = 29.201 \quad (8-51)$$

$$(N) \quad -2.490x_1 + 2.240x_2 + 1.480x_3 + 0.210x_4 = 17.888 \quad (8-52)$$

$$(\Lambda) \quad 0.015x_1 - 0.015x_2 + 0.210x_3 + 0.755x_4 = 0.819 \quad (8-53)$$

It should be noted here that the normal equations are to be formed exactly according to the rules of Section 7.4 and that no simplification or cancellation should be made in the equations. This is because the coefficients of the normal equations have a significance which is not limited to the determination of the values of the x_i . An alteration in the equations which would not alter the solution (such as the cancellation of a common factor in one of the equations or even the reordering of the equations in the set) can destroy the identification of the coefficients of the normal equations as the weight matrix of the solution.

The error (or variance) matrix of the solution is the inverse of the matrix of the coefficients of the normal equations. Hence the error matrix is

$$V = \begin{pmatrix} 0.1989 & 0.5760 & -0.5603 & 0.1633 \\ 0.5760 & 3.4478 & -4.4319 & 1.2898 \\ -0.5603 & -4.4319 & 6.7167 & -1.9452 \\ 0.1633 & 1.2898 & -1.9452 & 1.8879 \end{pmatrix} \quad (8-54)$$

and the solution for the variables is

$$\begin{aligned} x_1 &= 3.92 \\ x_2 &= 13.72 \\ x_3 &= -2.37 \\ x_4 &= 1.94 \end{aligned} \quad (8-55)$$

The value of χ^2 for this solution is

$$\chi^2 = 3.25 \quad (8-56)$$

This is to be compared to the value 52.1 which was obtained in the preliminary adjustment of Section 8.2. The major change in the variables caused by the deletion of those data suspected of syste-

matic error is an increase in x_3 of 2.23 and an attendant decrease in x_4 of 2.35; this corresponds to a change in Avogadro's number N of 22.3 ppm and a change in the conversion factor Λ of -23.5 ppm.

The value of χ^2 can be expressed equivalently in terms of the ratio of external to internal consistency

$$r_e/r_i = \sqrt{\chi^2/(n - q)} = 1.041$$

The 90 per cent confidence interval for r_e/r_i with three degrees of freedom is $0.594 < r_e/r_i < 2.795$. Hence there is no particular compunction to use internal rather than external consistency measures; our data tell us only that the two measures are consistent.

Table 8-5. Variance, Covariance, and Correlation Coefficients
(Recommended least-squares adjustment)

	<i>e</i>	<i>m</i>	<i>h</i>	α	Λ	<i>N</i>	<i>F</i>
<i>e</i>	374	560	685	62.5	140	-480	-107
<i>m</i>	<i>0.949</i>	940	1057	60.4	226	-778	-219
<i>h</i>	<i>0.996</i>	<i>0.971</i>	1264	103.5	262	-899	-216
α	<i>0.698</i>	<i>0.426</i>	<i>0.628</i>	21.5	17.7	-60.6	1.7
Λ	<i>0.507</i>	<i>0.516</i>	<i>0.515</i>	<i>0.267</i>	204	-211	-71
<i>N</i>	<i>-0.922</i>	<i>-0.941</i>	<i>-0.938</i>	<i>-0.484</i>	<i>-0.548</i>	726	246
<i>F</i>	<i>-0.469</i>	<i>-0.607</i>	<i>-0.509</i>	<i>0.035</i>	<i>-0.421</i>	<i>0.774</i>	141
<i>Standard Errors (ppm)</i>							
	19.3	30.6	35.5	4.6	14.3	26.9	11.8

We shall, however, quote our final error matrix in terms of external consistency since this is the larger measure (albeit not significantly so). Furthermore, the error matrix (8-54) will be reexpressed in terms of relative parts per million in the variables e , m , h , α , Λ , N , F . The error matrix and correlation coefficients are given in Table 8-5. Since the matrix of the covariances and the matrix of the correlation coefficients are both symmetric, we can conserve space and present them in a single square array. The variances appear on the diagonal of this array, the covariances in the upper right triangle, and the correlation coefficients in italics in the lower left triangle.

8.5 OUTPUT VALUES. RECOMMENDED (1955) LEAST-SQUARES ADJUSTMENT

The 1955 adjustment is based, as has been explained earlier, on the determination of four primary unknowns α , e , N , and Λ , by

least-squares adjustment from seven independent sources of experimental input data combined with a number of auxiliary constants whose values are known so much more accurately than the afore-mentioned input data that they are negligible error contributors. These auxiliary constants are listed in Table 8-6 with a star. The unstarred auxiliary constants in Table 8-6 either were used merely for computing the derived values of Table 8-7 and therefore

Table 8-6. 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

$$R_{\text{H}} = 109677.576 \pm 0.012 \text{ cm}^{-1}$$

$$R_{\text{D}} = 109707.419 \pm 0.012 \text{ cm}^{-1}$$

$$R_{\text{H}^3} = 109717.345 \pm 0.012 \text{ cm}^{-1}$$

$$R_{\text{H}^4} = 109722.267 \pm 0.012 \text{ cm}^{-1}$$

Velocity of light*

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

Atomic mass of neutron (physical scale)

$$M_n = 1.008982 \pm 0.000003$$

Atomic mass of hydrogen (physical scale)

$$H = 1.008142 \pm 0.000003$$

Atomic mass ratio of hydrogen to proton*

$$H/M_p = 1.00054461 \text{ (computed using atomic mass of electron)} \\ Nm = 0.00054875)$$

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*

$$D/M_d = 1.00027244 \text{ (computed using atomic mass of electron,)} \\ Nm = 0.00054875) \text{ (physical scale)}$$

Ratio of electron magnetic moment to proton magnetic moment 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 of electron*

$$\mu_e/\mu_0 = (1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 1.00114536 \\ \text{(Computed using the value } 1/\alpha = 137.037)$$

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)

$$V_0 = 22420.7 \pm 0.6 \text{ cm}^3 \text{ atm mole}^{-1}$$

^a S. H. Koenig, A. G. Prodell, and P. Kusch, *Phys. Rev.*, **88**, 191 (1952).

Table 8-7. Least-Squares Adjusted Output Values

The quantity following each \pm sign is the standard error. 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 error matrix of Table 8-5 must be used.

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)	$F = Ne = (2.89366 \pm 0.00003) \times 10^{14} \text{ esu (g mole)}^{-1}$ $F' = Ne/c = (9652.19 \pm 0.11) \text{ emu (g mole)}^{-1}$
Charge-to-mass ratio of the electron	$e/m = (5.27305 \pm 0.00007) \times 10^{17} \text{ esu g}^{-1}$ $e'/m = e/(mc) = (1.75890 \pm 0.00002) \times 10^7 \text{ emu g}^{-1}$
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	$H/M_p = \left[1 - \frac{Nm}{H} (1 - \alpha^2/2) \right]^{-1}$ $= 1.000544613 \pm 0.00000006$

^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 $m(1 - \alpha^2/2 + \dots)$.

Table 8-7. Least-Squares Adjusted Output Values (continued)

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

$$\mu = mM_p/H = (9.1034 \pm 0.0003) \times 10^{-28} \text{ g}$$

Schrodinger constant for a fixed nucleus

$$2m/\hbar^2 = (1.63836 \pm 0.00007) \times 10^{27} \text{ erg}^{-1} \text{ cm}^{-2}$$

Schrodinger 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

$$\begin{aligned} a_0 &= \hbar^2/(me^2) = \alpha/(4\pi R_\infty) \\ &= (5.29172 \pm 0.00002) \times 10^{-9} \text{ cm} \end{aligned}$$

Radius of electron orbit in normal H¹, referred to center of mass

$$a_0' = a_0(1 - \alpha^2)^{1/2} = (5.29158 \pm 0.00002) 10^{-9} \text{ cm}$$

Separation of proton and electron in normal H¹

$$a_0'' = a_0'R_\infty/R_H = (5.29446 \pm 0.00002) \times 10^{-9} \text{ cm}$$

Compton wavelength of the electron

$$\begin{aligned} \lambda_{ce} &= h/(mc) = \alpha^2/(2R_\infty) = (24.2626 \pm 0.0002) \times 10^{-11} \text{ cm} \\ \lambda_{ce} &= \lambda_{ce}/(2\pi) = (3.86151 \pm 0.00004) \times 10^{-11} \text{ cm} \end{aligned}$$

Compton wavelength of the proton

$$\begin{aligned} \lambda_{cp} &= h/(m_p c) = (13.2141 \pm 0.0002) \times 10^{-14} \text{ cm} \\ \lambda_{cp} &= \lambda_{cp}/(2\pi) = (2.10308 \pm 0.00003) \times 10^{-14} \text{ cm} \end{aligned}$$

Compton wavelength of the neutron

$$\begin{aligned} \lambda_{cn} &= h/(m_n c) = (13.1959 \pm 0.0002) \times 10^{-14} \text{ cm} \\ \lambda_{cn} &= \lambda_{cn}/(2\pi) = (2.10019 \pm 0.00003) \times 10^{-14} \text{ cm} \end{aligned}$$

Classical electron radius

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

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

$$\begin{aligned} \Delta E_H &= (1/16) R_H \alpha^2 [1 + \alpha/\pi + (5/8 - 5.946/\pi^2)\alpha^2] \\ &= 0.365871 \pm 0.000003 \text{ cm}^{-1} \\ &= 10968.56 \pm 0.10 \text{ Mc sec}^{-1} \end{aligned}$$

Fine structure separation in deuterium

$$\begin{aligned} \Delta E_D &= \Delta E_H R_D/R_H = 0.365970 \pm 0.000003 \text{ cm}^{-1} \\ &= 10971.54 \pm 0.10 \text{ Mc sec}^{-1} \end{aligned}$$

Zecman 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

$$\begin{aligned} k &= R_0/N = (1.38044 \pm 0.00007) \times 10^{-16} \text{ erg deg}^{-1} \\ k &= (8.6167 \pm 0.0004) \times 10^{-5} \text{ ev deg}^{-1} \\ 1/k &= 11605.4 \pm 0.5 \text{ deg ev}^{-1} \end{aligned}$$

Table 8-7. Least-Squares Adjusted Output Values (continued)

 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

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

Wien's displacement law constant^b

$$\lambda_{\max} T = c_2/(4.96511423) = 0.289782 \pm 0.000013 \text{ cm deg}$$

Stefan-Boltzmann constant

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

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

$$(S_0/R_0)_{\text{Ph}} = \frac{5}{2} + \ln\{(2\pi R_0)^{3/2} h^{-3} N^{-4}\}$$

$$= -5.57324 \pm 0.00007$$

$$(S_0)_{\text{Ph}} = -(46.3524 \pm 0.0014) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1}$$

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

$$(S_0/R_0)_{\text{Ch}} = -5.57256 \pm 0.00007$$

$$(S_0)_{\text{Ch}} = -(46.2467 \pm 0.0014) \times 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1}$$

Bohr magneton

$$\mu_0 = he/(4\pi mc) = e\lambda_{ce}/2$$

$$= (0.92731 \pm 0.00002) \times 10^{-20} \text{ erg gauss}^{-1}$$

Anomalous electron moment correction

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

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

Magnetic moment of the electron

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

Nuclear magneton

$$\mu_n = he/(4\pi m_p c) = \mu_0 N m/H^+$$

$$= (0.505038 \pm 0.000018) \times 10^{-23} \text{ erg gauss}^{-1}$$

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

$$1 \text{ g} = (5.61000 \pm 0.00011) \times 10^{26} \text{ Mev}$$

$$1 \text{ electron mass} = 0.510976 \pm 0.000007 \text{ Mev}$$

$$1 \text{ atomic mass unit} = 931.141 \pm 0.010 \text{ Mev}$$

$$1 \text{ proton mass} = 938.211 \pm 0.010 \text{ Mev}$$

$$1 \text{ neutron mass} = 939.505 \pm 0.010 \text{ Mev}$$

^b The numerical constant 4.96511423 is the root of the transcendental equation, $x = 5(1 - e^{-x})$.

Table 8-7. Least-Squares Adjusted Output Values (continued)

Quantum energy conversion factors

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

de Broglie wavelengths, λ_D , of elementary particles^a

Electrons

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

Protons

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

Neutrons

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

Energy of 2200 m/sec neutron

$$\begin{aligned}
 E_{2200} &= 0.0252973 \pm 0.0000003 \text{ ev} \\
 T_{2200} &= 293.585 \pm 0.012 \text{ }^\circ\text{K} \\
 &= 20.435 \pm 0.012 \text{ }^\circ\text{C}
 \end{aligned}$$

The Rydberg and related derived constants

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

Hydrogen ionization potential

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

^a 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 $\lambda_D = \lambda_c[\epsilon(\epsilon + 2)]^{-1/2}$, 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.

entered the computations only after the least-squares adjustment had been effected, or are given simply for their intrinsic utility.

The physical scale of atomic weights is used almost exclusively

in these tables, the Sackur-Tetrode constant (given on both physical and chemical scales) being the sole exception. The conversion factor between these scales, $r = 1.000272 \pm 0.000005$ calculated by R. T. Birge on the basis of the abundance ratio for the oxygen isotopes, $O^{16} : O^{18} : O^{17} = (506 \pm 10) : 1 : (0.204 \pm 0.008)$, is adopted here as a definition for the chemical scale. These abundance ratios, and the value of r implied by them, are subject to variation depending on the source of the oxygen. The value of the O^{16}/O^{18} ratio can vary from approximately 495 for oxygen from air or carbonates to 515 for oxygen from water and rocks. Corresponding to this variation is a variation in the value of r from 1.000278 to 1.000268 (4, 5). The International Commission on Atomic Weights is at present (1957) considering the arbitrary redefinition of the chemical scale of atomic weights in terms of the physical scale and the value, $r = 1.000275$. The accuracy ascribed to our adopted value is such that these two numbers do not differ significantly (approximately one-half the standard error).

The new Kelvin scale of temperature adopted October 1954 in Paris at the Tenth General Conference on Weights and Measures is here used. On this scale the triple point of water is assigned the temperature 273.16° K exactly. This changes the numerical value of the gas constant, R_0 , slightly from that used in earlier evaluations and gives the value of the ice point as $273.1500 \pm 0.0002^\circ$ K. Absolute electrical units are used exclusively, the "international" electrical units having been abolished in 1948.

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Author Index

- Aamodt, R. L., 38, 39 (ref. 22), 46 (ref. 22), 48 (ref. 22), 93
Aggson, T. L., 65, 96
Airy, Sir G. B., 14
Aitken, A. C., 226 (ref. 9), 246
Alford, W. L., 80 (ref. 171), 100
Allison, S. K., 121 (ref. 23), 142 (ref. 53), 180, 181
Alvarez, L. W., 61 (ref. 82), 69 (ref. 116a), 70 (ref. 126, 128), 71, 75, 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 95, 98, 99
Alvial, G., 66 (ref. 107), 77 (ref. 107), 97
Amaldi, E., 59 (ref. 71), 63 (ref. 94), 64, 77, 79, 94-96, 99, 100
Ambler, E., 64, 75 (ref. 96b), 96
Anand, B. M., 47, 93
Anderson, C. D., 32 (ref. 9), 63 (ref. 94), 79 (ref. 166), 87 (ref. 186), 88 (ref. 196), 91 (ref. 196), 92, 96, 100, 101
Anderson, F., 66 (ref. 107), 77 (ref. 107), 97
Anderson, W. C., 108, 111, 112, 184, 179
Annis, M., 66 (ref. 106), 78 (ref. 106), 97
Arago, D. F. J., 106
Armenteros, R., 66 (ref. 105), 69 (ref. 117), 77 (ref. 156), 79 (ref. 164), 87 (ref. 185), 91 (ref. 185), 97-101
Arnold, W. H., Jr., 69 (ref. 115), 70 (ref. 120), 71 (ref. 120), 76 (ref. 150, 151), 79 (ref. 115), 87 (ref. 189), 91 (ref. 189), 98, 99, 101
Arnowitt, R., 206 (ref. 42), 221
Aron, W. A., 66 (ref. 104), 97
Ascoli, G., 52, 94
Ashkin, J., 34 (ref. 15), 92
Aslakson, C. I., 109, 184, 188, 220
Astbury, J. P., 69 (ref. 118), 70 (ref. 118), 72 (ref. 135), 78 (ref. 160), 81 (ref. 174), 87 (ref. 160), 98-100
Astier, A., 77 (ref. 156), 99
Bäcklin, E., 118, 121, 124, 172
Ballam, J., 66 (ref. 104), 70 (ref. 120), 71 (ref. 120), 76 (ref. 150, 151), 87 (ref. 189), 88 (ref. 199), 91 (ref. 189), 97-99, 101, 102
Banerjea, G. B., 116 (ref. 14), 179
Barkas, W. H., 34 (ref. 16, 17), 36, 37 (ref. 21), 52, 56 (ref. 21), 57, 65, 66, 67 (ref. 111), 74 (ref. 101), 77 (ref. 111), 82, 92, 93, 96, 97, 100
Barker, K. H., 79 (ref. 164), 87 (ref. 185), 91 (ref. 185), 100, 101
Barker, P. R., 70 (ref. 124), 98
Baroni, G., 77 (ref. 159), 90
Barrett, P. H., 87 (ref. 192), 101
Bates, S. J., 23, 249, 28
Batuecas, T., 19, 28
Baxter, G. P., 19, 28
Bearden, J. A., 116 (ref. 14), 121, 122, 124-126, 142 (ref. 54), 143, 144 (ref. 58), 147 (ref. 58, 65), 149 (ref. 58, 65), 151, 167, 172, 173, 177, 211 (ref. 58, chap. 5), 212, 214, 249, 251, 180, 181
Beattie, J. A., 8, 13
Beets, H. N., 122, 126, 180

- Belinfante, F. J., 59, *95*
 Bell, W. E., 60, 61, 62, *95*
 Benoit, J. R., 4, *18*
 Bergstrand, E., 108, 109, 110, 111, 183, 188, 251, *179*
 Beringer, R., 202, 203, 254, *221*
 Berley, D., 72 (ref. 140b), 73, *99*
 Berthelot, D., 8, *13*
 Beth, R. A., 163, *182*
 Bethe, H. A., 33, 34 (ref. 15), 49 (ref. 10), 142, 204, *92, 181, 221*
 Binnie, D. M., 70 (ref. 124), *98*
 Birge, R. T., 1, 8, 11, 12, 16, 18, 19, 20, 25, 26, 103-105, 107, 109, 110, 112, 124, 125, 127-131, 150, 151, 158-164, 177, 184, 226, 250, 263, 271, 3, 13, 28, *180-182, 246, 271*
 Birge, R. W., 66 (ref. 108), 67, *97*
 Birnbaum, W., 36 (ref. 19), 37 (ref. 21), 52 (ref. 21), 56 (ref. 21), 57 (ref. 21), *92, 93*
 Bishop, A. S., 34 (ref. 16), *92*
 Bjerhammer, A., 226 (ref. 12), *246*
 Bjørnerud, E. K., 69 (ref. 119), 70 (ref. 119), 84 (ref. 119), *98*
 Blackett, P. M. S., 63 (ref. 94), *96*
 Blaine, L. R., 184, 188, *220*
 Blatt, J. M., 49 (ref. 44), *94*
 Bloch, F., 188 (ref. 8), 193, 194, 251, 260, *220*
 Bloembergen, N., 188 (ref. 9), *220*
 Blumenfeld, H., 72 (ref. 139), 73 (ref. 139), 79 (ref. 139), 80 (ref. 139), 81 (ref. 139), *98, 99*
 Bogachev, N. P., 50 (ref. 50), *94*
 Bøggild, J., 66 (ref. 107), 77 (ref. 107), *97*
 Bohr, N., 36, *92*
 Bol, K., 184, 188, *220*
 Bollman, V. L., 119 (ref. 17, 18), 143 (ref. 56), 144 (ref. 56), 147 (ref. 56), 149 (ref. 56), 150, 172, *180, 181*
 Bond, W. N., 116 (ref. 14), 161, *179, 182*
 Bonetti, A., 66 (ref. 107), 77 (ref. 107), 81 (ref. 174), *97, 100*
 Booth, E. T., 44 (ref. 35), 45 (ref. 35), 54 (ref. 35, 62), 72 (ref. 139), 73 (ref. 139), 78 (ref. 162a), 79 (ref. 139), 80 (ref. 139), 81 (ref. 139), *93, 94, 98, 100*
 Boys, C. V., 16, *28*
 Bradley, J., 106
 Bradner, H., 34, 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), *92, 98*
 Bragg, Sir Lawrence, 125, 250, *180*
 Bragg, Sir William, 117, 119, 121, *180*
 Breit, G., 204 (ref. 33, 34), *221*
 Brene, N., 66 (ref. 107), 77 (ref. 107), *97*
 Bridge, H. S., 62, 66 (ref. 106), 72 (ref. 137), 78, 79 (ref. 137), 80 (ref. 137), 87 (ref. 89a), *96-98*
 Brode, R. B., 34, 51, 52, *92, 94*
 Brown, D. C., 226 (ref. 13), *246*
 Brown, R. H., 64 (ref. 97), *96*
 Buchanan, J. S., 69 (ref. 118), 70 (ref. 118), 72 (ref. 135), *98*
 Bucherer, A. H., 134-136, 141, *180*
 Budde, R., 72 (ref. 140a), 73, 74, 80 (ref. 140a), 81 (ref. 140a), *99*
 Burgess, G. K., 11 (ref. 10), *13*
 Burwell, J. R., 68 (ref. 114), 78 (ref. 161), *98, 100*
 Busch, H., 140-142, *181*
 Buskirk, A. V., 78 (ref. 161), 79 (ref. 163), *100*
 Butement, F. D. S., 60 (ref. 73a), *95*
 Butler, C. C., 79 (ref. 164), 87 (ref. 185), 91 (ref. 185), *100, 101*
 Byfield, H., 44 (ref. 35), 45 (ref. 35), 54 (ref. 35), *93*
 Cachon, A., 87 (ref. 185), 91 (ref. 185), *101*
 Camac, M., 41, *93*
 Camerini, U., 64 (ref. 97), *96*
 Cartwright, W. F., 49, 50 (ref. 45), *94*
 Case, K. M., 78 (ref. 162c), *100*
 Casado, F. L., 19 (ref. 5b), *28*
 Castagnoli, C., 77 (ref. 159), 87 (ref. 193), *99, 101*
 Cauchois, Y., 121 (ref. 25), *180*

- Cavendish, H., 16, 28
 Ceccarelli, M., 66 (ref. 107), 77 (ref. 107), 81 (ref. 174), 82, 97, 100
 Chaffee, E. L., 134, 137, 180
 Chamberlain, O., 43 (ref. 32), 45 (ref. 32), 93
 Chang, W. Y., 72 (ref. 140), 73 (ref. 140), 80 (ref. 140), 81 (ref. 140), 99
 Chappuis, P., 8, 13
 Cheston, W., 49 (ref. 43), 93
 Chinowsky, W., 47, 49, 51, 72 (ref. 139), 73 (ref. 139), 78 (ref. 162a), 79 (ref. 139), 80 (ref. 139), 81 (ref. 139), 93, 94, 98, 100
 Chippendale, P., 69 (ref. 118), 70 (ref. 118), 98
 Chretien, M., 72 (ref. 140a), 73 (ref. 140a), 74 (ref. 140a), 80 (ref. 140a), 81 (ref. 140a), 83 (ref. 181), 85 (ref. 181), 88 (ref. 181), 99, 101
 Christy, R. F., 58 (ref. 70), 167, 177, 94
 Chrzanowski, P., 16, 28
 Chupp, W. W., 67, 70 (ref. 132), 82, 84, 97, 98, 100, 101
 Clark, D. L., 49, 50 (ref. 46), 94
 Classen, J., 140, 181
 Clews, C. J. B., 155, 177
 Coates, M. S., 79 (ref. 164), 100
 Cohen, E. R., 29 (ref. 1), 125, 160 (ref. 77c), 161 (ref. 77d, g), 197 (ref. 25), 206 (ref. 44), 214 (ref. 49), 218 (ref. 50), 224 (ref. 1), 226 (ref. 11), 245 (ref. 14), 253 (ref. 1), 261 (ref. 3), 92, 182, 221, 246, 271
 Cohn, H. O., 78 (ref. 161), 100
 Collington, D. J., 193, 194, 260, 220
 Collins, G. B., 72 (ref. 140b), 73, 99
 Compton, A. H., 117, 119, 120, 121 (ref. 23), 122, 126, 142 (ref. 53), 180, 181
 Condon, E. U., 132 (ref. 35), 180
 Connor, W. S., 184, 188, 220
 Conversi, M., 61 (ref. 80), 95
 Cooper, L. N., 54 (ref. 69), 59 (ref. 71), 94, 95
 Corben, H. C., 41 (ref. 27), 54 (ref. 27), 93
 Cork, J. M., 55 (ref. 65), 57, 94
 Cornu, M. A., 16, 106, 111
 Cortini, G., 77 (ref. 159), 87 (ref. 193), 99, 101
 Costa, G., 74 (ref. 144), 99
 Courant, H., 66 (ref. 106), 78 (ref. 106), 97
 Cowan, C. L., 91 (ref. 205), 102
 Cowan, E. W., 79 (ref. 165), 87 (ref. 186, 187), 88 (ref. 196), 91 (ref. 186, 187), 100, 101
 Cragoe, C. S., 19, 28
 Craig, D. N., 26, 27, 28
 Crane, L., 66 (ref. 107), 77 (ref. 107), 97
 Crawford, F. S., Jr., 50 (ref. 48), 70 (ref. 128), 71 (ref. 128), 75 (ref. 128a, 147), 94, 98, 99
 Cresti, M., 78 (ref. 162), 100
 Crittenden, E. C., 5, 13
 Crowe, K. M., 38, 39, 53 (ref. 60), 56 (ref. 23), 58, 93, 94
 Crussard, J., 66 (ref. 110), 76, 77, 97, 99
 Dahanayake, C., 87 (ref. 191), 101
 Dalitz, R. H., 47, 63 (ref. 94), 74, 77 (ref. 155), 78 (ref. 155), 93, 96, 99
 Dallaporta, N., 81 (ref. 174), 90 (ref. 204), 100, 102
 D'Andlan, C., 77 (ref. 156), 99
 Daniel, R. R., 77, 80, 99, 100
 David, F. N., 224 (ref. 7), 246
 Davies, J. H., 66 (ref. 107), 77 (ref. 107), 84, 97, 101
 Dayhoff, E. S., 185, 194, 197, 250, 263, 220, 221
 De Benedetti, S., 41 (ref. 26), 56 (ref. 26), 82 (ref. 178), 93, 100
 De Foe, O. K., 122, 126, 180
 de Hoffmann, F., 33, 49 (ref. 10), 92
 Dellis, A. N., 193, 194, 260, 220
 De Staebler, H. C., 66 (ref. 106), 77 (ref. 156), 78 (ref. 106), 97, 99
 Deutschmann, M., 72 (ref. 136), 78, 80 (ref. 136), 98, 100
 Dicke, R. H., 204-206, 221

- diCorato, M., 66 (ref. 107), 77 (ref. 107), 97
 Dilworth, C., 62, 66 (ref. 107), 77 (ref. 107), 87 (ref. 85), 95, 97
 Doan, R. L., 120, 180
 Dorsey, N. E., 111, 112, 179
 Driggers, F. E., 58 (ref. 70), 94
 Driscoll, R. L., 189, 250, 263, 220
 Duane, W., 147 (ref. 60), 150, 172, 181
 Dudziak, W., 53 (ref. 59), 82 (ref. 176a), 94, 100
 DuMond, J. W. M., 42, 119 (ref. 17-19), 125, 143 (ref. 56), 144 (ref. 56, 57), 147 (ref. 56, 57, 66), 149 (ref. 56, 57, 66), 150, 154, 157, 160 (ref. 77a-c), 161 (ref. 77d-g), 166 (ref. 77a), 169 (ref. 77b), 172, 177, 206 (ref. 44), 212, 214, 215 (ref. 49), 216 (ref. 57, chap. 5), 218 (ref. 50), 226 (ref. 11), 251, 261 (ref. 3), 93, 180-182, 221, 246, 271
 Dunnington, F. G., 134, 137, 138, 152-154, 160 (ref. 75), 173, 177, 180, 181
 Durbin, R. P., 45, 49, 50 (ref. 47), 93, 94
 Dwyer, P. S., 226 (ref. 10), 246

 Eckart, C., 118, 180
 Eddington, A. S., 16
 Eisenberg, Y., 87, 101
 Ekspong, A. G., 76 (ref. 152), 77 (ref. 152), 99
 Escribano, A., 19, 28
 d'Espagnat, B., 90, 102
 Essen, L., 6, 184, 187, 188, 13, 220
 Etter, L. R., 78 (ref. 161), 79 (ref. 163), 100
 Evans, D., 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 97, 101

 Fabri, E., 64 (ref. 98), 74, 96
 Fabry, C., 4, 13
 Fahy, E. F., 58 (ref. 70), 94
 Falk-Vairant, P., 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 98
 Feder, H., 147 (ref. 61), 150, 172, 181
 Feld, B. T., 74 (ref. 142), 75 (ref. 142), 99
 Felt, G. L., 147 (ref. 66), 149 (ref. 66), 212, 214, 251, 181
 Fermi, E., 204, 221
 Fideraro, G., 59 (ref. 71), 94, 95
 Fields, T. H., 50 (ref. 49), 94
 Fisher, R. A., 259 (ref. 2), 271
 Fitch, V., 54 (ref. 63), 56 (ref. 63), 60, 70 (ref. 129, 130), 71, 78, 94, 95, 98
 Fizeau, H. L., 106
 Florman, E. F., 184, 188, 220
 Foucault, J. L., 106
 Fouché, V., 66 (ref. 110), 97
 Fournet, D. M., 70 (ref. 131), 72 (ref. 131), 98
 Fowler, P. H., 64 (ref. 97), 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 96, 97, 101
 Fowler, W. A., 29 (ref. 1), 30, 92
 Fowler, W. B., 82 (ref. 177), 85, 86, 88 (ref. 177), 100, 101
 Fox, J. G., 50 (ref. 49), 94
 Francois, P. E., 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 87 (ref. 191), 97, 101
 Franzinetti, C., 77 (ref. 159), 81 (ref. 174), 99, 100
 Freden, S. C., 84, 101
 Fretter, W. B., 51, 63 (ref. 94), 65 (ref. 102), 69, 70 (ref. 122), 71, 72 (ref. 134), 79 (ref. 134), 80 (ref. 134), 82 (ref. 179), 87 (ref. 188), 91 (ref. 188), 94, 96, 98, 100, 101
 Friedlander, M. W., 66 (ref. 107), 77, 79, 80, 81 (ref. 174), 84 (ref. 182), 87 (ref. 190), 97, 99, 100, 101
 Friesen, E. W., 65 (ref. 102), 69 (ref. 116), 70 (ref. 122), 71 (ref. 122), 82 (ref. 179), 87 (ref. 188), 91 (ref. 188), 96, 98, 100, 101
 Froome, K. D., 184, 186-188, 251, 220
 Fry, W. F., 68, 77 (ref. 155), 78 (ref. 159), 82, 83, 84, 85, 88, 97, 99-102
 Fujimoto, Y., 87 (ref. 191), 101
 Fung, S., 66 (ref. 109), 67, 97

- Gardner, E., 34, 36, 92
 Gardner, J. H., 32, 197, 200, 201, 203, 221
 Garelli, C. M., 82 (ref. 178), 100
 Garwin, R. L., 59, 60, 64, 75 (ref. 72b), 95
 Gauss, C. F., 224 (ref. 6), 246
 Gayther, D. B., 72, 80 (ref. 133), 98
 Gell-Mann, M., 33, 88, 90, 92, 102
 George, E. P., 59 (ref. 71), 95
 Gilbert, F. C., 68, 70 (ref. 131), 72 (ref. 131), 82, 84, 97, 98, 100
 Giles, P. C., 82 (ref. 176a), 100
 Gill, P., 58 (ref. 70), 94
 Ginnings, D. C., 20, 28
 Gnan, J., 155, 167, 173, 177
 Godfrey, T. N. K., 62 (ref. 83), 95
 Goldhaber, G., 66 (ref. 109), 67, 70 (ref. 131, 132), 72 (ref. 131, 132), 76 (ref. 152), 77 (ref. 152), 82 (ref. 180), 84 (ref. 181a), 97-101
 Goldhaber, M., 90, 91 (ref. 205), 102
 Goldhaber, S., 66 (ref. 109), 67, 70 (ref. 126), 70 (ref. 131, 132), 71, 72 (ref. 131, 132), 82 (ref. 180), 84 (ref. 181a), 97, 98, 100, 101
 Good, M. L., 70 (ref. 128), 71 (ref. 128), 75 (ref. 128a, 147), 98, 99
 Gow, J. D., 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 98
 Green, A. E. S., 144 (ref. 57), 147 (ref. 57), 149 (ref. 57), 150, 177, 216 (ref. 57, chap. 5), 181
 Greening, W. D. B., 78 (ref. 162), 100
 Gregory, B., 66 (ref. 105), 69 (ref. 117), 77 (ref. 156), 87 (ref. 185), 91 (ref. 185), 97-99, 101
 Grilli, M., 66 (ref. 107), 77 (ref. 107), 82 (ref. 175), 97, 100
 Grunstra, B. G., 41 (ref. 27), 54 (ref. 27), 93
 Guerriero, L., 78 (ref. 162), 100
 Guillaume, C. E., 5, 17 (ref. 3), 13, 28
 Gupta, I. C., 72 (ref. 140), 73 (ref. 140), 80 (ref. 140), 81 (ref. 140), 99
 Haddock, R. P., 65, 66 (ref. 108), 67 (ref. 108), 74 (ref. 100), 96, 97
 Hadley, J., 38, 39 (ref. 22), 46 (ref. 22), 48 (ref. 22), 93
 Halbert, M. L., 41 (ref. 25), 93
 Hammer, W., 133, 180
 Hansen, L. F., 65 (ref. 102), 96
 Hansen, W. W., 184, 188, 220
 Harrington, E., 115-117, 122, 179
 Harris, D. R., 76 (ref. 150), 99
 Harris, G., 48, 70 (ref. 127), 71, 74 (ref. 143), 93, 98, 99
 Harris, J. N., 147 (ref. 66), 149 (ref. 66), 212, 214, 251, 181
 Harrison, F. B., 62 (ref. 83), 95
 Haskin, D. M., 77 (ref. 154), 99
 Haun, R. D., Jr., 6, 13
 Havens, W. W., 45, 93
 Hayward, R. W., 64 (ref. 96b), 75 (ref. 96b), 96
 Heald, M. A., 202, 203, 254, 221
 Heckman, H. H., 65 (ref. 101), 66 (ref. 101, 111), 67, 74 (ref. 101), 77, 82 (ref. 176a), 96, 97, 100
 Heitler, W., 207 (ref. 46), 221
 Helm, R. H., 53 (ref. 60), 94
 Hemenway, C. L., 152 (ref. 67), 181
 Hendel, A., 66 (ref. 105), 97
 Henley, E. M., 33, 54 (ref. 69), 92, 94
 Hennessy, J., 66 (ref. 110), 97
 Henning, F., 8, 12 (ref. 11), 13
 Henri, V. P., 44 (ref. 34), 45 (ref. 34), 93
 Hercus, E. O., 20, 28
 Herzberg, G. I., 132 (ref. 36), 180
 Heuse, W., 8, 13
 Heyl, P. R., 16, 28
 Hilberry, N., 60 (ref. 74), 61 (ref. 74), 95
 Hillier, R., 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 97, 101
 Hincks, E. P., 60, 61, 62, 95
 Hipple, J. A., 25, 32, 189, 190, 191, 198, 201, 250, 251, 260, 263, 220
 Hoag, J. B., 60 (ref. 74), 61 (ref. 74), 95

- Hoang, T. F., 64 (ref. 98), 70 (ref. 127a), 71, 76 (ref. 149), 96, 98, 99
- Hodson, A. L., 66 (ref. 104), 76, 88 (ref. 199), 97, 99, 102
- Hoffman, J. I., 26, 27, 28
- Hooper, J., 66 (ref. 107), 77 (ref. 107), 97
- Hoppes, D. D., 64 (ref. 96b), 76 (ref. 96b), 96
- Hornbostel, J., 67, 97
- Hornyak, W. F., 29 (ref. 1), 92
- Houston, W. V., 116, 132, 173, 179, 180
- Houterman, F. G., 53 (ref. 58), 94
- Hoyt, H. C., 154, 157, 181
- Hudson, R. P., 64 (ref. 96b), 75 (ref. 96b), 96
- Huggett, R. W., 68 (ref. 114), 78 (ref. 161), 98, 100
- Hulubei, H., 121 (ref. 25), 180
- Hyams, B. D., 70 (ref. 124), 98
- Iloff, E. L., 70 (ref. 131, 132), 72, 98
- Impeduglia, J., 78 (ref. 162a), 100
- Ingelstam, E., 121 (ref. 24), 180
- Ingelstam, E. C., 55 (ref. 67), 94
- Inman, F. W., 82 (ref. 176a), 100
- Iredale, P., 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 87 (ref. 191), 97, 101
- Jaeger, W., 12 (ref. 11), 20, 13, 28
- Jakobson, M., 43, 45 (ref. 33), 93
- Janes, C. D., 72 (ref. 135), 98
- Jeffries, C. D., 193, 194, 251, 260, 220
- Jenkins, F. A., 18, 112 (ref. 7), 28, 179
- Johnson, F. T., 144 (ref. 58), 147 (ref. 58), 149 (ref. 58), 211 (ref. 58, chap. 5), 212, 251, 181
- Johnson, M. H., 49 (ref. 43), 93
- Johnston, R. H. W., 66 (ref. 107), 77 (ref. 107), 97
- Joule, J. P., 8, 13
- Kane, J. A., 50 (ref. 49), 94
- Kannangara, M. L. T., 59 (ref. 71), 95
- Kaplon, M. F., 70 (ref. 127a), 71, 76 (ref. 149), 77 (ref. 158), 98, 99
- Karplus, R., 88, 197 (ref. 23), 202 (ref. 23), 204 (ref. 32), 206, 102, 221
- Karzmark, C. J., 78 (ref. 161), 78 (ref. 163), 100
- Kaufman, W., 134, 180
- Kayas, G., 66 (ref. 110), 97
- Keefe, D., 66 (ref. 107), 77 (ref. 153, 107), 79 (ref. 167), 84 (ref. 182), 87 (ref. 190), 97, 99-101
- Keesom, W. M., 8, 13
- Keller, J. M., 167, 177
- Kellström, G., 116 (ref. 14), 179
- Kepler, R. G., 65 (ref. 102), 96
- Kerth, L. T., 66 (ref. 108), 67 (ref. 108), 97
- Kessler, J., 44 (ref. 35), 45 (ref. 35), 54 (ref. 35), 93
- Keuffel, J. W., 62, 70 (ref. 123), 95, 98
- Kimm, Y. B., 78 (ref. 161), 100
- Kinsler, L. E., 132, 173, 180
- Kirchner, F., 133, 134, 136, 137, 155, 160 (ref. 76), 173, 177, 180, 181
- Kirkpatrick, P., 147 (ref. 62), 150, 156, 167, 172, 173, 181
- Klarmann, J., 77 (ref. 158), 99
- Klein, A., 206, 221
- Klein, D. J., 154, 157, 181
- Koenig, S. H., 201-203, 254, 266, 221
- Koshiba, M., 77 (ref. 154), 99
- Koslov, S., 54, 56 (ref. 63), 94
- Kraushaar, W. L., 44, 45 (ref. 34), 93
- Kretschmar, G. G., 155, 173
- Kroll, N. M., 54 (ref. 68), 197 (ref. 23), 202 (ref. 23), 204 (ref. 32), 206, 94, 221
- Kuchner, J. A., 49 (ref. 37a), 93
- Kulenkampff, H., 208, 221
- Kusaka, S., 58 (ref. 70), 94
- Kusch, P., 201-206, 254, 266, 221
- Laby, T. H., 20, 28
- Lagarrigue, A., 65 (ref. 102), 66 (ref. 105), 69 (ref. 116, 117), 70 (ref. 122), 71 (ref. 122), 82 (ref. 179), 87 (ref. 185), 91 (ref. 185), 96-98, 100
- Lal, D., 80, 100

- Lamb, W. E., Jr., 194, 195, 197, 250, 220, 221
- Landau, L. D., 49 (ref. 53), 94
- Lande, K., 78 (ref. 162a), 100
- Langer, L. M., 53 (ref. 58), 94
- Lannutti, J. E., 70 (ref. 131, 132), 72 (ref. 131, 132), 98
- Laplace, P. S., 224 (ref. 4) 246
- Lapp, R. E., 58 (ref. 70), 94
- Lattes, C. M., 34, 92
- Lauritsen, C. C., 29 (ref. 1), 30, 92
- Lawlor, G., 66 (ref. 107), 77 (ref. 107), 97
- Lawrence, E. O., 153, 160, 173, 189
- Layton, T. W., 218 (ref. 50), 261 (ref. 3), 221, 271
- Lazarus, A. J., 59 (ref. 72), 95
- Lederman, L. M., 44, 45 (ref. 35), 53 (ref. 61), 54, 59, 64 (ref. 72b), 72 (ref. 139), 73 (ref. 139), 75 (ref. 72b), 78 (ref. 162a), 79 (ref. 139), 80 (ref. 139), 81 (ref. 139), 93-95, 98, 100
- Lee, T. D., 63, 75, 78 (ref. 162d), 96, 99, 100
- Leide, A., 55 (ref. 66), 94
- Leighton, R. B., 69 (ref. 119), 70 (ref. 119, 121), 71, 79 (ref. 166), 80 (ref. 171), 84 (ref. 119), 87 (ref. 186), 88 (ref. 196), 91 (ref. 186), 98, 100, 101
- Leipuner, L., 41 (ref. 26), 56 (ref. 26), 93
- Leitner, J., 72 (ref. 140a), 73 (ref. 140a), 74 (ref. 140a), 80 (ref. 140a), 81 (ref. 140a), 83 (ref. 181), 85 (ref. 181), 88 (ref. 181), 99, 101
- Leontic, B., 59 (ref. 71), 95
- Leprince-Ringuet, L., 62, 63 (ref. 94), 66 (ref. 105, 110), 69 (ref. 117), 77 (ref. 156), 87 (ref. 84, 185), 91 (ref. 185), 95-99, 101
- Levi-Setti, R., 66 (ref. 107), 77 (ref. 107), 97
- Lévy, M., 90 (ref. 204), 102
- Lewis, H. W., 36 (ref. 18), 92
- Li, C. W., 29 (ref. 1), 30, 92
- Lind, D. A., 157, 181
- Lindeberg, G. K., 76 (ref. 151), 87 (ref. 189), 91 (ref. 189), 99, 101
- Lindenfeld, P., 47, 93
- Lindhard, J., 36 (ref. 18), 92
- Lipson, H., 125
- Loar, H. H., 45, 49, 50 (ref. 47), 93, 94
- Lock, W. O., 64 (ref. 98), 96
- Lokanathan, S., 42 (ref. 29), 93
- Longacre, A., 61 (ref. 82), 95
- Longmire, C., 142, 204, 181, 221
- Lorentz, H. A., 141
- Loria, A., 78 (ref. 162), 100
- Low, F. E., 206 (ref. 45), 221
- Lukirsky, P., 172
- Lyons, H., 6, 13
- MacInnes, D. A., 27, 28
- Mack, J. E., 54 (ref. 65), 57, 94
- Mackenzie, I. C. C., 110, 111, 188, 179
- Maenchen, G., 85 (ref. 184), 86 (ref. 184), 101
- Manescu, I., 55 (ref. 64), 94
- Manfredini, A., 77 (ref. 159), 87 (ref. 193), 99, 101
- Mariani, F., 59 (ref. 71), 94
- Markoff, A. A., 224 (ref. 5), 246
- Marshak, R. E., 49 (ref. 43), 62, 87 (ref. 87), 90 (ref. 204), 94, 96, 102
- Martin, W., 69 (ref. 115), 79 (ref. 115), 88 (ref. 199), 98, 102
- Martinelli, E. A., 42, 43, 45 (ref. 31), 93
- Masek, G. E., 59 (ref. 72), 95
- Maskelyne, N., 14
- Mason, C. J., 82 (ref. 176a), 100
- May, M. M., 72 (ref. 134), 79 (ref. 134), 80 (ref. 134), 98
- Mayo, R. L., 177
- McDiamid, B., 59 (ref. 71), 95
- McGuire, A. D., 41 (ref. 25), 93
- Menon, M. G. K., 66 (ref. 107), 77 (ref. 107, 153), 79 (ref. 167), 84 (ref. 182), 87 (ref. 190), 97, 99-101
- Merlin, M., 66 (ref. 107), 77 (ref. 107), 79 (ref. 167), 82 (ref. 175), 97, 100
- Merrison, A. W., 49 (ref. 37a), 93
- Meshcheryakov, M. G., 50 (ref. 50), 94
- Meyer, A. J., 62 (ref. 83), 95
- Meyerott, E. R., 204 (ref. 33), 221

- Mezzetti, L., 70 (ref. 123), 98
 Michelson, A. A., 106, 107, 108, 110, 111, 112, 184, 179
 Mickelwait, A. B., 41 (ref. 27), 54 (ref. 27), 93
 Millar, D. D., 69 (ref. 118), 70 (ref. 118), 72 (ref. 135), 98
 Miller, P. H., 119 (ref. 19), 130
 Millikan, R. A., 112-118, 122, 173, 179
 Millman, S., 201 (ref. 29), 221
 Milone, A., 66 (ref. 107), 77 (ref. 107), 97
 Moellering, W. M., 206 (ref. 45), 221
 Moffat, R. J. D., 53 (ref. 58), 94
 Mohler, N., 66 (ref. 109), 67 (ref. 109), 97
 Moles, E., 19, 28
 Morellet, D., 66 (ref. 110), 97
 Motley, R., 70 (ref. 129, 130), 71, 98
 Mozley, R. F., 43 (ref. 32), 45 (ref. 32), 93
 Muirhead, H., 64 (ref. 97), 96
 Muller, D. E., 154, 157, 181
 Muller, F., 66 (ref. 105), 69 (ref. 117), 77 (ref. 156), 87 (ref. 185), 91 (ref. 185), 97-99, 101
 Murrill, T. A., 8, 13

 Nafe, J. E., 204, 221
 Nakada, M. P., 72 (ref. 134), 79 (ref. 134), 80 (ref. 134), 98
 Nakano, T., 90 (ref. 201), 102
 Neddermeyer, S. H., 32 (ref. 9), 92
 Neganov, B. S., 50 (ref. 50), 94
 Nelson, E. B., 204, 221
 Nereson, N., 61 (ref. 78), 95
 Neugebauer, G., 87 (ref. 186), 91 (ref. 186), 101
 Nevin, T. E., 66 (ref. 107), 77 (ref. 107), 97
 Newcomb, S., 106, 111
 Newcomb, W. A., 206 (ref. 43), 221
 Newth, J. A., 69 (ref. 118), 70 (ref. 118), 72 (ref. 135), 80 (ref. 172), 98, 100
 Neyman, J., 224 (ref. 7), 246
 Nier, A. O., 129, 271, 180, 271
 Nijboer, B. R. A., 209, 221
 Nikols, N. A., 82 (ref. 176a), 100
 Nilsson, A., 144 (ref. 59), 147 (ref. 59), 153, 181
 Nishijima, K., 90, 102
 Noon, J. H., 77 (ref. 158), 99

 Occhialini, G. P. S., 62 (ref. 85), 66 (ref. 107), 77 (ref. 107), 87 (ref. 85), 95, 97
 O'Ceallaigh, C., 66 (ref. 107), 77 (ref. 107), 97
 Odian, A., 74 (ref. 142), 75 (ref. 142), 99
 Oehme, R., 78 (ref. 162d), 100
 Ogren, V. G., 61 (ref. 82), 95
 Ohlin, P., 147 (ref. 64), 150, 209, 181
 Olbert, S., 66 (ref. 106), 78 (ref. 106), 97
 Olpin, A. R., 172
 Orear, J., 48, 63 (ref. 96), 70 (ref. 127), 71, 74 (ref. 143), 93, 96, 98, 99
 Ortel, W. G., 66 (ref. 107), 77 (ref. 107), 97
 Osborne, N. S., 20, 28
 Osher, J. E., 72 (ref. 140c), 73, 74 (ref. 140c), 99

 Packard, M., 188 (ref. 8), 220
 Page, D. I., 69 (ref. 118), 70 (ref. 118), 72 (ref. 135, 138), 80, 100
 Pais, A., 78 (ref. 162c), 88, 100, 102
 Pal, Y., 77, 99
 Palmer, H. H., 147 (ref. 60), 150, 172, 181
 Panofsky, W. K. H., 38, 39 (ref. 22), 42, 43, 45 (ref. 31), 46, 48, 59 (ref. 72), 78, 144 (ref. 57), 147 (ref. 57), 149 (ref. 57), 150, 177, 216 (ref. 57, chap. 5), 93, 95, 100, 181
 Parry, J. V. B., 6, 13
 Pearson, F., 107, 108, 110, 111, 112, 184, 179
 Pease, F. G., 107, 108, 110, 111, 112, 184, 179
 Peaslee, D. C., 90 (ref. 204), 102
 Perkins, D. H., 66 (ref. 107, 108), 67 (ref. 108), 77 (ref. 107), 84 (ref. 182), 97, 101

- Perot, A., 4, 13
 Perry, C. T., 134, 137, 180
 Peters, B., 63 (ref. 94), 96
 Peterson, J. R., 66 (ref. 108), 67 (ref. 108, 108a), 97
 Pevsner, A., 66 (ref. 109), 67 (ref. 109), 70 (ref. 131, 132), 72 (ref. 131, 132), 97, 98
 Peyrou, C., 66 (ref. 105, 106), 69 (ref. 117), 72 (ref. 137), 77, 78 (ref. 106), 79 (ref. 137), 80 (ref. 137), 87 (ref. 185), 91 (ref. 185), 97-99, 101
 Phillips, R. H., 38, 39, 56 (ref. 23), 58, 93
 Piccioni, O., 61 (ref. 80), 78 (ref. 162c), 95, 100
 Plackett, R. L., 224 (ref. 3), 246
 Plano, R., 86, 101
 Platt, J. B., 41 (ref. 25), 93
 Plattanaik, B., 116 (ref. 14), 179
 Plyler, E. K., 184, 188, 220
 Polkinghorne, J., 90 (ref. 204), 102
 Pollock, F., 206, 221
 Pound, R. V., 188 (ref. 9), 220
 Powell, C. F., 62, 63 (ref. 94), 64 (ref. 97), 66 (ref. 107), 77 (ref. 107), 84 (ref. 182), 87 (ref. 86), 95-97, 101
 Powell, W. M., 85 (ref. 184), 86 (ref. 184)
 Poynting, J. H., 16, 28
 Prentki, J., 90, 102
 Preston, T., 112 (ref. 8), 179
 Prilezaev, S., 172
 Prodell, A. G., 201-206, 254, 266, 221
 Prokofiev, A. Y., 91 (ref. 206), 102
 Purcell, E. M., 32, 188 (ref. 9), 197, 201, 203, 220, 221
 Rabi, I. I., 201 (ref. 29), 221
 Rainwater, J., 54 (ref. 63), 56 (ref. 63), 59 (ref. 71), 60, 94, 95
 Ramsey, N. F., 190, 220
 Rasetti, F., 61 (ref. 77), 95
 Rau, R. R., 76 (ref. 150, 151), 88 (ref. 199), 99, 102
 Rawitscher, G. H., 59 (ref. 72a), 95
 Ray, B. B., 55 (ref. 67), 94
 Redding, J. L., 59 (ref. 71), 95
 Rediker, R. H., 78 (ref. 161), 79 (ref. 163), 100
 Reines, F., 91 (ref. 205), 102
 Renard, F., 66 (ref. 110), 97
 Retallack, J. G., 51, 94
 Retherford, R. C., 194 (ref. 18, 19, 21), 221
 Reynolds, G. T., 62 (ref. 83), 66 (ref. 104), 70 (ref. 120), 71 (ref. 120), 76, 88 (ref. 199), 95, 97-99, 102
 Richardson, J. R., 42, 45 (ref. 30), 93
 Richman, C., 49 (ref. 45), 50 (ref. 45), 94
 Ridgway, S. L., 72 (ref. 140b), 73, 99
 Rigden, P. J., 116 (ref. 14)
 Rinehart, M., 53 (ref. 61), 94
 Ritson, D. M., 64 (ref. 97), 66 (ref. 109), 67 (ref. 109), 70 (ref. 131, 132), 72 (ref. 131, 132), 74 (ref. 142), 75 (ref. 142), 96-99
 Roberts, A., 49 (ref. 46), 50 (ref. 46), 94
 Robinson, C. F., 31, 92
 Robinson, G., 224 (ref. 2), 246
 Robinson, H. R., 155, 167, 173, 177
 Robinson, K., 70 (ref. 125), 98
 Robson, J. M., 91 (ref. 206), 102
 Rochester, G. D., 59 (ref. 71), 63 (ref. 94), 95, 96
 Roebuck, J. R., 8, 13
 Rogers, K. C., 53 (ref. 61), 94
 Rollett, J. S., 218 (ref. 50), 261 (ref. 3), 221, 271
 Römer, O., 105
 Rosa, E. B., 22 (ref. 10), 111, 112, 28, 179
 Rosenfeld, A. H., 49 (ref. 52), 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 94, 98
 Ross, P. A., 147 (ref. 62), 150, 156, 167, 172, 173, 181
 Rossi, B., 60, 61 (ref. 74, 78), 63 (ref. 94), 66 (ref. 106), 72 (ref. 137), 78 (ref. 106), 79 (ref. 137), 80 (ref. 137), 95-98
 Rossini, F. D., 20, 28

- Rough, J. D., 152 (ref. 67), 181
 Rout, R. J., 70 (ref. 124), 98
 Ruderman, M. A., 33, 88, 92, 102
 Rutgers, G. A. W., 157, 181
 Rymer, T. B., 154, 155, 181
 Rytz, A., 69 (ref. 118), 70 (ref. 118),
 72 (ref. 135), 98
- Sachs, A., 47, 93
 Sachs, R. G., 78 (ref. 162c), 88 (ref.
 195), 90, 100-102
 Safford, R., 66 (ref. 106), 72 (ref. 137),
 78 (ref. 106), 79 (ref. 137), 80 (ref.
 137), 97, 98
 Sagane, R., 53, 94
 Sahair, A. B., 69 (ref. 118), 70 (ref.
 118), 72 (ref. 135), 98
 Salam, A., 90 (ref. 204), 102
 Salandin, G., 66 (ref. 107), 77 (ref. 107),
 82 (ref. 175), 97, 100
 Salant, E. O., 67, 97
 Salpeter, E. E., 206 (ref. 43), 221
 Samios, N. P., 72 (ref. 140a), 73 (ref.
 140a), 74 (ref. 140a), 80 (ref. 140a),
 81 (ref. 140a), 83 (ref. 181), 85 (ref.
 181), 86 (ref. 184a), 88 (ref. 181), 99,
 101
 Sanders, J. H., 193, 194, 260, 220
 Sands, M., 60 (ref. 74), 61 (ref. 74),
 95
 Sandweiss, J., 66 (ref. 108), 67 (ref.
 108), 97
 Saphir, G., 85 (ref. 184), 86 (ref. 184),
 101
 Sard, R. F., 60 (ref. 74), 61 (ref. 74), 95
 Sargent, C. P., 53 (ref. 61), 94
 Scarsi, L., 62 (ref. 85), 64 (ref. 98), 66
 (ref. 107), 77 (ref. 107), 87 (ref. 85),
 95-97
 Schaitberger, G., 147 (ref. 63), 150, 172,
 181
 Scharff, M., 36 (ref. 18), 66 (ref. 107),
 77 (ref. 107), 92, 97
 Schein, M., 58 (ref. 70), 77 (ref. 154),
 94, 99
 Schneps, J., 68 (ref. 113b), 77 (ref. 155),
 78 (ref. 155), 82 (ref. 176), 83 (ref.
 113b), 84 (ref. 183), 85 (ref. 183), 88,
 97, 99-102
 Schulte, H. J., 41 (ref. 25), 93
 Schulz, A., 43 (ref. 33), 45 (ref. 33), 93
 Schwartz, M., 72 (ref. 140a), 73 (ref.
 140a), 74 (ref. 140a), 80 (ref. 140a),
 81 (ref. 140a), 83 (ref. 181), 85 (ref.
 181), 86 (ref. 184a), 88 (ref. 181), 99,
 101
 Schwarz, G., 147 (ref. 65), 149 (ref. 65),
 151, 212, 251, 181
 Schwinger, J., 90 (ref. 204a), 197 (ref.
 22), 202 (ref. 22), 102, 221
 Scott, A. F., 26, 28
 Sechi, B., 66 (ref. 107), 77 (ref. 107),
 82 (ref. 175), 97, 100
 Seymour, D. W., 60, 61 (ref. 75), 95
 Shacklett, R., 42, 93
 Shane, C. D., 31, 173, 92
 Shapiro, A. M., 62, 96
 Shapiro, M. M., 62, 96
 Shaw, A. E., 134, 139, 140, 173, 181
 Sheppard, J., 70 (ref. 124), 98
 Shiba, K., 116 (ref. 14), 179
 Shortley, G. H., 132 (ref. 35), 180
 Shrikantia, G. S., 59 (ref. 71), 95
 Shutt, R. P., 59 (ref. 71), 82 (ref. 177),
 85 (ref. 184), 86 (ref. 184), 88 (ref.
 177), 95, 100, 101
 Sidrov, V. M., 50 (ref. 50), 94
 Siegbahn, K., 153, 154, 181
 Siegbahn, M., 117, 119, 121, 122, 125,
 178, 180
 Silsbee, F. B., 10, 22 (ref. 9, chap. 2), 13
 Smith, F. M., 34 (ref. 16, 17), 36, 37
 (ref. 21), 52 (ref. 21), 56 (ref. 21), 57
 (ref. 21), 65 (ref. 101), 66 (ref. 101,
 111), 67 (ref. 111), 74 (ref. 101), 77
 (ref. 111), 82 (ref. 176a), 92, 93, 96,
 97, 100
 Snow, G. A., 68 (ref. 113b), 74 (ref.
 140d), 77 (ref. 155), 78 (ref. 155), 82
 (ref. 176), 83 (ref. 113b), 84 (ref.
 183), 85, 97, 99-102
 Snyder, A. L., 72 (ref. 140), 73 (ref.
 140), 80 (ref. 140), 81 (ref. 140), 99
 Söderman, M., 121, 124, 172

- Sokolov, V. S., 91 (ref. 206), 102
 Solmitz, F. T., 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 98
 Sommer, H., 32, 190, 191, 198, 201, 251, 260, 263, 220
 Sorrels, J. D., 87 (ref. 186), 91 (ref. 186), 101
 Sosnovsky, A. N., 91 (ref. 206), 102
 Sowerby, M. G., 79 (ref. 164), 100
 Spedding, F. H., 31, 173, 92
 Spivac, P. E., 91 (ref. 206), 102
 Sreckantan, B. V., 66 (ref. 106), 78 (ref. 106), 97
 Stadler, H. L., 50 (ref. 51), 94
 Stallwood, R. A., 50 (ref. 49), 94
 Starkweather, H. W., 19, 28
 Stearns, M., 41, 56 (ref. 26), 93
 Stearns, M. B., 41, 56 (ref. 26), 93
 Steinberger, J., 33, 42, 43 (ref. 32, 33), 45 (ref. 32, 33), 47, 49, 50 (ref. 47), 51, 72 (ref. 140a), 73 (ref. 140a), 74 (ref. 140a), 80 (ref. 140a), 81 (ref. 140a), 83, 85, 86 (ref. 184a), 88 (ref. 181), 92-94, 99, 101
 Stenström, W., 123, 180
 Stevenson, M. L., 50 (ref. 48), 70 (ref. 128), 71 (ref. 128), 75 (ref. 128a, 147), 94, 98, 99
 Stewart, R. L., 139, 181
 Stimson, H. F., 20, 28
 Stork, D. H., 66 (ref. 108), 67 (ref. 108), 97
 Stranathan, J. D., 131 (ref. 34), 180
 Sutton, R. B., 50 (ref. 49), 94
 Swami, M. S., 68 (ref. 113b), 77 (ref. 155), 78 (ref. 155), 82 (ref. 176), 83 (ref. 113b), 84 (ref. 183), 85 (ref. 183), 88, 97, 99, 100-102
 Swann, W. F. G., 60, 61 (ref. 75), 95
 Taffara, L., 74 (ref. 144), 99
 Tallone, L., 82 (ref. 178), 100
 Tautfest, G. W., 53 (ref. 60), 94
 Taylor, S., 48, 70 (ref. 127), 71, 74 (ref. 143), 93, 98, 99
 Thibaud, J., 120, 180
 Thirring, W., 53 (ref. 58), 94
 Thomas, H. A., 32, 189, 190, 191, 198, 201, 250, 251, 260, 263, 220
 Thomas, J. E., 44 (ref. 34), 45 (ref. 34), 93
 Thomas, R. E., 61 (ref. 82), 95
 Thompson, R. W., 62, 63 (ref. 94), 68, 78, 79 (ref. 163), 84 (ref. 182), 87 (ref. 88, 89), 96, 98, 100, 101
 Thomson, G. P., 131 (ref. 33), 180
 Thomson, J. J., 112, 131 (ref. 33), 134, 179, 180
 Thomson, Sir William, 8, 13
 Thorndike, A. M., 82 (ref. 177), 85 (ref. 184), 86 (ref. 184), 88 (ref. 177), 100, 101
 Ticho, H. K., 61 (ref. 79), 84, 95, 101
 Tinlot, J., 54 (ref. 62), 77 (ref. 156), 94, 99
 Tollestrup, A., 29 (ref. 1), 92
 Tolman, R. C., 2
 Tomasini, G., 66 (ref. 107), 77 (ref. 107), 81 (ref. 174), 97, 100
 Toral, T., 19, 28
 Tornabene, S., 49 (ref. 37a), 93
 Torrey, H. C., 188 (ref. 9), 220
 Touschek, B., 64 (ref. 98), 74 (ref. 141), 96, 99
 Townes, C. H., 177
 Townsend, J. S., 112, 179
 Treiman, S. B., 76 (ref. 150, 151), 78 (ref. 162c), 88 (ref. 195, 199), 99-102
 Trent, P., 59 (ref. 71), 95
 Triebwasser, S., 194, 197, 250, 220, 221
 Trigger, K. R., 194, 260, 220
 Trilling, G. H., 65, 70 (ref. 121), 71 (ref. 121), 79 (ref. 166), 87 (ref. 186), 91 (ref. 186), 96, 98, 100, 101
 Tripp, R. D., 69 (ref. 116a), 80 (ref. 116a), 81 (ref. 116a), 85 (ref. 116a), 98
 Tu, Y. C., 119 (ref. 16), 180
 Turberfield, K. C., 193, 194, 260, 220
 Tuyn, W., 8, 13
 Tyrén, F., 121, 124, 178, 249
 Van Atta, L. C., 153, 173

- Van Lint, V. A. J., 65, 79 (ref. 166),
 87 (ref. 186, 189), 88, 91 (ref. 186,
 189), *96, 100, 101*
 Van Patter, D. M., 30, *92*
 Van Rossum, L., 77 (ref. 153), *99*
 Vedder, J., 53 (ref. 59), *94*
 Vigone, M., 82 (ref. 178), *100*
 Vinal, G. W., 22 (ref. 10), 23, 25, 177,
 249, *28*
 Violet, C. E., 68, 70 (ref. 131), 72 (ref.
 131), 82 (ref. 176b), 84 (ref. 176b),
97, 98, 100
 Vitale, B., 64 (ref. 98), *96*
 von Friesen, S., 155, 167, 173, 177
 von Steinwehr, H., 20, *28*

 Waddington, C. J., 87 (ref. 191), *101*
 Wagner, E., 208, *221*
 Waldman, B., 65 (ref. 102), *96*
 Walker, W. D., 85, 86, *101*
 Wapstra, A. H., 31, *92*
 Warren, B. E., 125
 Washburn, E. W., 23
 Watson, B. B., 157, *181*
 Watson, K. M., 33, *92*
 Wattenberg, A., 74 (ref. 142), 75 (ref.
 142), *99*
 Watts, H. M., 144 (ref. 58), 147 (ref.
 58), 149 (ref. 58), 211 (ref. 58, chap.
 5), 212, 251, *181*
 Webb, F. H., 67, 82 (ref. 180), 84 (ref.
 181a), *97, 100, 101*
 Weichert, E., 132, *180*
 Weinrich, M., 59, 64 (ref. 72b), 75
 (ref. 72b), *95*
 Weisskopf, V. F., 49 (ref. 44), *94*
 Wensel, H. T., 157, 172, *181*
 Whaling, W., 29 (ref. 1), 30, *92*
 Wheeler, J. A., 40, 142 (ref. 54), *93, 181*
 Whiddington, R., 153, 172
 White, H. E., 112 (ref. 7), *179*
 White, R. S., 68, 70 (ref. 131), 72 (ref.
 131), 82 (ref. 176b), 84 (ref. 113c,
 176b), *97, 98, 100*
 Whitehead, M. N., 49 (ref. 45), 50
 (ref. 45), 66 (ref. 108), 67 (ref. 108),
94, 97
 Whittaker, E., 224 (ref. 2), *246*
 Whittemore, W. L., 59 (ref. 71), 82
 (ref. 177), 85 (ref. 184), 86 (ref. 184),
 88 (ref. 177), *95, 100, 101*
 Wichers, E., 130
 Wick, G. C., 51 (ref. 54a), *94*
 Wickman, E. H., 54 (ref. 68), *94*
 Widgoff, M., 66 (ref. 109), 67 (ref.
 109), *97*
 Wiegand, C. E., 43, 45 (ref. 32), *93*
 Wightman, A. S., 51 (ref. 54a), *94*
 Wigner, E. P., 51 (ref. 54a), *94*
 Wilcox, H. A., 49 (ref. 45), 50 (ref. 45), *94*
 Williams, D. B., 77, *99*
 Williams, R. C., 31, 173, *92*
 Wilson, H. A., 112, *179*
 Wilson, R., 49 (ref. 46), 50 (ref. 46), *94*
 Wittke, J. P., 204-206, *221*
 Wold, D. C., 68 (ref. 113b), 83 (ref.
 113b), *97*
 Wolf, F., 142, *181*
 Wolfendale, A. W., 59 (ref. 71), *95*
 Wolz, K., 134, *180*
 Woodroffe, E. G., 153, 172
 Wright, K. H. R., 154, 155, *181*
 Wright, R. W., 85 (ref. 184), 86 (ref.
 184), *101*
 Wu, C. S., 64, 75 (ref. 96b), *96*
 Wyld, H. W., 69 (ref. 115), 79 (ref.
 115), *98*
 Yang, C. N., 49, 63, 75, 78 (ref. 162d),
94, 96, 99, 100
 Yasin, M., 87 (ref. 191), *101*
 Yates, J. G., 6, *18*
 Yeh, C. S., 147 (ref. 60), 150, 172, *181*
 Yekutieli, G., 70 (ref. 127a), 71, 76
 (ref. 149), *98, 99*
 York, C. M., 69 (ref. 119), 70 (ref. 119),
 84, 87 (ref. 185), 88 (ref. 196), 91
 (ref. 185), *98, 101*
 Yukawa, H., 32, *92*
 Zacharias, J. R., 6, 201 (ref. 29), *13, 221*
 Zago, G., 78 (ref. 162), *100*
 Zemach, A. C., 206 (ref. 45), *221*
 Zorn, G. T., 66 (ref. 109), 67 (ref. 109), *97*
 Zwicky, F., 119

Subject Index

- Absolute electromagnetic system, 9-11
- Acceleration of gravity, 14, 17
- Analysis of variance, 261
- Anomalous magnetic moment of the electron, 202, 253, 269
- Atomic clock, 6
- Atomic constants, 103
 - history of, 103
 - least squares adjustment of, 247
 - preliminary (1952) adjustment, 258
 - recommended values (1957), 262, 265
- Atomic mass, 29. See also *Atomic weight*.
- Atomic mass, of electron, 31, 267
 - of certain nuclei, 30, 266
- Atomic weight, scales of, 129, 271
- Avogadro's number, 126, 252, 267
- Axiom of Maximum Likelihood, 223, 240
- Axiom of maximum weight, 238
- Beta decay, of K^+ meson, 77
 - of μ meson, 53
- Birge-Bond diagram, 161, 162
- Bivariate normal distribution, 228
- Bohr radius, 117, 268
- Boltzmann's constant, 117, 268
- Bragg reflection, 119, 120
- Bremsstrahlung, 207
- Cerenkov radiation, 33
- Charge-to-mass ratio for the electron, 25, 130, 267
- Chemical scale of atomic weight, 129
- Chi-square, 225
- Compton wavelength, of electron, 155, 268
 - of proton, 268
- Consistency, measures of, 226
- Conversion factor, from x-units to milliangstroms, 124, 178, 250, 267
- Correlation as the result of a linear transformation, 229
- Correlation coefficients, 227, 235, 243
 - geometrical interpretation, 232
- Coulometer, 23. See also *Voltmeter*.
 - iodine, 23
 - sodium oxalate, 26
- Covariance, 235
- Cozonal planes, 164
- Critical evaluation of data, Birge's method, 159
 - need for, 158
 - resolution of discrepancies, 160
- Cyclotron frequency, of electron, 32, 198
 - of proton, 32, 189
- Detailed balancing, in pion production, 49
- Eclipses of Jupiter's moon, 105
- Electrical units, 9
- Electron charge, 112, 126, 267
 - relation to other constants, 116
 - x-ray value "discrepancy," 118
- Electron diffraction, 155
- Electron magnetic moment, 197, 253, 269
- Ellipse of standard deviation, 229
- Ellipsoid of error, 235

- e/m , for electrons, 130, 267
 Energy and mass, relativistic equivalence, 29
 Energy balance in nuclear reactions, 29
 Error matrix, 226, 235, 243
 Errors, random *vs.* systematic, 248
- Faraday, 250, 260, 267
 electrochemical determinations of, 21
 Fine structure separation in deuterium, 194, 250, 268
- Gamma rays, from pion capture, 38
 from pion decay, 46
 Gas constant, 18, 19, 252, 266
 Gaussian distribution, 223, 227
 Grating space, 124
 effective, 123
 Gyromagnetic ratio, of muon, 58
 of proton, 188, 198, 250, 269
- h/e , measurements of, 143
 discrepancies in, 147
 excitation potentials, 144, 152
 photoelectric effect, 144
 SWL of x-rays, 144
 Hypercharge, 90
 Hyperfine structure shift in hydrogen, 204
 Hyperonic charge. See *Hypercharge*.
 Hyperons, properties of, 78. See also *Mesons*.
- Indirect value of input numeric, 259
 International Electrical Units, 9
 International Gravity Formula, 17
 International Temperature Scale, 7, 271
 Inverse cyclotron, 193
 Isochromats, method of, 146-151, 207-220
 Isofermionic charge. See *Hypercharge*.
 Isometric consistency chart, 163, 168, 171
 in 1940, 172
 in 1947, 175, 176
- Isotopic abundance ratios for oxygen, 129, 271
 Joule equivalent, 20
 Kelvin Temperature Scale, 7, 8, 271
 Kilogram, definition of, 4
 K-mesons. See *Mesons*.
 "Knees," in isochromats, 147
- Lambda meson, 79. See also *Mesons (hyperons)*.
 Lamb-Retherford shift, 194, 196
 Least squares, method of, 222
 generalized theory, 237
 Least-squares analysis, selection of data for, 247
 Length, mass, and volume, definition of units, 4
 Lifetime, K-meson, 69, 70, 91
 lambda meson, 80, 91
 mesons and hyperons, 91
 muon, 60, 91
 pion, 47, 91
 sigma particles, 84, 91
 theta meson, 72, 91
 Limiting gas densities, 18
 Liter, definition of, 5
- Magnetic moment, of muon, 58
 of proton, 251, 269
 Magnetic resonance frequency of the proton, 189
 Marginal probability distributions, 230
 Mass, of electron, 267
 of heavy mesons, 82, 84, 91
 of hyperons, 78-84, 86, 87
 of K-mesons, 62, 65, 67, 91
 of light mesons, 32-42, 51-58, 91
 of mesons and hyperons (table), 91
 of muon, 51, 54, 58, 91
 of neutron, 91, 267
 nuclear, from reaction energies, 29-31
 of pion, 46, 58, 91
 of proton, 91, 267
 of tau meson, 64, 91
 of theta meson, 68, 91
 units of, 4

- Mass and energy, relativistic equivalence, 29
 Mass ratio, pion-muon, 52
 proton-electron, 201, 268
 Mesic energy levels, 41
 Mesic x-rays, 40-42, 54-58
 and mass of negative muon, 55
 Meson, gyromagnetic ratio of μ^+ , 58
 kappa meson, 76
 magnetic moment of μ , 58
 parity, 48, 74
 spin, 48, 50, 58, 74
 Meson decay, 43, 53
 of K-meson, 77
 Meson lifetime, 42, 60, 69, 70, 72, 80, 84, 91
 Meson mass, 46, 51, 54, 58, 62, 64, 65, 67, 68, 80, 82, 84, 91
 from mesic x-rays, 42
 Mesons, classification and nomenclature, of hyperons, 78
 of K-particles, 62
 Mesons, hyperfragments, 87
 Mesons, (hyperons), lifetime of Λ^0 , 80
 lifetime of Σ , 84
 mass of Λ^0 , 80
 mass of Σ^+ , 82
 mass of Σ^- , 84
 xi particles, 86
 Mesons, masses and properties, 32, 91
 of hyperons, 78, 91
 of K-mesons, 62, 75
 Mesons, "strange" particles, 88
 Meter, definition of, 4
 Method of isochromats, 146
 Minimum error, 239
 Mitbewegung des Kerns, 31
 Mole volume of an ideal gas, 18
 Muon lifetime, 60

 Natural constants, 3
 Normal equation, 225
 Normal gravity, 17
 Nuclear forces, charge dependence, 49

 Ohlin "valleys," 148, 219

 Oil-drop experiment, 112-115
 Omegatron, 190-193

 Parity, conservation in meson decay, 60, 64
 Parity, intrinsic, 51
 of mesons, 48, 74
 Photoelectric determinations of h/c , 151
 Physical constants as units, 2
 Physical scale of atomic weights, 129, 271
 Pi-meson, 34-51
 capture γ -rays, 38
 lifetime, 42, 47
 mass, 34, 46
 momentum, 34
 parity, 48
 pi-mu decay, 43
 range, 34
 spin, 48, 50
 Planck's constant, h , 103, 117
 Point of maximum bending, 149, 210, 216
 Postulate of reproducibility, 2
 Probability distribution, conditional, 230
 marginal, 230
 Probability hill, 229
 Propagation of errors, 231, 242
 correlated variables, 233
 generalized law, 244
 Proton cyclotron frequency, 190
 Proton magnetic moment, 197
 Proton magnetic resonance, 27

 Quantum limit of the continuous x-ray spectrum, 207

 Radiation constants, 156
 Range straggling, 36
 Refractive index of x-rays, 123
 in diamond, 142
 Regression line, 230
 Relative fractional error, 223
 Residual, 223
 Rydberg constant, 253, 266

- Second, definition of, 5
- Short wavelength limit of the continuous x-ray spectrum, 207, 251
"discrepancy," 211, 213
- Sidereal time standards, 6
- Siegbahn-Avogadro number, 127, 250
- Siegbahn's scale of wavelength, 121
- Spin, of mesons, 48, 50, 58, 74
- Standard atmosphere, 11
- Standard errors, 227
- Stefan-Boltzmann law, 156
- "Strangeness," 88
- "Strange" particles, 88
- Tauons. See *Mesons, classification and nomenclature, of K-particles.*
- Temperature, 7
- Temperature Scale, International, 7
Kelvin, 7, 271
- Thermochemical calorie, 20
- Thermodynamic scale of temperature, 8
- Thetons. See *Mesons, classification and nomenclature, of K-particles.*
- Time, 5
- Unitary nature of electrical charge, 114
- Units of measurement, 3
- Universal constant of gravitation, 14-17
measurements of, 16
- Universal gas constant. See *Gas constant.*
- Variance, 235
of residues, 244
- Velocity of light, measurement of, 105-112, 183-188, 251, 266
by cavity resonance, 184
by eclipse of Jovian moon, 184
by geodimeter, 109
by Kerr cell, 108
by microwave interferometer, 186
by rotating mirror, 107
by Shoran, 109
by toothed wheel, 106
- Viscosity of air, 115
- Voltmeter, iodine, 23
silver, 22
sodium oxalate, 26
- Volume, definition of units, 4
- V-particles, 88. See also *Mesons, hyperfragments.*
- Wavelength of annihilation radiation, 157
- Weight, of observational equation, 225
- Weight matrix, 226
- Wien's displacement law, 156
- Work function, 145
- X-ray photoelectric effect, 154
- X-ray quantum limit, 212
- X-rays, mesic, 40
- X-ray spectrum, thick target, 208
thin target, 208
- X-ray wavelengths, ruled grating measurements, 118
- X-unit, 121
definition in terms of calcite, 121
- Y-particle. See *Mesons, hyperfragments.*