1980

The precision measurement of mass

James Steven Gibson
Iowa State University

Recommended Citation

Gibson, James Steven, "The precision measurement of mass " (1980). *Retrospective Theses and Dissertations*. 7372.
https://lib.dr.iastate.edu/rtd/7372

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University
Microfilms
International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND

GIBSON, JAMES STEVEN

THE PRECISION MEASUREMENT OF MASS

Iowa State University PH.D. 1980

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106 18 Bedford Row, London WC1R 4EJ, England

The precision measurement of mass

by

James Steven Gibson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1980

TABLE OF CONTENTS

I. INTRODUCTION

During 1975 and 1976, Koch and Diehl (66) and Koch *et al.* (68) reported the results of high-precision, coulometric titrations of highly purified 4-aminopyridine, results which enabled them to calculate a new value for the faraday, the fundamental constant interrelating chemistry and electricity. Somewhat earlier, physicists (28) had rejected the then current value for the faraday, a value obtained by Craig, Hoffman, Law and Hamer (31) at the National Bureau of Standards by the anodic dissolution of silver, in favor of a value calculated from other physical data. The Craig experimental value was presumably "subject to some serious error". The new value of Diehl and co-workers (see table on next page) was identical to that of Craig as successively recalculated (41) for the change in the basis of the atomic weight scale, for two changes in the definition of the volt, for a determination of the isotope ratio of the silver used by Craig, and for a more generous statistical treatment of his data than was given by Craig. The experimental, electrochemical value of Craig and of Diehl was reinstated by the physicists (97) but there remains a discrepancy of 20 parts per million (p.p.m.) between the experimental and the calculated values, disturbing because the discrepancy is some five times the uncertainty estimated for the experimental value and ten times that estimated for the calculated value.

Table I-1. Recent values for the faraday

F 1972 NBS coulombs per g.-eq.-wt. (Uncertainty)[a]	Worker. Location. Year. Method.
96,486.72 (σ = 6.8 p.p.m.)	Craig, Hoffman, Law and Hamer (31). NBS. 1960. Anodic dissolution of silver, as recalculated (41).
96,486.57 (σ = 4.9 p.p.m.)	Koch and Diehl (66), Koch *et al.* (68). Iowa State University. 1975, 1976. Titration of 4-aminopyridine.
96,484.56 (σ = 2.8 p.p.m.)	Cohen and Taylor (28). NBS. 1973. Calculation involving least squares treatment of other physical data.

---

[a] Combined random and systematic uncertainties expressed as the standard deviation of the mean, the systematic uncertainties being estimated at the 70 per cent confidence level.

The Craig-Diehl value for the faraday is two orders of magnitude better than the accuracy and precision characteristic of essentially all chemical work, industrial, clinical and academic; chemists could hardly care less about resolving the discrepancy just mentioned. However, the physicists report that a backlog of experimental and theoretical work has accumulated because a high-precision value for the faraday is lacking. Moreover, they have undertaken (97) an exhaustive re-examination of the various experimental measurements used in arriving at their value. The source of the discrepancy, though, may lie in the chemical work. If so, however, the fault is something common to the electrolysis of aqueous solutions involving such diverse reactions as the anodic dissolution of silver, the anodic generation of hydrogen ion, and the cathodic generation of hydroxyl ion. Because the calculated value is smaller than the direct, electrochemical value, it appears as if a very small portion of the electricity passing through the electrochemical cell does so without effecting a chemical change at the electrodes. During the work on the faraday at Iowa State University, unexplained phenomena having to do principally with the change in pH through the equivalence-point region had been observed which accorded with some astonishing results of electrolysis experiments reported by the Indian chemist Palit (76-82); together these observations call into question the assumption that 100.0000 per cent current efficiency in electrolysis is or can be obtained. Passing from water as the solvent for the coulometric titration to a nonaqueous solvent also promised to shed light on the problem.

The apparently genuine need of the physicists and the intriguing character of the problem brought on a renewed effort at Iowa State University to extend the earlier work on the faraday. Inasmuch as the physicists were asking that the uncertainty be reduced to less than 1 p.p.m., a necessary prelude to any such effort was a re-examination of the uncertainties in the various measurements involved in the determination just completed followed by steps to reduce each to less than 1 p.p.m. These uncertainties were treated in detail in the original work (reference 66, page 511) and were discussed by Professor Diehl in a lecture given in Indianapolis on October 4, 1978, and published in *Analytical Chemistry* (33) in March of 1979. In this paper, he reviews the work published in 1975-1976 and tells about the various steps which have been taken to reduce the uncertainty in the measurements of current, potential, time, purity, molecular weight and mass, and the design of a titration cell. The present dissertation is devoted to one phase of this more general problem, namely the high-precision measurement of mass.

In the review paper just mentioned, Professor Diehl states that in his opinion the greatest error in the current values for the faraday is the measurement of mass; he believes that mass has never been measured more accurately than 10 p.p.m. This opinion was derived from extended and thorough examination of the various factors involved: the correction for the buoyancy of air during a weighing and the concomitant measurements of barometric pressure, temperature, relative humidity, and the densities of object and weights which are entailed, and the calibration of weights. In his own experience, the problem of calibration had been exacerbated by mistaken and unfortunate calibrations of his weights at the National Bureau of Standards. These and other considerations raised doubt in his mind about the quality of the dissemination of mass from the prototype kilogram to the working one- and two-gram weights used in the chemical work on the faraday.

One of the overall objectives of the physics of this century is to place each of the fundamental units of measurement on a natural, or "absolute", basis so that no arbitrary character is involved and reproduction of a given unit can be achieved independently by anyone anywhere with sufficient effort. Admirable success was achieved early in this century in referring the unit of length to a particular line of an easily obtained spectrum; currently the basis of length is the orange line in the spectrum of kryptron, although by proposals now under consideration, this basis may soon be shifted to the distance light travels in one second. Success in placing the ampere on an absolute basis, after a long and frustrating period extending back to 1885, was achieved in 1948, and during the early 1970's the international ampere was officially shifted to the absolute standard. Shortly thereafter, the international ohm and the international volt were shifted to absolute standards. Similar success has not been achieved with the measurements of temperature and mass.

A possible way to place mass on an absolute basis occurred to Professor Diehl during the course of the faraday work at Iowa State University. The concept is to use as the fundamental natural standard of mass the silicon-28 atom. This idea emerged following his study of the publication in 1974 of a new determination of the Avogadro constant by nine scientists (32) at the National Bureau of Standards, work which involved in a very fundamental way highly-purified, elemental silicon. Professor Diehl went so far as to prepare a set of weights of elemental silicon and to attempt the calibration. The work was defeated by the highly-hygroscopic character of the surface of elemental silicon. The attempt was never publicized; the set of weights languishes in the laboratory at Iowa State University, and although Professor Diehl has had several ideas for rendering the surface of the silicon nonabsorbent, the work has not been pressed further. This aborted effort, however, is having direct consequences on the concept and usage of weights currently employed for high-precision work as will be detailed later in this dissertation.

Establishing an experimental value for the faraday presents the chemist with an unusual demand not faced by earlier chemists dealing with high-precision analyses, that is, with the determination of atomic weight or the establishment of a primary standard. Mass must be measured in absolute terms. In the old atomic weight work, it was sufficient that a set of weights be calibrated so as to be internally consistent inasmuch as the work was all relative. In the faraday work, on the other hand, the weights used must be in terms of absolute mass and "traceable" to the International Kilogram so that the value obtained for the faraday will be on the same basis as other fundamental standards. At the p.p.m. level it is this "tracing" or "dissemination" to, or from, the International Kilogram which requires critical examination at every point and is the subject of the latter part of this dissertation.

A major consideration in the determination of mass is the buoyant effect of the air displaced by the object being weighed and by the weights. The correction is applied using the equation

$$T_o = W_{o,a}[(1 - (d_a/d_W))/(1 - (d_a/d_o))] \qquad \text{(I-1)}$$

from a knowledge of the densities of the object (d_o), the weights (d_W), and the air (d_a), T_o being the mass (mass in vacuum) of the object and $W_{o,a}$ the sum of the weights when the object is weighed in air. Three densities are involved in a specific application of this formula. Nothing appears easier than a determination of the density of a solid, one or the other of the two Archimedes methods being called into play and use made of modern tables of the density of water as a function of temperature. Yet few measurements lead to such discordant and baffling results. Some of the problems and what has been done about them are described in Chapter II, below. The density of air, of course, varies with locality and with changing climatic conditions. I dealt with this problem in my thesis for the degree of Master of Science (38) and I continue with it in the present dissertation, Chapters III through IX. In my Master of Science thesis, there is provided a general introduction to the problem of making hydrostatic weighings and corrections for buoyancy and there are discussed certain other important aspects of the problem of measuring mass; because I will draw on it heavily, I have for convenience reproduced the Table of Contents of the thesis here, Figure I-1. In my thesis I report an investigation of certain aspects of the problem of correcting a determination of mass made by the weighing of an object in air for the buoyancy of the air on the object and on the weights; the ultimate goal of the work was to enable the determination of mass to be made with an uncertainty of less than 1 part per 1,000,000. As will be seen from the Table of Contents, Figure I-1, a convenient symbolism was therein offered for handling the theoretical aspects of the problem and the calculations involved.

Figure I-1. Table of contents of the Master of Science thesis of J. S. Gibson, "Devices for the Rapid Determination of the Density of Air"

TABLE OF CONTENTS

Particular attention was focused on the problems of measuring the density of air. There was reported a re-investigation of the so-called *Baxter's globe*, a hollow glass vessel, from the weighing of which in air the density of the air can be calculated, thus obviating measurement of the prevailing temperature, barometric pressure and humidity, and an involved calculation.

In the course of the present work I have devised an *absolute density cylinder* with which I have shown that the density of air cannot be calculated with accuracy from the barometric pressure, temperature and relative humidity prevailing in laboratories in which people are working. This is in direct support of certain claims of Pontius (86) of the National Bureau of Standards although his claim that the discrepancies observed result from the failure of moist air to conform to the gas laws is probably incorrect. In the course of fabricating this cylinder, which is really a logical extension of the Baxter's globe treated in my Master of Science thesis, it was necessary to invent two other devices, most notably a *vacuum weighing bottle*. This device, described in Chapter VII, proved useful also in the proposed re-examination of the dissemination of the kilogram (high-precision subdivision down to the gram).

One feature of the operation of weighing as it has been conducted in the past, is that water and other gases adsorbed on the surface or absorbed into the body of the weight has been completely ignored. Not only do the relative amounts of these gases increase with increase in the surface area relative to the mass on passing to smaller weights, but the amounts of such gases change with changes in barometric pressure, temperature, and composition of the surrounding gas. The latter is shown directly by experiment but is, of course, common experience: the "wetness" of the surfaces of solids is greatly affected by the prevailing conditions; witness also the connotations of such English words as clammy, damp, and moist. In Chapter X, I deal with this subject and have shown now, by coating a weight suitably, adsorbed gases can be removed from a surface to a mild vacuum by placing the object in the vacuum weighing bottle and the true mass thus obtained.

The boldest proposal of this dissertation is that the prototype kilogram, the so-called *International Kilogram*, be replaced by a mass of stainless steel, properly surface-treated, and weighed in an actual vacuum. The rationale for this is discussed in Chapter X and a beginning on the experimental work of fabricating such a weight and the weights necessary to effect its dissemination is reported in Chapters X and XI. A suitable stainless steel has been selected, machines for the fabricating of the weights have been perfected, a novel sequence for the various weights which permits numerous cross checking during the calibration has been adopted, and fabrication and calibration have been started.

II. MEASURING THE DENSITY OF A SOLID. THE DENSITY OF 4-AMINOPYRIDINE

A. Measuring the Density of a Solid

The concept of density originated still earlier, but the hydrostatic methods of measuring density go back to Archimedes (287-212 B.C.). It is not entirely clear whether Archimedes solved the problem of the adulteration with silver of the gold wreath by direct (hydrostatic) weighing or by the displacement (pycnometer) method, although the mathematics for handling both are given clearly in his *On Floating Bodies, Book One* (35,46); Heath (46) believes the evidence favors the weighing method.

The concept and measurement of density has played a long and important role in the development and practice of science and technology and even today a greater volume and value of industrial chemical is sold on the basis of specific gravity than on any other method of analysis. The measurement of density appears straightforward and simple but for anything much better than one part in 100 this simplicity is deceptive and a more accurate value difficult to obtain.

In the determination of the density of a single-bodied, irregular solid by hydrostatic weighing, the problem of suspending the solid can usually be solved satisfactorily by a suitable choice of suspension cord and by care to eliminate all obvious bubbles on the surfaces and at the contacts of cord and object. In my experience, the best suspension cord is Nylon monofilament fish line, for which the surface tension effect at the interface and the creepage of liquid are minimal. Not so easy to eliminate is the film of gas adhering to the surface of the solid object. This problem, together with other objections to the use of water, led Bowman, Schoonover and Carroll (8) to recommend that a solid be used as the standard of density and that water be replaced by another liquid as the "transfer liquid". As the solid for the density standard, they selected elemental silicon which they worked neatly into a redetermination (32) of the Avogadro constant. As the transfer liquid, they found the ideal liquid in the completely fluorinated hydrocarbon, FC-75, a liquid having the extraordinary property of dissolving large amounts of oxygen and nitrogen. Using this remarkable liquid as a transfer liquid in a hydrostatic weighing (the term is retained for lack of a better term not implying the use of water), gases on the surface of the solid are dissolved away and, as evidenced by the Avogadro constant work, reproducibility and accuracy to the p.p.m. level made possible.

In the present dissertation, the problem of measuring the density of single-body, irregular solids has arisen at several points and preparations were made to perform hydrostatic weighings using FC-75. In the early part of the work, that with the absolute density cylinder, the density needed was calculated from actual weight in vacuum (vacuum weighing bottle) and a volume calculated from accurate measurements of the external dimensions of the object. For the preliminary work on the weights of stainless steel described in the later chapters of this dissertation, values obtained using water as the transfer liquid were sufficiently satisfactory. Before this set of weights, when completed, however, can be calibrated reliably to the 1-p.p.m. level, an accurate determination of the density of each individual weight must be made using FC-75 as the transfer liquid.

This last statement may seem surprising inasmuch as the weights are being fabricated from the same stainless steel alloy. Some six different heats of the alloy are being used, however, and the densities (two measurements on each heat) vary from 8.089,8 g./cm.^{3} to 8.114,0 g./cm.^{3}; see Table X-1. Dr. David Peterson, Professor of Material Science and Engineering, Iowa State University, was not surprised at this finding and he stated that in his experience, reproducibility in the density of the same piece of alloy was seldom obtained, variations of several parts in 1,000 being common. The causes of these variations he thought were microinclusions and variations in composition with position produced by inhomogeniety in the melt and produced by selective crystallization during freezing. Nor in his experience was agreement ever obtained between values obtained by direct measurement and from X-ray diffraction data.

B. Density of 4-Aminopyridine

Because of the central role of 4-aminopyridine in the recent determination of a value for the faraday (66,68), the density of this substance is a matter of significance; an accurate value for the density must be known to enable the calculation of the correction for the buoyancy of air during a weighing.

In the course of my thesis for the degree Master of Science (reference 38, page 8), I evaluated the partial derivative of the correction for the buoyancy of air with respect to the density of the object being weighed

$$\frac{\partial(BC)}{\partial(d_o)} = W_{o,a}\left(\frac{d_W - d_a}{d_W}\right)\left[\frac{-d_o}{(d_o - d_a)^2} + \frac{1}{(d_o - d_a)}\right] \quad \text{(II-1)}$$

and evaluated it for 4-aminopyridine in air of density 0.001,15 g./cm.^{3} and weights of density 7.89 g./cm.^{3}:

$$\frac{\partial(BC)}{\partial(d_{4ap})} = W_{4ap,a}\left(\frac{d_W - d_a}{d_W}\right)\left[\frac{-d_{4ap}}{(d_{4ap} - d_a)^2} + \frac{1}{(d_{4ap} - d_a)}\right] = -0.000,716 \text{ ml.} \quad \text{(II-2)}$$

That is, a quantity of 4-aminopyridine indicated by the sum of the weights required during a weighing to be 1.000,000 g. has a mass of 1.000,761 g. If the permissible error in the correction is 1 p.p.m., the uncertainty in the density of the 4-aminopyridine must be less than

$$\Delta d_{4ap} = 0.001,398 \text{ g./cm.}^3$$

To date, a value this good has not been obtained although a number of measurements of varying sophistication have been made, Table II-1.

The value last used in a reported result for the faraday is the 1.2682 g./cm.^{3} value of Diehl and Koch. This value was obtained by applying a vacuum to the pycnometer when filled with just sufficient xylene to cover the 4-aminopyridine with the idea of pulling off the air trapped in the bundles of the lath-like crystals of the 4-aminopyridine (as obtained by sublimation). Later, Koch was not able to reproduce this result and application of a vacuum before introducing the xylene and after gave results from 1.2631 g./cm.^{3} to 1.2665 g./cm.^{3} On continued application of the vacuum, a stream of bubbles continued to be evolved, although slowly; a puzzling business.

The source of these troubles in measuring the density of 4-aminopyridine was uncovered during a microscopic examination of the material by Professor Donald L. Biggs of

Table II-1. Density of 4-aminopyridine

Value g./cm.^{3}	Method. Author. Date. Comment.
1.2695	Pycnometer using mineral oil. W. C. Hoyle (54). 1973. This value used in the main faraday paper (68).
1.2682	Pycnometer using xylene and vacuum.[a] W. F. Koch (68). 1975. This value used in the additional results paper (66).
1.2631 to 1.2665	Pycnometer using xylene and vacuum.[b] W. F. Koch at the National Bureau of Standards. 1976. Unpublished work.
1.25	Flotation. Brown and Zabsky (14). 1963.
1.27	Calculated from preliminary X-ray diffraction data. Brown and Zabsky (14). 1963.
1.2636	Flotation in solutions of sodium perchlorate; value very uncertain.[c] H. Diehl and J. C. Clardy (27). 1975.
1.2710	Calculated from precision X-ray diffraction data. J. C. Clardy (27). 1975. The outer limits of uncertainty are 1.2702 g./cm.^{3} and 1.2718 g./cm.^{3}.

---

[a] The xylene was previously saturated with 4-aminopyridine, the pycnometer was filled only partially and a vacuum was applied to the xylene-4-aminopyridine mixture to remove bubbles before final filling

[b] Same as a but the vacuum was applied before the xylene was introduced and afterward. See text for comment on the phenomena observed.

[c] Flotation in solutions of sodium perchlorate of slightly varying density. Results very uncertain; as the density for the liquid and crystal became closer, some crystals fell and some rose.

the Department of Earth Sciences, Iowa State University. The long, needle-like crystals of 4-aminopyridine obtained by sublimation have long cavities in the form of tubes, some running the entire length of the crystals, Figures II-1 and II-2. Usually one end and frequently both ends appear open. These cavities are undoubtedly the source of the slow continual stream of bubbles observed by Diehl and Koch and of the wide variation in the values obtained for the density.

Values for the density of crystals obtained from X-ray diffraction data are invariably much higher than those obtained by hydrostatic weighing and Professor Biggs, as well as Professor J. C. Clardy of the Department of Chemistry, Iowa State University, and Professor D. Peterson of the Department of Materials Science and Engineering of Iowa State University, authorities on the crystal structure of inorganic, organic, and metallurgical materials, respectively, expressed no surprise at the discordant values reported for 4-aminopyridine in Table II-1.

As of this writing (June 1979), it is not clear which value for the density should be used in making the correction for the buoyant force of air during a weighing of 4-aminopyridine; probably none would really reflect the prevailing or effective density at the time of weighing. It would seem that the only way this problem can be solved is

Figure II-1. Tubular cavities in 4-aminopyridine prepared by sublimation. Magnification: 100X. Photomicrograph taken by Professor Donald L. Biggs

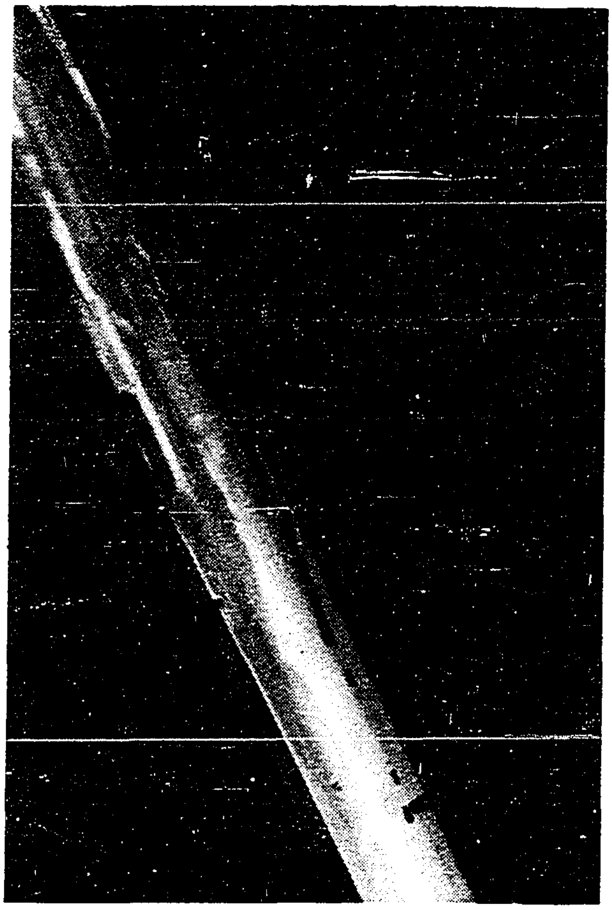


Figure II-2. Tubular cavities in 4-aminopyridine prepared by sublimation. Magnification: 100X. Photomicrograph taken by Professor Donald L. Biggs to melt the 4-aminopyridine, then to solidify it into a single mass which can then be crushed, and this material, presumably free from the tubular voids, used for the high-precision coulometric titrations and for a measurement of density. The high volatility of 4-aminopyridine at the melting point probably will make it necessary to effect the fusion under mild gas pressure, and of course, an inert gas should be used.

III. MEASURING THE DENSITY OF AIR

A. Introduction

Of the corrections which are applied in the precise determination of mass, that which looms largest, particularly for objects of low density, is for the buoyancy of air on the object being weighed and on the weights. Given the densities of the object (d_o), weights (d_W), and air (d_a), the mass of the object (mass in vacuum, T_o) is obtained from the sum of the weights ($W_{o,a}$) by

$$T_o = W_{o,a}\ (1 - (d_a/d_W))/(1 - (d_a/d_o)) \qquad \text{(III-1)}$$

This correction is discussed in the texts on analytical chemistry, see for example Diehl (ref. 34, page 37) for a somewhat simplified version of equation (III-1). The correction is treated in detail and the derivation of equation (III-1) is given in my thesis for the degree Master of Science (38), a thesis in which the groundwork is laid for the definitive treatment necessary to make the correction with such accuracy that the measurement of mass may be reliable to one part per million (1 p.p.m.). The very recent papers (19,20,61,102) which have appeared on the subject of the correction for the buoyancy of air deal with the trivial variation in applying it when the measurement of mass is made with the single-pan balance. In the present chapter, I deal with the general problems and with preliminary experiences with the determination of the density of air.

Rearrangement of equation (III-1) yields the correction (BC) for the buoyancy of air, equation (III-2), of more direct applicability in evaluating the accuracy necessary in the measurement of the density of air:

$$BC = T_o - W_{o,a} = W_{o,a} \left\{ \left[\frac{1 - \frac{d_a}{d_W}}{1 - \frac{d_a}{d_o}} \right] - 1 \right\} \qquad \text{(III-2)}$$

The partial derivative of the correction with respect to the density of air is

$$\frac{\partial(BC)}{\partial(d_a)} = \frac{W_{o,a}d_o}{d_W} \left[\frac{d_W - d_a}{(d_o - d_a)^2} - \frac{1}{(d_o - d_a)} \right] \qquad \text{(III-3)}$$

Equation (III-3) may be used to calculate the permissible uncertainty in the density of air for a given uncertainty in the correction for buoyancy. This has been done for four common substances, Table III-1, for a weighing of 1.000,000 g. of material with an accuracy of 1 p.p.m., using stainless steel weights, $d_W = 7.89$ g./cm.^{3}, and a typical density of air, $d_a = 0.001,150$ g./cm.^{3}. Clearly, the density of air must be known to one part per thousand (1 p.p.t.) or better if weighings are to be good to 1 p.p.m.

Table III-1. Uncertainty permissible in the density of air for an uncertainty of one part per million in the correction for the buoyancy of air in the weighing of one gram of material

Substance (Use or reference)	Density of Substance	$\frac{\partial(BC)}{\partial(d_a)}$	$\Delta(d_a)$	
	g./cm.^{3}	cm.^{3}	mg./cm.^{3}	Parts per 10,000
Water (Calibration of volumetric glassware)	1.000,000	0.875,3	0.001,14	9.9
4-Aminopyridine (Refs. 66,68)	1.268,2	0.663,0	0.001,51	13.1
Metallic Silver (Ref. 31)	10.500,0	-0.031,51	-0.031,7	-276
Platinum-iridium alloy (Mass transfer from standard kilogram to stainless steel kilogram working standards)	21.55	-0.080,3	-0.012,4	-108

Traditionally, the density of air has been calculated from the barometric pressure, temperature, and relative humidity using an equation such as (III-4) which is based on the ideal gas law and the law of additivity of partial pressures:

$$d_a = \frac{0.001{,}292{,}3[P_{bp} - 0.378{,}02\ P_{H_2O,t}(\text{Rel. Hum.}/100)]}{(1 + (0.003{,}660{,}99)(t))(760.0)} \tag{III-4}$$

In this equation, P_{bp} is the barometric pressure in mm. Hg, and $P_{H_2O,t}$, the vapor pressure of water at temperature t in °C, is multiplied by the relative humidity expressed as a fraction. A derivation of this equation appears in my M.S. thesis (Ref. 38, pp. 14-17). Various numerical quantities enter into the derivation of this equation: the molecular weight of air, 28.964,5 g./mole; the molecular weight of water, 18.015,34 g./mole; and the gas constant, 82.056,8 $\text{cm.}^3\cdot\text{atm./mole}\cdot{}^\circ\text{K}$. More elaborate equations have been derived which include additional corrections such as the compressibility factor (59).

To obviate the need for measuring the barometric pressure, temperature, and relative humidity each time a weighing was made, Baxter (3) employed a sealed glass globe, determined its exterior volume, and determined its weight in air of known density. These quantities enabled him at a later date to obtain the density of air from a single weighing of the globe. A *Baxter's globe*, weighing approximately 27.2 g. and having a volume and density of 118.3 cm.^3 and 0.23 g./cm.^3, respectively, was used by Diehl and coworkers in their work on primary standards and the value of the faraday (66,68).

On several occasions since the Baxter's globe was described, sealed, hollow vessels have been used to determine the density of air; by Ulbricht (100) who used a light bulb (42 g., 190 cm.^{3}, 0.22 g./cm.^{3}); by Bowman et al. (9) who used hollow and solid weights of stainless steel (difference in weight only stated, 35.466 mg., 42.7 cm.^{3}); by Brulmans and Eschbach (18) who used an aluminum can filled with helium (23.1 g., 69.4 cm.^{3}, 0.33 g./cm.^{3}) and a counterpoise of stainless steel; and by Toropin and Snegov (99) who used a sealed globe of molybdenum glass (72.5 g., 556 cm.^{3}, 0.15 g./cm.^{3}) and a counterpoise in the form of a cylindrical tube made of the same glass. The external volume of each of these devices was determined by hydrostatic weighing, with corrections presumably being made for the buoyant effect of air on the weights used. The mass in vacuum of three of the devices, those of Baxter, Ulbricht, and Brulmans and Eschbach, was determined by weighing in air and making the correction for buoyancy using the density of air calculated from the prevailing conditions. It has been stated, private communication only, that the mass in vacuum of the hollow vessel of Bowman and Schoonover was determined by weighing in an actual vacuum using a commercial apparatus; measurement of mass in an actual vacuum, in an absolute way rather than relative or changes in mass, is extremely difficult and it is likely that the private communication just referred to is in error. The mass in vacuum of the glass globe of Toropin and Snegov was in effect obtained by weighing the two objects of the same glass of approximately equal mass in air then sealing one in the form of a globe, presumably without losing any glass. The difference in mass of the two glass objects was in terms of weights of brass or of stainless steel without correction for buoyancy and was taken as mass in vacuum on the assumption that, because of the way the devices were made, an error was suffered just about equal to the error in the weighings made.

These devices yield values for the density of air agreeing with values calculated from the prevailing conditions to about one part per thousand or slightly better. The precision of this "tracking" indicates that for relative changes in the density of air over the range in which barometric pressure, temperature, and relative humidity vary in any one laboratory, a formula such as equation (III-4) does describe the behavior of moist air. None of these devices, however, provides a check on the conformity of moist air to the gas laws in the absolute sense of yielding an independent value for the density inasmuch as the equation itself was used in determining the characteristics of the device. That moist air conforms to the gas laws has been questioned by Pontius (86).

In January 1976, work was begun at Iowa State University to make and calibrate stainless steel cylinders to be used as Baxter's globes for the determination of the density of air. The material and the cylindrical shape were chosen to (1) improve the sensitivity by reducing weight and density, (2) obviate electrostatic effects by passing from glass to metal, (3) reduce the mass to less than 20 g. so that weighing could be performed on a modern, single-pan microbalance, and (4) determine the physical characteristics in such a manner as not to involve a prior knowledge of the density of air (as obtained by calculation using a formula involving the gas laws such as equation (III-4)). The last of these objectives was prompted by the paper of Pontius (86).

In my M.S. thesis (38), I described the fabrication and calibration of a hollow cylinder of stainless steel formed by the electron-beam welding of "re-entrant" caps into the ends of thin-walled, stainless steel tubing. Three such cylinders were made, each having about the dimensions: 15.2 g., 37.9 cm.^{3}, and 0.4 g./cm.^{3}. The interior of these cylinders was evacuated owing to the welding technique used. These cylinders met the first three of the objectives listed above. The nature of the re-entrant caps which formed the ends of the cylinders precluded obtaining the exterior volume of the cylinders by measurement of the external dimensions.

It was necessary, therefore, to determine the volume of the cylinders by hydrostatic weighing and to calculate the mass (in vacuum) of the cylinder from the volume and a weighing in air of known density. These cylinders were used in a series of determinations of the density of air, the weight of a solid stainless steel counterweight being obtained at the same time. The values obtained agreed with the values calculated from the prevailing conditions to about 1 p.p.t. Again, these re-entrant-cap cylinders did not provide a check on the claim of Pontius that moist air does not conform to the gas laws inasmuch as the cylinders were calibrated using air of known density.

Of the various regular solids for which the exterior volume can be calculated from the dimensions, the right cylinder is the only one which can be constructed with precisely true configurations as a thin-walled shell of minimum weight. A right cylinder meeting all four objectives outlined above was made possible in April 1976 when Dr. Diehl proposed a method of sealing flat faces onto stainless steel tubing. Fabrication of such a cylinder, referred to as an *absolute density cylinder*, was begun in late April of 1976. The fabrication and calibration of the absolute cylinder are described in detail in Chapter VI of this dissertation and the use of the absolute density cylinder for the determination of the density of air is the subject of Chapter VIII.

The problem of obtaining directly the mass in vacuum of this hollow cylinder was solved in April 1976 by the invention of a metal *weighing bottle*. The weighing bottle consisted of a chamber which could be evacuated, which was large enough to accommodate the hollow cylinder, but which was light enough that it, together with the hollow cylinder, could be weighed on a modern, single-pan semimicrobalance (capacity 160 g., sensitivity 10 μg.). The construction of the weighing bottle and its use to determine directly mass in vacuum is described in detail in Chapter VII.

Thus, as early as late May 1976, the various devices necessary to determine the density of air and to check the conformity of moist air to the gas laws were on hand at Iowa State University. Work began at that time to check the claim made by Pontius under improved conditions in the laboratory. In the remainder of this chapter and in Chapter IV are described why and how certain improvements were made in the laboratory to facilitate a precise check on the conformity of moist air to the gas laws.

B. Relative Effects of the Prevailing Conditions on the Density of Air

Partial differentiation of equation (III-4) with respect to barometric pressure, temperature, vapor pressure of water, and relative humidity, respectively, gives:

$$\frac{\partial(d_a)}{\partial(P_{bp})} = \frac{0.001{,}292{,}3}{(1 + (0.003{,}660{,}99)(t))(760.0)} \qquad \text{(III-5)}$$

$$\frac{\partial(d_a)}{\partial(t)} = \frac{-(0.001{,}292{,}3)[P_{bp} - 1.051{,}78(P_{H_2O})(\text{Rel. Hum.}/100)]}{[1 + (0.003{,}660{,}99)(t)(760.0)]^2} \qquad \text{(III-6)}$$

$$\frac{\partial(d_a)}{\partial(P_{H_2O})} = \frac{-(0.000{,}488{,}51)(\text{Rel. Hum.}/100)}{(1 + (0.003{,}660{,}99)(t))(760.0)} \qquad \text{(III-7)}$$

$$\frac{\partial(d_a)}{\partial(\text{Rel. Hum.})} = \frac{-(0.000{,}004{,}885{,}1)(P_{H_2O})}{(1 + (0.003{,}660{,}99)(t))(760.0)} \qquad \text{(III-8)}$$

The relationship between the vapor pressure of water and temperature is given by Jones (59):

$$P_{H_2O} = 1.314{,}6 \times 10^9 \exp(-5{,}315.56)/(t + 273.15) \qquad \text{(III-9)}$$

in which P_{H_2O} is in mm. Hg, and t is in °C, and the symbol exp means to calculate the natural antilogarithm of the value in parentheses following the symbol. Substitution of equation (III-9) into equation (III-4) and differentiation with respect to temperature gives a more exact expression relating the density of air to temperature:

$$\frac{\partial(d_a)}{\partial(t)} = \frac{-(0.003{,}595{,}6)[P_{bp} - (4.969{,}45)(10^8)^{\P\P}}{[(1 + (0.003{,}660{,}99)(t))(760.0)]^2}$$

$$^{\P\P}(\text{Rel. Hum.}/100)\exp(-(5{,}315.56)/(273.15 + t))]$$

$$\text{(III-10)}$$

The uncertainty in the barometric pressure, temperature, vapor pressure of water, and relative humidity permissible for the determination of the density of air at certain levels of accuracy can be illustrated by evaluating equations (III-5), (III-6), (III-7) and (III-8) for typical conditions in the laboratory: P_{bp} = 744.01 mm. Hg; t = 23.2°; Rel. Hum. = 32 per cent; $P_{H_2O,23.2°}$ = 21.324 mm. Hg, and d_a = 0.001,162,1 g./cm.^{3}. This gives

$$\frac{\partial(d_a)}{\partial(P_{bp})} = 0.000,001,567 \text{ g./cm.}^3\cdot\text{mm. Hg} \qquad \text{(III-11)}$$

$$\frac{\partial(d_a)}{\partial(t)} = -0.000,003,921 \text{ g./cm.}^3\cdot{}^\circ \qquad \text{(III-12)}$$

$$\frac{\partial(d_a)}{\partial(P_{H_2O})} = -0.000,000,188 \text{ g./cm.}^3\cdot\text{mm. Hg} \qquad \text{(III-13)}$$

$$\frac{\partial(d_a)}{\partial(\text{Rel. Hum.})} = -0.000,000,126 \text{ g./cm.}^3\cdot\text{per cent} \qquad \text{(III-14)}$$

Evaluation of the more rigorous equation (III-10) gives a result identical with that of equation (III-12).

For the permissible uncertainty in the density of air to be 1 p.p.t., that is 0.000,001,2 g./cm.^{3}, the uncertainties in the measurements of the barometric pressure, the temperature, and the relative humidity must not exceed the following values:

$$\Delta P_{bp} = 0.742 \text{ mm. Hg} \tag{III-15}$$

$$\Delta t = 0.296° \tag{III-16}$$

$$\Delta(\text{Rel. Hum.}) = 9.201 \text{ per cent} \tag{III-17}$$

$$\Delta P_{H_2O} = 6.18 \text{ mm. Hg} \tag{III-18}$$

To determine the density of air to 1 p.p.t., or preferably better, and to check the conformity of moist air to the gas laws at the same level of precision, the uncertainty in the measurement of each of the variables must be at least to the level of precision listed above and the conditions in the laboratory must be stable and measurable of the same degree.

C. Preliminary Experience with the Measurement of Temperature

The preliminary investigation into the use of stainless steel cylinders for the determination of the density of air, including the work described in my M.S. thesis (38), was done in Room 137A of the Chemistry Hall, Iowa State University. Room 137A is 6.9 meters (22.75 ft.) long, aligned north-south, 3.0 meters (9.9 ft.) wide, and 3.9 meters (12.8 ft.) high. The volume of the room is thus about 81 cubic meters (2860 cubic ft.). The room has one window located on the north wall; the window is 2.9 meters (9.4 ft.) high and 1.7 meters (5.6 ft.) wide. During the course of the earlier work on primary standards and on the value of the faraday and during the preliminary work of this dissertation, the room was considerably modified. It was sealed from the ventilating system of the Chemistry Hall and was partially insulated by covering the window with a sheet of Styrofoam, 1 in. thick. The temperature of the room was regulated by the interplay of a Sears Coldspot Air Conditioner mounted in the window and a steam radiator also located on the north wall; the compressor of the air conditioner was controlled by a thermostat located on the south wall. Annually, the temperature of the room ranged between 23.5° and 25.5° depending on the season, the prevailing outside temperature, and the pressure in the steam line to the radiator. Hourly, the temperature of the room varied cyclically over a range of 1.5° to 2.0° reflecting the operation of the air conditioner. A cycle of the air conditioner averaged about 40 minutes in length with the compressor being on about half of this time. The length of the cycle and the maximum and minimum temperatures of the room reached during any cycle depended primarily on the outside temperature and the pressure in the steam line.

The variation of temperature inside the case of a balance located in Room 137A was as great at 0.5° during the 40-minute cycle of the air conditioner. As shown by equation (III-16), the uncertainty in temperature must be less than 0.3° if the density of air calculated by equation

(III-4) is to be reliable to 1 p.p.t. Clearly, a check on the conformity of moist air to the gas laws to better than 1 p.p.t. could not be made unless the temperature inside the balances used was controlled better than could be done under the conditions existing in Room 137A. To obtain the control necessary, a constant temperature room was constructed inside Room 137A; this constant temperature room is described in Chapter IV.

D. Preliminary Experience with Barometers

During the summer of 1976, measurements of the density of air were made with absolute density cylinder Number 1 at Ames, Iowa, Gaithersburg, Maryland, Boulder, Colorado, and Laramie, Wyoming, with the object of showing that moist air conforms to the gas laws. The variation in altitude of these localities provided a greater range of barometric pressure than experienced by the day-to-day changes in any one locality. The barometric pressure at these places was measured with mercurial barometers which were the property of and housed in the various laboratories. Intercomparison of the barometers was made with three travelling aneroid barometers:

a) A high-precision aneroid barometer, Model PMB-1, manufactured by American Paulin System of Los Angeles, California, the property of the Ames Laboratory of the Department of Energy and on loan courtesy of Professor Harry J. Svec. This instrument was readable to 0.001 in.

b) A digital read-out, aneroid barometer with electronic balancing (neon glow tube used as zero indicator) manufactured by Mechanisms Limited of Croydon, Great Britain, the property of the National Center for Atmospheric Research, Boulder, Colorado, and on loan through the courtesy of Dr. Robert McBeth.

c) An Air Force altimeter, reading in meters, manufactured by the Wallace and Tiernan Company, the property of Professor Victor Ryan, Department of Chemistry, University of Wyoming, Laramie.

Simultaneous readings of these three portable barometers were made at:

a) A bench mark (United States Geological Survey (USGS)) on the southeast corner of the campus of the University of Colorado.

b) The porch of the stone church in Lyons, Colorado.

c) Several bench marks along Colorado Highway 7 in the vicinity of Allenspark, Colorado, at an elevation of about 8200 feet as established by the USGS and the Colorado Highway Commission.

d) A USGS bench mark in the City Park, Missouri Valley, Iowa.

e) Room 170 Chemistry Hall, Iowa State University.

The disconcerting discovery was made that no real agreement could be obtained between these instruments, or with a house instrument at the sites where one was available. The differences were unpredictable, the readings on any one instrument being sometimes high and sometimes low. This erratic behavior was traced to temperature effects, and these were found to be particularly bad in the field; the erratic variations often were equivalent to 2 m. in elevation. Surprisingly, if all the aneroid barometers and the house barometer in Room 170 Chemistry Hall (a Fortin ship-board model mounted on gimbals, Model 751-B, manufactured by Julien Friez and Sons of Baltimore, Maryland) were placed together overnight (in Room 170 of the Chemistry Hall) with doors and windows shut so that the temperature of all the instruments became the same to within 0.1°, all instruments gave identical readings to within 0.01 in. Hg. It was necessary to take the readings immediately on entering the room in the morning. Such agreement was obtained repeatedly in this manner over the course of two months.

The conclusion was drawn that barometers, both aneroid and mercurial, are exceptionally temperature dependent. It was concluded also that the measurements of the density of air made at Boulder and Laramie with absolute density cylinder Number 1 were at best only first approximations as a check on the validity of the cylinder for the determination of the density of air and for the conformity of moist air to the gas laws. It was concluded further that measurements of the density of air with this or other hollow cylinders (as described in my M.S. thesis) were not much more reliable, the weighings described in my M.S. thesis having been made in Room 137A and the barometric pressure measurements in Room 170. It became obvious that it would be necessary to house the barometers in a constant temperature room if reliable measurements were to be obtained.

E. Preliminary Experience with Measurements of Relative Humidity

The measurement of relative humidity in the work described in my M.S. thesis was made using an Airguide, Model 113B, Hygrometer. Subsequently, a Weathermeasure, Model H311, Hygrothermograph was purchased. The Hygrothermograph recorded that the relative humidity in Room 137A varied cyclically with the operation of the air conditioner, as did the temperature. During periods of high relative humidity outside the Chemistry Hall, the relative humidity in Room 137A varied over a range of 5 to 12 per cent for one cycle of the air conditioner; during periods of lower prevailing relative humidity, the range in Room 137A was 1 to 3 per cent. It was also discovered that the response of the Airguide Hygrometer was sluggish compared to the more sensitive Hygrothermograph. While the two devices agreed to 2 per cent in a quiesent room (Room 145 of the Chemistry Hall), they disagreed by up to 5 per cent under the conditions in Room 137A. As shown by equation (III-17), the uncertainty in the measurement of relative humidity must be less than 9 per cent if the density of air is to be reliable to 1 p.p.t. The conditions in Room 137A were marginal at best for checking the performance of the absolute density cylinders and the conformity of moist air to the gas laws. It was concluded that conditions more favorable for such work would exist only inside a constant temperature room.

The calibration of the devices for measuring relative humidity was also a matter of concern. The Airguide Hygrometer had been calibrated against a sling psychrometer in 1975 but some question existed as to the reliability of this calibration. The Weathermeasure Hygrothermograph was calibrated according to the manufacturer's instructions by coating the bundle of hair with water and setting the pen to 95 per cent. This method appeared approximate at best and the agreement between the two hygrometers was probably fortuitous. A method for determining the moisture content of air by a gravimetric method was developed; this method is described in Chapter IV.

IV. CONSTANT TEMPERATURE BOX

A. Construction of the Constant Temperature Box

A constant temperature room constructed from sheets of insulating material was built in the southeast corner of Room 137A of the Chemistry Hall, Iowa State University, during June 1977; hereinafter, this constant temperature room will be referred to as the "constant temperature box" to differentiate the box from Room 137A which was also at a controlled temperature (±1°). The constant temperature box was built to house the balances, barometers, and other devices used in the work described in this dissertation as well as to act as a controlled environment in which the calibration of weights and high-precision weighings could be performed in the future. The placement of the box in Room 137A and the door of the box are shown in Figure IV-1.

The exterior of the constant temperature box was 3.27 m. (10.7 ft.) long, aligned north-south, 1.46 m. (4.79 ft.) wide, and 2.59 m. (8.50 ft.) high. The box was constructed from 1.0-in. thick (R=8) and 1.5-in. thick (R=12) sheets of Thermax, a foil-covered brand of high-thermal, insulating Styrofoam (Celtex Corporation); these sheets were nailed to a wooden framework of 2x4-in. studs. The walls and ceiling of the box consisted of a layer of the 1.0-in. thick sheet

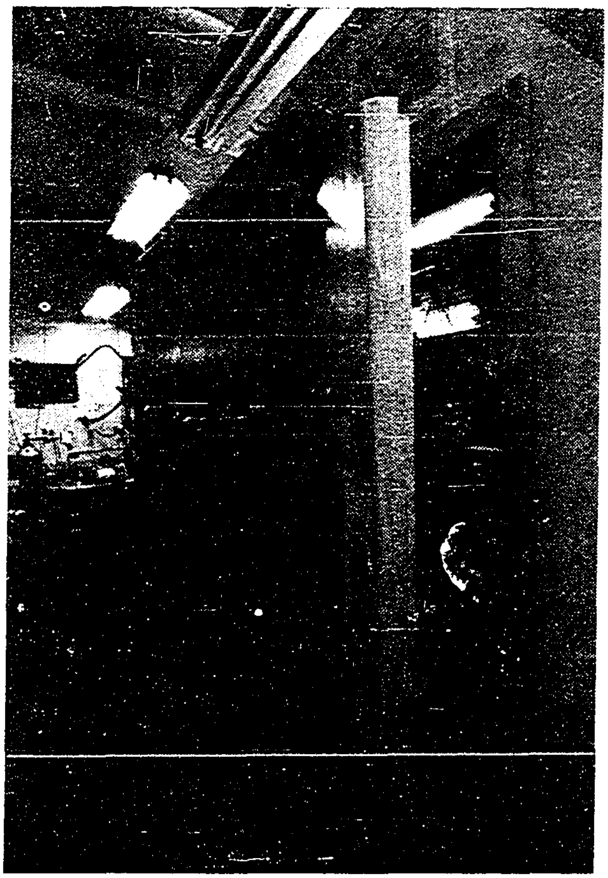


Figure IV-1. Constant temperature box in Room 137A

Door to box open. Air conditioner and block fan in insulation covering window sandwiched between two layers of the 1.5-in. thick sheet to give a total thickness of 4.0-in. The layers were staggered so that the gap between any two sheets of insulating material in a layer was covered by a full sheet on at least one side. The gaps between sheets were sealed with strips of 2-in. duct tape. The floor of the box consisted of a 1.0-in. sheet of Thermax sheet covered by a sheet of plywood which was also 1.0-in. thick. The door to the box was made by sandwiching a hollow-core door between two sheets of 1.5-in. thick sheeting. The interior dimensions of the box were: length, 3.05 m. (10.0 ft.); width, 1.25 m. (4.14 ft.); and height, 2.41 m. (7.92 ft.). The area of the floor and the volume of the interior of the box were about 3.82 m.^{2} (41.3 ft.^{2}) and 9.19 m.^{3} (327.1 ft.^{3}), respectively. The arrangement of the various piers and equipment described in the remainder of this chapter reduced the working area of the box to about 1.58 m.^{2} (16.9 ft.^{2}). See Figure IV-2 and Figure IV-4.

The location of the box in the southeast corner of Room 137A disrupted both the circulation of air in the room and the control of temperature; the box blocked direct access of the air from the air conditioner to the thermostat which was isolated in the quiescent space two feet wide between the box and the south wall of the room. The cycle of the air conditioner became longer (up to 1.5 hours) and

Figure IV-2. Floor plan of the constant temperature box

A. Pier carrying the balances

B. Mettler, Model M5/SA microbalance

C. Mettler, Model H51AR semimicrobalance

D. Shelf carrying the gas pipet

E. Pier carrying barometer

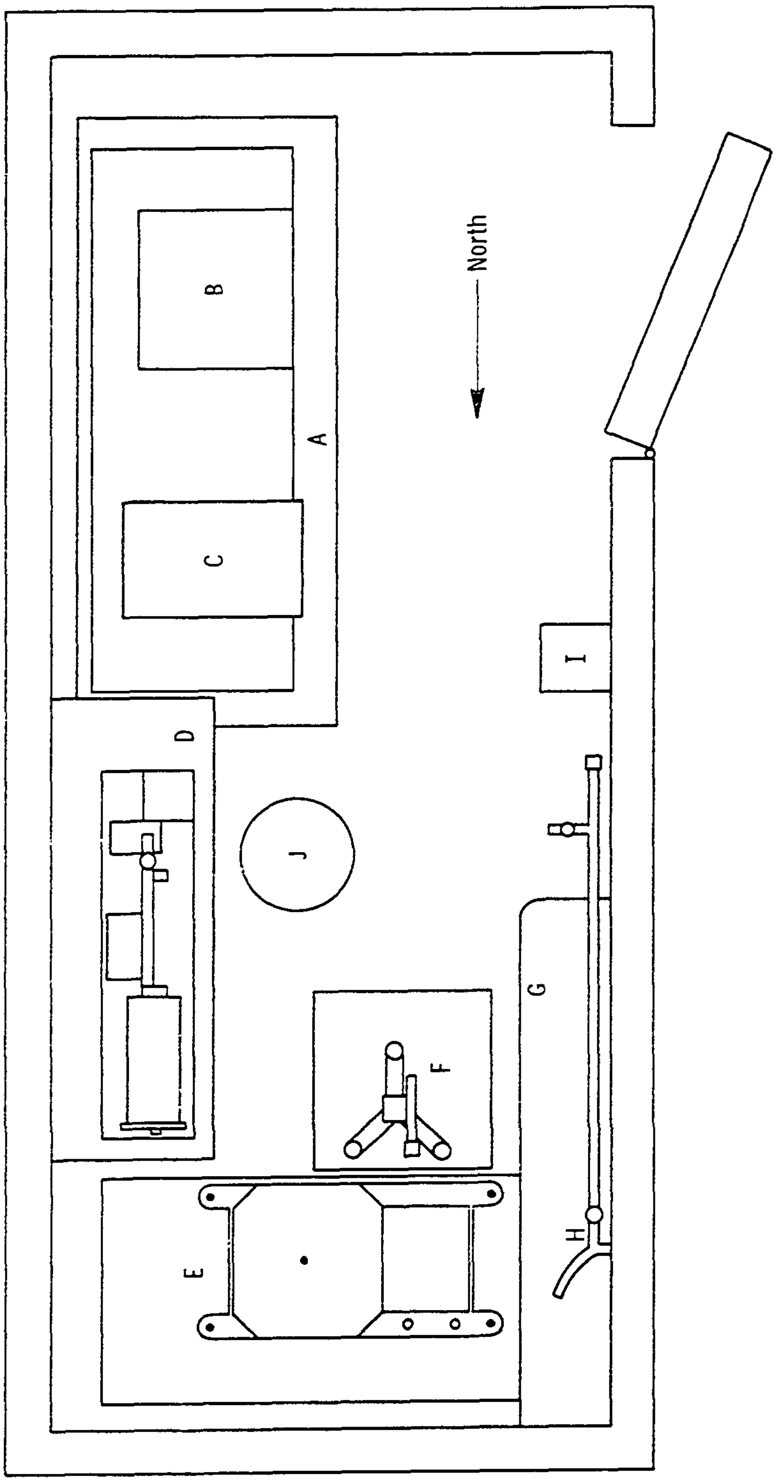
F. Pier carrying cathetometer

G. Shelf

H. Vacuum system including attachment to barometer (north leg) and pumping station (end of south leg)

I. Friez, mercurial barometer

J. Position of the reflector carrying the bulb which was turned off to compensate for body heat


North
A
B
C
D
E
F
G
H
I
J

the range of temperature recorded during the cycles increased (up to 3.5°). Satisfactory circulation in Room 137A was regained by (1) using a fan, with 12-in. blades to force air down the outside of the west wall of the box toward the thermostat, and by (2) mounting two so-called block fans in the insulation covering the window of Room 137A. These block fans, located 3 ft. above the blower of the air conditioner and directed into the room, forced air to the southern end of the room and furthermore relieved the strain on the air conditioner, particularly in the winter, since these fans drew air from a dead space formed between the window and the insulation covering the window.

The ventilation of the constant temperature box and the distribution and mixing of air within the box were accomplished using block fans (75 $ft.^3/min.$). These fans were mounted in metal boxes and forced air through sheet metal pipes (4-in. diameter), some with adjustable elbows. The ventilating system of the box is shown in Figure IV-3.

Air entering the box was drawn from the quiescent space between the box and the southeast corner of Room 137A. The air was drawn through a sheet metal box (12 in. x 12 in. in cross section by 14 in. high) and over heating elements (light bulbs) in the metal box, drawn through the block fan, blown through a duct, and released amid the concrete blocks which made up the pier carrying the barometer. The heating

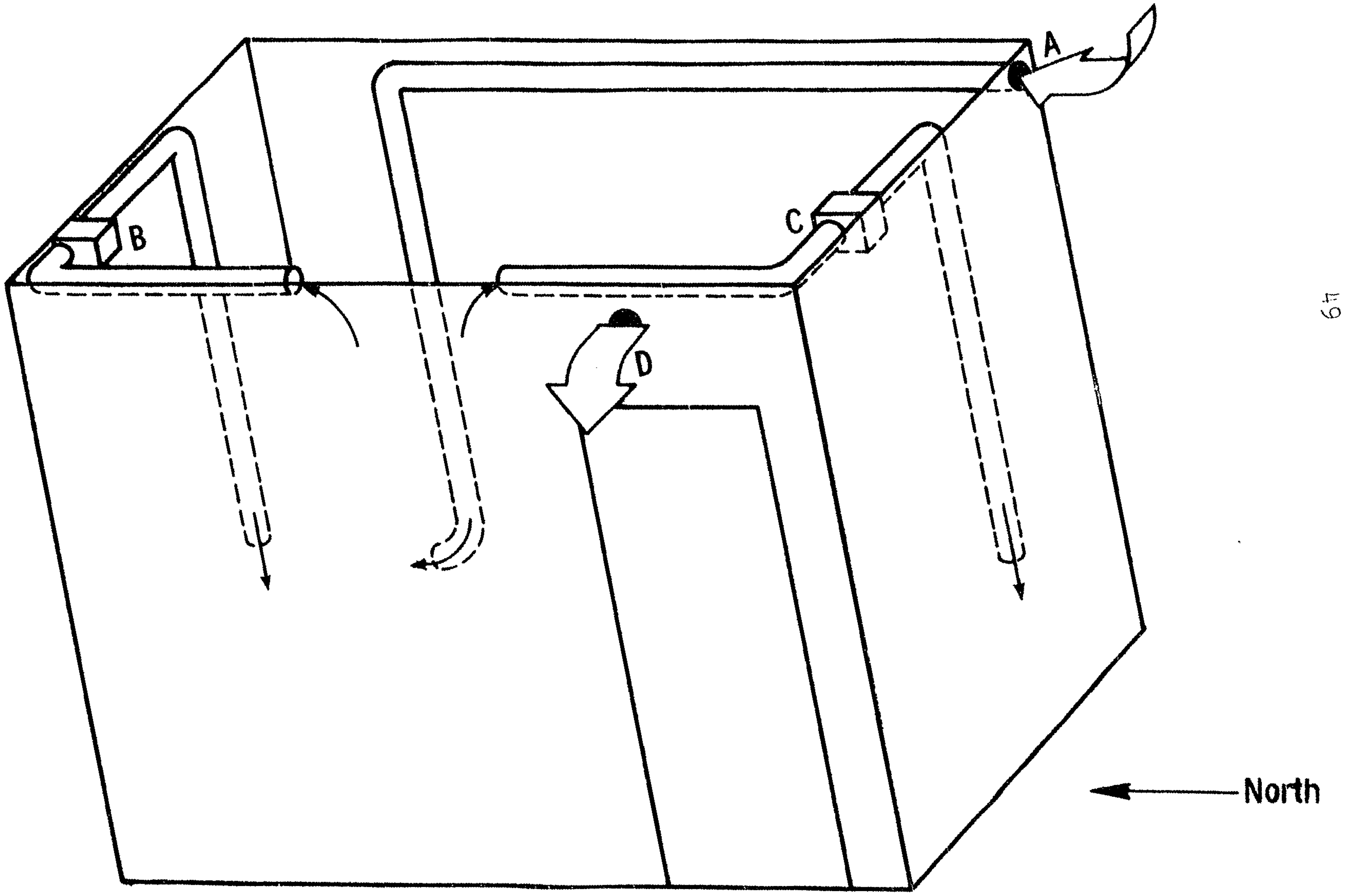
Figure IV-3. Ventilating system for the constant temperature box

A. Point of entry of air into the box. This air is blown into the concrete blocks of the pier carrying the barometer

B. North, recirculation system

C. South, recirculation system

D. Vent


A
B
C
D
North

elements in this system consisted of a 200-watt light bulb and a 200-watt infrared heating lamp. A thermistor temperature regulator, custom manufactured by the electrical engineers of the Hach Chemical Company, Loveland, Colorado, was used to control these heating elements. The sensor for the thermistor regulator was located at the mouth of the duct into the box and directly behind the fan. Thus, any heating of the air was done prior to entry into the box. Early attempts to use a second thermistor regulator located inside the box and light bulbs located in the duct work of the recirculating system inside the box failed; the light bulbs simply supplied too much heat to the highly insulated box. An attempt to use another port close to floor level on the south wall of the box also failed; the air entering through the lower port did not have sufficient time to equilibrate with the air in the box before entering the general circulation within the box.

The air was distributed and mixed within the box by two recirculating systems, B and C in Figure IV-3, which drew air from near the ceiling of the box and released it among the concrete blocks of the piers carrying the barometer and the balances. In such a fashion, full use was made of the concrete blocks of the piers as sinks for heat and the disruptive effects of moving air were minimized. Each recirculating system consisted of sheet metal duct and a box carrying a block fan.

The box was vented by (1) four holes, each 1 in. in diameter, which were drilled 2 in. off the floor on the west wall of the box and (2) a block fan, D in Figure IV-3, mounted on the west wall over the door. An adjustable elbow of duct was placed inside the box before the fan to preferentially draw air from the northern end of the box rather than the area directly around the balances; this avoided any disruption of the balances by air moving in the vicinity of the balances while partially venting body heat, carbon dioxide, and water vapor from the operator. Further details on control of temperature in the box are discussed in Section C of this chapter.

B. Piers to Carry the Balances, Barometer, and Cathetometer

In theory, a pier on which instruments are mounted should be connected to the earth by both a still and a loose coupling. In the present instance the stiff coupling was through massive slabs of concrete and concrete blocks and the loose coupling through pads of plastic foam sheet 0.25 in. thick; a large volume of water, in plastic, 1-gallon jugs, placed within the piers probably constituted the equivalent of a loose coupling.

The floor of Room 137A, a remnant of the original flooring laid in 1910-1912 when the Chemistry Hall was constructed, consists of cast concrete (or a rather poor quality poured as both flooring and supporting beams) and a 2-in. layer of asphalt. Before the constant temperature box was constructed, the asphalt over areas sufficient for two piers was removed and slabs of concrete, 3.5 in. thick, were poured directly on the concrete of the flooring and beam work of the building. After hardening, these slabs were coated with varnish to prevent dusting and the piers built on them. Care was taken that at no point did the piers or apparatus mounted on them touch the walls of the constant temperature box.

The pier for the balances consisted of layers of, successively from bottom up: 0.25-in. plastic foam; four courses of concrete block; a sheet of plastic foam; a sheet of plywood 0.75 in. thick; a box made of 0.75-in. plywood in the top of which was cast a concrete slat 3 in. thick; a sheet of plastic foam; and finally, a sheet of Alberene stone 1 in. thick and weighing 70 pounds. Jugs of water were placed inside the box and within the piers wherever possible. The piers for the barometer and cathetometer were similarly constructed but without the wood box but, at the top, with a sheet of plywood and two slabs of Alberene stone, the top one of these stone slabs being supported by six Number 9 rubber stoppers.

These assemblies provided the instruments, particularly important for the balances, with support which was free of the vibration of the building, either that caused by foot traffic in the corridors, auto and truck traffic on nearby streets, or trains on the Chicago and Northwestern Railroad (evident in the basement of the new Physics Building and in Room 137A). The interior of the constant temperature box including the piers for the balances, barometer, and cathetometer is shown in Figure IV-4.

On the suggestion of physicists, the upper, Alberene stone slab of the pier carrying the balances was mounted on partially inflated inner tubes (six tubes, each 4 in. internal diameter) and although these also provided against the transmittal of vibrations, the level of the balance mounted on the slab changed on the addition of a 1-kg. weight and this mounting had to be abandoned. Although the 0.25-in. sheets of plastic foam and the rubber stoppers probably did not provide the loose coupling ideally desired, they had the merit that the levels of the stone slabs were not affected by large weights.

C. Control and Measurement of Temperature

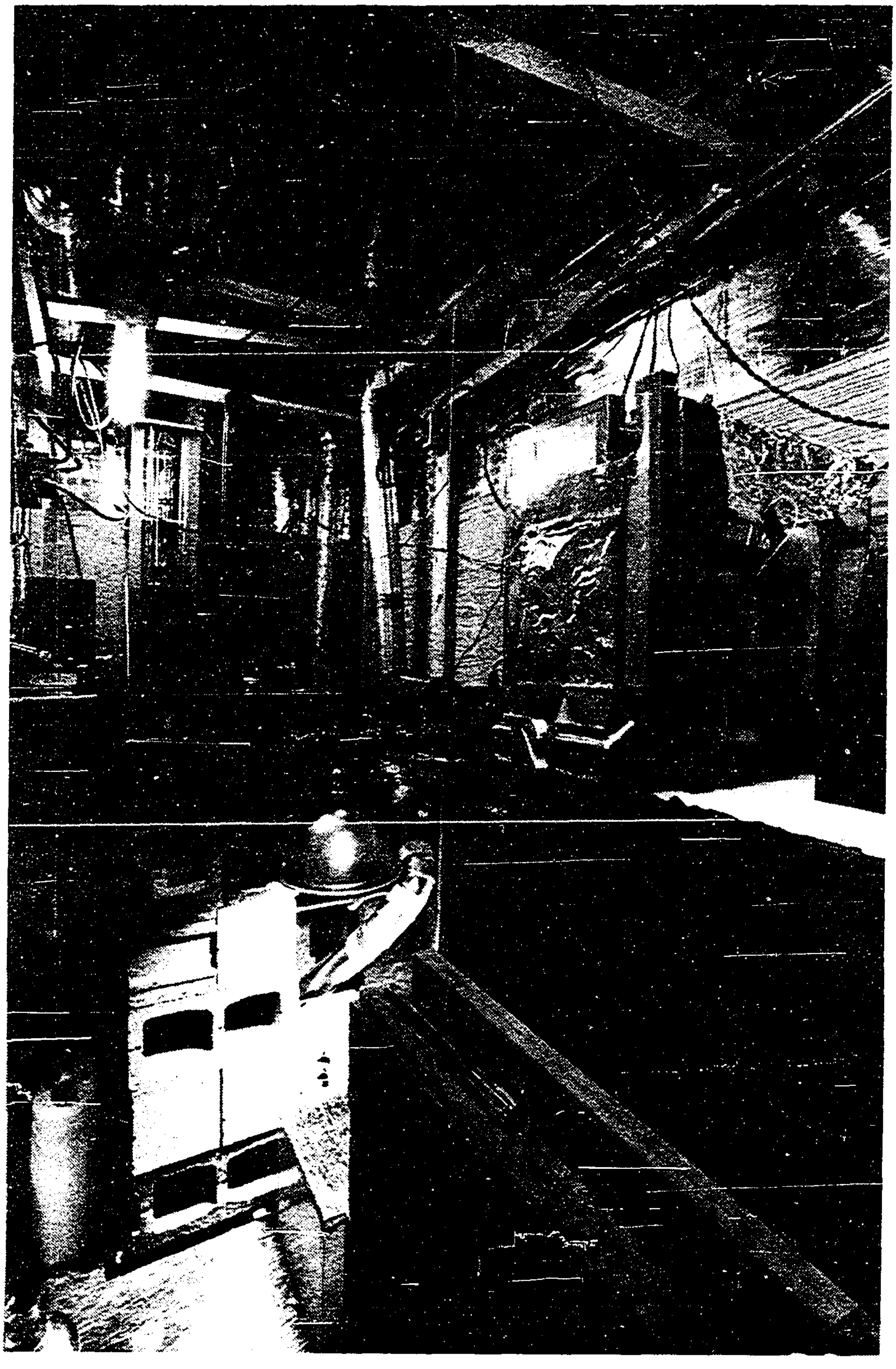
The temperature within the constant temperature box was maintained at 28.2°, some 4.5° above the temperature of the

Figure IV-4. Interior of the constant temperature box

Left to right: The piers carrying the barometer and the cathetometer, the shelf carrying the gas pipet and the compensating bulb, and the balance pier. The balance shown is the Mettler H51AR semimicrobalance, covered with insulation.

The duct carrying air from outside the box into the blocks of the barometer pier is at the upper right. The recirculation system at the north end of the box is shown at the upper left.

This photograph was taken with a camera equipped with a wide-angle lens.



constant temperature room, Room 137A. The higher temperature of the box resulted from the slow dissipation of the heat generated by equipment within the box through the highly insulated walls; temperatures as high at 35° were recorded before it was realized that all superfluous, heat-generating equipment had to be excluded from the box. The temperature within the box, if undisturbed by the presence of the operator or by the opening of the door, was maintained to ±0.075° over one cycle of the air conditioner, as recorded by a platinum resistant thermometer mounted on the west wall.

The temperature maintained within the box was, after the exclusion of all superfluous sources of heat from the box, a trade-off between one which allowed a reasonable degree of comfort for the operator and one which permitted regulation to within a desired level. Regulation of the temperature was maintained by: (1) careful adjustment of the volume and the temperature of the air entering; (2) use of concrete blocks and a large quantity of water as heat sinks; and (3) regulation of sources of heat within the box including consideration for the body heat of the operator.

Careful regulation of the amount of air entering the box and its temperature was necessary. Experiments involving several ports through which air entered the box resulted in lower temperatures within the box but with greater variations in temperature, sometimes approaching that of Room 137A. It was found that the best control was obtained by using the single port described in Section A above. Air entering through this port was regulated to ±0.5° by preheating with light bulbs which were turned on and off by a thermistor. This heated air was then blown through 12 feet of metal duct work which allowed some equilibration with the temperature in the box. This incoming air was released amid the concrete blocks of the barometer pier.

The sixty concrete blocks, each weighing 40 pounds, which made up the piers carrying the balances, barometer, and cathetometer, proved ideal as heat sinks. Additional control was gained by placing some seventy gallons of water, in 1-gallon, plastic jugs and large plastic carboys, in every available space within the box, including the spaces between the blocks of the various piers. While the blocks and water did not prevent short-term variations in temperature within the box, these materials mitigated against large, long-term changes in temperature caused by changes or failures in the operation of the air conditioner in Room 137A and prolonged power failures.

Further regulation of temperature was obtained by maintaining a constant input of heat within the box. One major and excessive source of heat within the box was the the fluorescent lighting; it was necessary to remove the ballasts from the fluorescent fixtures and to locate the ballasts outside the box. The heat generated by the operator was a large and intermittent disruption which was solved by turning on a 150-watt lamp delivering 120 watts (regulation by an autotransformer) when the operator was absent. The 120-watt figure was determined to be close to the heat dissipated by the operator (Mr. J. S. Gibson in the present dissertation).

Temperature inside the box was measured using three Matheson, mercury thermometers graduated to 0.1°. These thermometers were located: (1) on the barometer, at the north end of the box, (2) on the west wall of the box, just south of the shelf, and (3) on the east wall, behind and between the balances.

More precise measurements of temperature within the box and the balances were made using three Degussa, platinum resistance thermometers, Type W63-01. These platinum resistance thermometers were calibrated by Mr. M. S. Anderson and Professor C. A. Swenson, Department of Physics of Iowa State University and the Ames Laboratory of the Department of Energy. The calibration involved the comparison of the resistance of the platinum resistance thermometers with the resistance of a standard platinum resistance thermometer which had been previously calibrated at the National Bureau of Standards. Platinum resistance thermometer Number 1

(10-77-01) and Number 3 (10-77-03) were positioned on the barometer, at the north end of the box, and on the west wall, next to the tenth degree thermometers, respectively. Platinum resistance thermometer Number 2 (10-77-02) was mounted in a one-hole, Number 9 rubber stopper which was mounted in the balances, either in the chamber housing the beam or in the chamber housing the pan as appropriate to the occasion.

The equipment used to measure temperature using the platinum resistance thermometers is shown in block form in Figure IV-5 and in photographic form in Figure IV-6. The current through the platinum resistance thermometers was determined by measuring the potential developed across a 100-ohm standard resistor (Julie Research Laboratories, New York City, Type CH46-T4) calibrated by Mr. Anderson. The measurement of potential was made using a White double potentiometer, Leeds & Northrup Company, Model Number 6273, Serial Number 1766847, feeding into a Linear Strip Chart Recorder, Model Number 141, Serial Number B001260; a Keithley Null Detector Microvoltmeter, Model Number 155, Serial Number 39632A, was interfaced between the potentiometer and the recorder. The constant currents necessary to power the platinum resistance thermometers and the potentiometer were supplied by power supplies designed on the Kroeger-Rhinehart circuit (69). The potentiometer was

Figure IV-5. Circuitry for measurement of temperature with platinum resistance thermometers

A. White double potentiometer, Leeds & Northrup, Model 6273

B. Constant current source for potentiometer

C. Standard cell

D. Null Detector Microvoltmeter, Keithley, Model 155

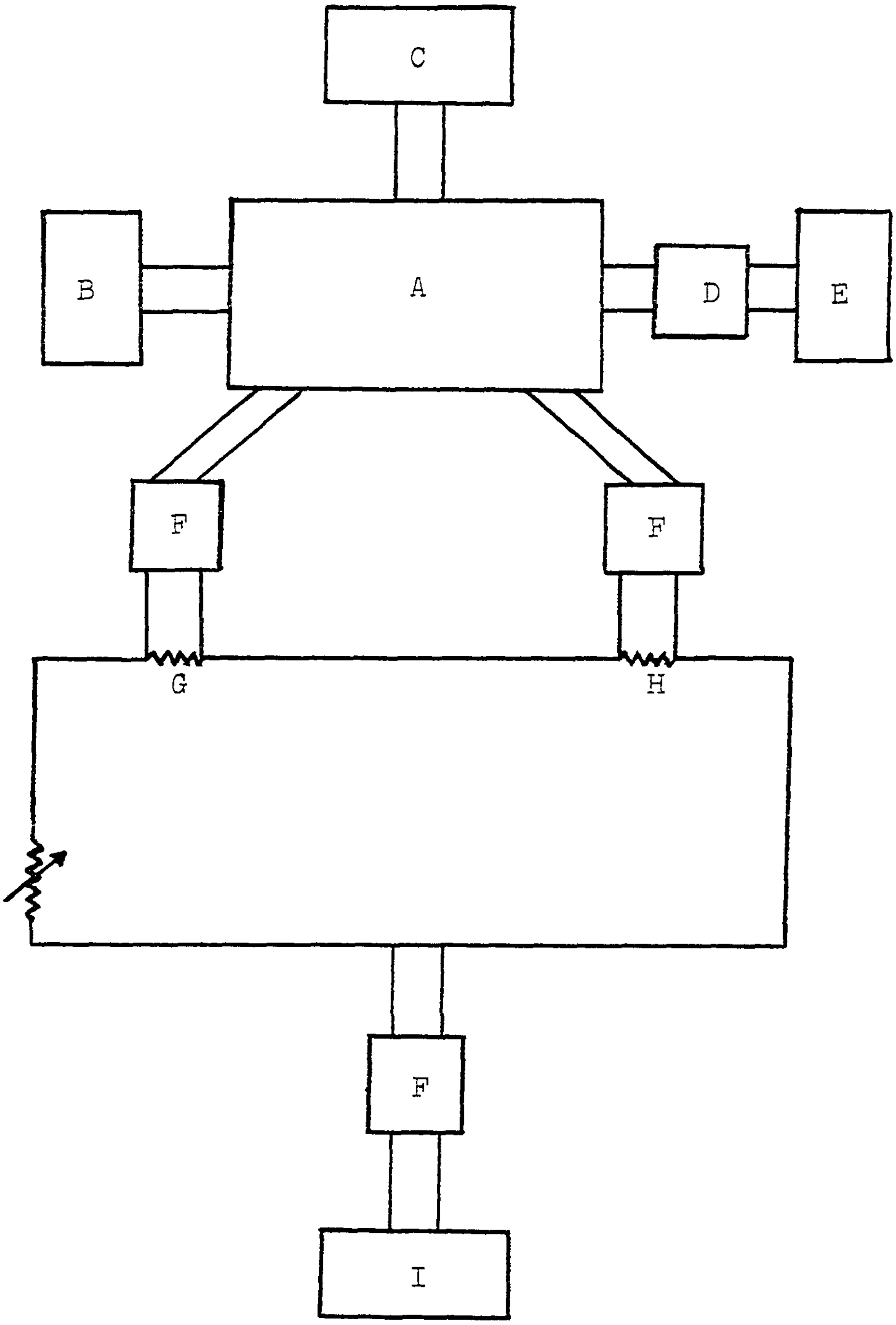
E. Strip chart recorder, Linear, Model 141

F. Double pole, rotary switch, Leeds & Northrup, Type 31

G. Standard resistor (100-ohms)

H. Platinum resistance thermometers

I. Constant current source for platinum resistance thermometers


C
B
A
D
E
F
F
G
H
F
I

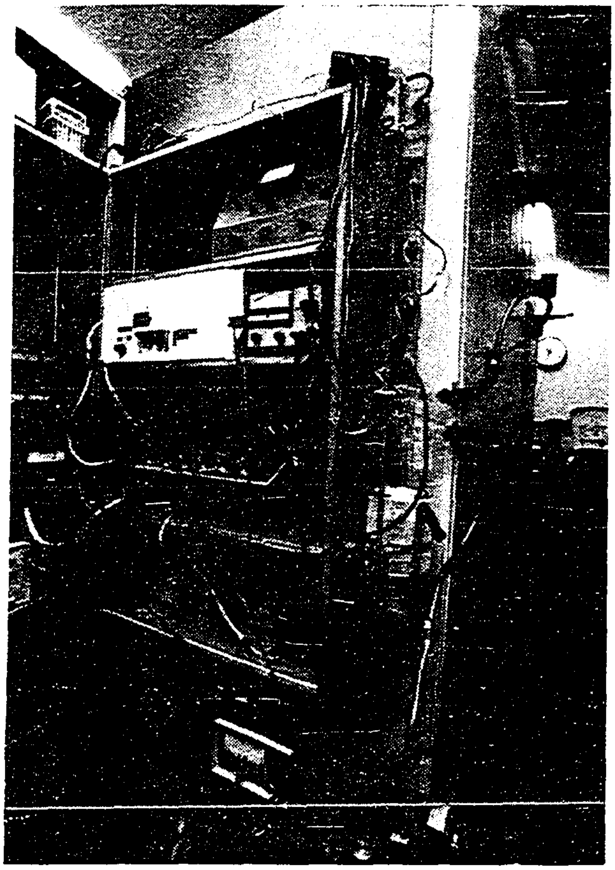


Figure IV-6. Equipment for measurement of temperature using platinum resistance thermometers

Shelf One: Meter for measurement of pressure in vacuum system
Shelf Two: Left- constant current supply for resistors. Right- Keithley micrometer
Shelf Three: Left- White double potentiometer
Shelf Four: Constant current supply for potentiometer
Shelf Five: Strip chart recorder

calibrated using a standard cell manufactured by Eppley Laboratories, Inc. (Newport, Rhode Island), Serial Number 791896. All switches were Leeds & Northrup Company, Type 31, double pole, rotary switches. Twisted wire was used throughout the circuitry to minimize interference by electromagnetic radiation.

The temperature, as measured by the platinum resistance thermometers, was given over the range of temperature in the box by the equation

$$y = mx + b \tag{IV-1}$$

in which y is the temperature in °C, x is the resistance of the platinum resistance thermometers in ohms, and for

Number 1, $m = 2.5818$ °C/ohm
$b = -257.885$ °C
Number 2, $m = 2.5800$ °C/ohm
$b = -257.807$ °C
Number 3, $m = 2.5840$ °C/ohm
$b = -258.090$ °C

Typical variation of temperature, as measured by platinum resistance thermometers, in: (1) a Mettler, Model H315, Kilogram Balance (direct from the factory without additional insulation) in the constant temperature box, and (2) the constant temperature box, is shown in Figure IV-7.

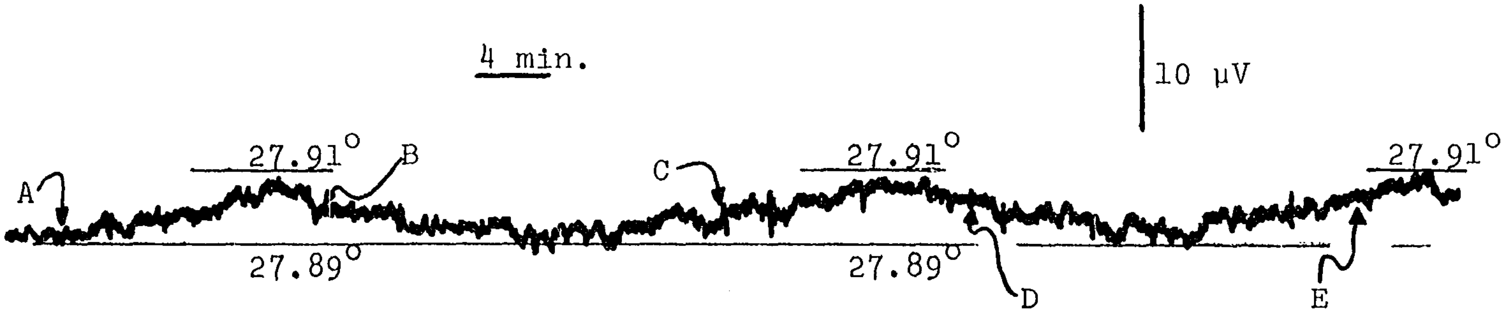
Figure IV-7. Variation of temperature as measured by platinum resistance thermometers

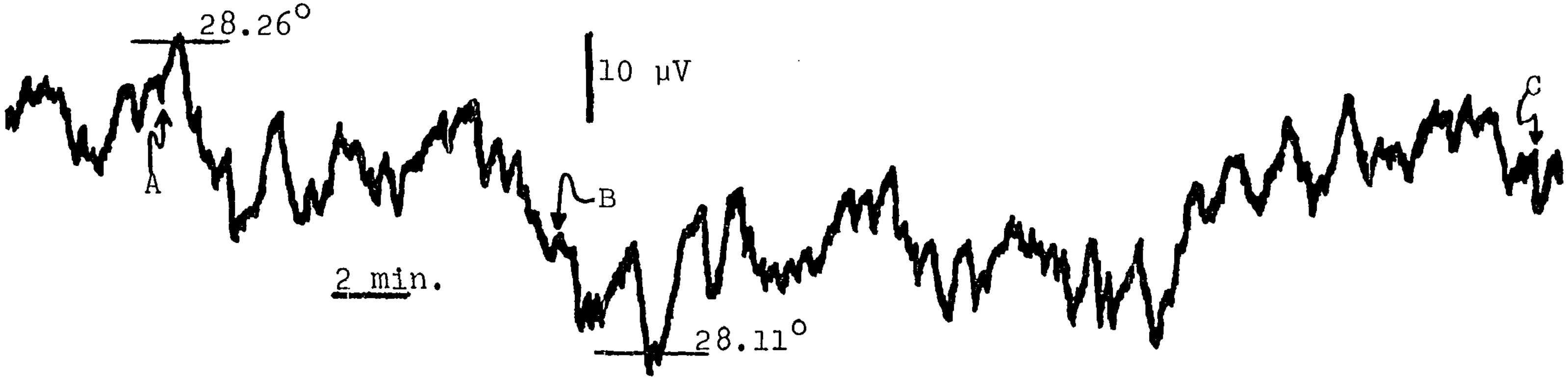
I. Variation of temperature in a Mettler, Model H315, Kilogram Balance (direct from factory, no additional insulation) in the constant temperature box as recorded by platinum resistance thermometer Number 2 located in the chamber housing the beam

A. Air conditioner turns on, 7:23 a.m.
B. Air conditioner turns off, 7:37 a.m.
C. Air conditioner turns on, 7:56 a.m.
D. Air conditioner turns off, 8:11 a.m.
E. Air conditioner turns on, 8:32 a.m.

II. Variation of temperature in the constant temperature box as recorded by platinum resistance thermometer Number 3 located on the west wall of the box

A. Air conditioner turns on, 8:37 a.m.
B. Air conditioner turns off, 8:48 a.m.
C. Air conditioner turns on, 9:14 a.m.


4 min.
10 μV
27.91°
27.91°
27.91°
A
B
C
D
E
27.89°
27.89°


28.26°
10 μV
A
B
C
2 min.
28.11°

D. Measurement of Barometric Pressure Within the Constant Temperature Box

Because of the discordant results obtained in our preliminary experiences with barometers, described in Chapter III, a mercurial barometer of our own design was constructed with which precise and reliable measurements of barometric pressure could be made. The new barometer was of the Fortin type. Other Fortin-type barometers with large cisterns had been constructed earlier by others and the measurement of the height of the mercury column with a cathetometer and the auxiliary measurement of the height of the mercury in the cistern with the aid of electrical indication were not new; a unique feature of the new instrument, however, was the incorporation in the space above the mercury column of a thermocouple gauge to measure the gas pressure above the mercury column. The barometer is shown in Figure IV-8.

The barometer consisted of two vertical tubes, 1.2 m. in height and 20 mm. inside diameter, and a large cistern containing 75 pounds of mercury, all carried on a steel frame supported by four leveling screws. The vertical tubes were each connected to the cistern, through the base, by stainless steel tubing of small bore (1.4 mm. inside diameter) through which the mercury flowed so slowly as to

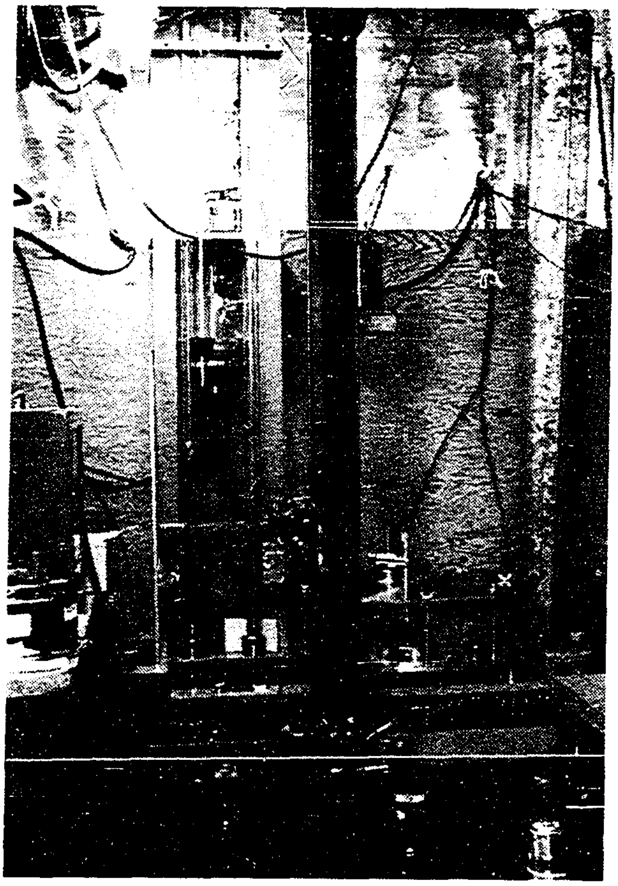


Figure IV-8. Barometer and cathetometer constructed to measure barometric pressure within the constant temperature box prevent damage to the instrument by rapid movement such as might be produced by sudden changes in pressures. Valves and outlets were provided below each tube and the cistern to enable drainage of the mercury when necessary. The vertical tubes were connected at the top through a vacuum stopcock. Each tube was fitted with an additional vacuum stopcock, the left tube so that it could be opened to the atmosphere, the right tube through glass tubing and ball joints into a glass manifold. The manifold carried a thermocouple vacuum gauge and connection to the vacuum system. The vacuum system is described below in Section E. For the cistern, a section of glass cylinder, 4 in. long and 12 in. in diameter, was obtained by cutting the bottom from a crystallizing dish. The ends of this tubing were ground flat. This tubing was clamped between stainless steel plates, the lower of which was carefully machined to provide: (1) a circular groove to house the gasket on which the glass tubing rested, and (2) a sloping floor so that mercury would drain to the openings located in the center (connections to the barometer tubes and drainage outlet). The assembly was drawn together and held by long stainless steel bolts and wing nuts. A hole was drilled through the upper plate to provide entry of a pointed, stainless steel shaft attached to a Mitutoyo micrometer head. The steel shaft was part of an electrical circuit powered by a 1.5-volt battery; contact of the point of the shaft with the mercury in the cistern caused a small light bulb to light. It proved necessary to clean the pointed tip of the shaft with emery cloth periodically. The micrometer was readable to 0.001 in. and thus the change in the position of the mercury level in the cistern could be determined accurately when mercury was drawn up into the barometer tubes.

The level of mercury in the barometer tubes was measured with a Wild Heerbrugg Cathetometer, Model 801, Serial Number 71, on loan from Professor H. J. Svec of the Ames Laboratory of the Department of Energy. The cathetometer, which had a glass scale and was readable to 0.01 mm., was fitted with an additional objective lens (upper telescope) which decreased the focusing range from 0.96 to 0.42 m., the distance separating the barometer tubes and the cathetometer.

The measurement of the barometric pressure in the constant temperature box involved four measurements. First, with the spaces above the mercury in both glass tubes open to the atmosphere, the height of the mercury in the two tubes, the same of course, was measured with the cathetometer, the cross hairs of the upper telescope being aligned with the top of the mercury meniscus and the scale of the cathetometer being read through the lower telescope. Second, the height of the mercury in the cistern (the same level, of course, as that in the two tubes) was measured by bringing the steel shaft into contact with the mercury and reading the micrometer (to 0.001 in.). Third, the right-hand tube was then evacuated, drawing the mercury up into the tube and at the same time lowering the levels in the left tube and in the cistern. After equilibrium was established, at a gas pressure in the right tube less than one micron, the height of the column in the right tube was read with the cathetometer. Fourth, contact with the mercury in the cistern was again made with the steel shaft and the height of the mercury measured with the micrometer. The drop in the level of the mercury in the cistern (and in the left barometer tube) was then subtracted from the initial reading of the cathetometer and thus the new lower level established. This reading subtracted from the upper reading gave the height of the mercury column.

Three corrections were made to the height of the mercury column obtained as just described: correction for the expansion of the soft-glass scale of the cathetometer from the temperature at which the scale was calibrated; correction for the height of the mercury column from room temperature to 0°; and correction of the height of the column to a standard acceleration of gravity.

The correction for the expansion of the soft-glass scale of the cathetometer was calculated by the equation

$$h_{t(\text{corr.})} = \frac{h_t}{1 + \alpha(t + t_o)} \qquad \text{(IV-2)}$$

in which $h_{t(\text{corr.})}$ is the corrected height of the column of mercury, h_t is the height of the column as measured at t°C, α is the coefficient of expansion of the glass scale, 95×10^{-7}/°C, and t_o is the temperature at which the scale was calibrated, 20°. The information about the coefficient of expansion of the glass scale and the temperature at which the scale was calibrated was obtained directly from the manufacturer (101). The correction for the expansion of the glass scale typically amounted to 0.06 mm. (for example, for h_t = 740.00 mm. and t = 28.00°, the correction is 0.056 mm.).

The reduction of the height of the mercury column to 0° was made using the equation

$$h_{0°(\text{corr.})} = \frac{h_{t(\text{corr.})}}{1 + \gamma(t - 0)} \qquad \text{(IV-3)}$$

in which $h_{0°}$ is the height of the column of mercury would have if it were at 0°, $h_{t(\text{corr.})}$ has the meaning given in the preceding paragraph, and γ is the cubical coefficient of expansion of mercury as obtained (10) from equation (IV-4):

$$\gamma \times 10^8 = 18{,}144.01 + 0.701{,}6t + 0.002{,}862t^2 + 0.000{,}002{,}617t^3 \qquad \text{(IV-4)}$$

The reduction amounted to about 3.8 mm. (for $h_{t(\text{corr.})}$ = 740.00 mm. and t = 28.00°, the correction is -3.745 mm.).

The height of the mercury column at a standard acceleration of gravity was calculated by

$$h_{s,0°(\text{corr.})} = h_{0°(\text{corr.})}(g/g_s) \qquad \text{(IV-5)}$$

in which the subscripts to $h_{s,0°(\text{corr.})}$ indicate that all three corrections have been applied, g is the local acceleration of gravity, 980.293 cm./sec.^{2}, and g_s is the standard acceleration of gravity (10) at 45 degrees longitude, 980.665 cm./sec.^{2}. The local acceleration of gravity was determined by Professors Hardy and Diehl and the author. Typically, in this work the correction reduced the height of the mercury column by 0.28 mm. (for $h_{0°(\text{corr.})}$ = 740.00 mm. and t = 28.00°, the height is decreased by 0.281 mm.).

E. Vacuum System in the Box

The vacuum system of the constant temperature box was made of copper tubing of 5/8 in. outside diameter. The system was evacuated by a Welch, Duo-Seal Vacuum Pump, Model 1400, Serial Number 141360, on loan from Dr. David Peterson of the Ames Laboratory and the Department of

Materials Science and Engineering. The pump was connected to a trap submerged in liquid nitrogen to prevent contamination of the vacuum system with pump oil and to prevent damage to the pump. The copper tubing was connected to the trap and entered the box through a 1-in. hole in the wall of the box. At this point, the system divided into two legs. The northern leg was connected to the manifold of the barometer. The thermocouple vacuum gauge, Type 501, manufactured by the National Research Corporation of Newton, Massachusetts, was mounted on the manifold and measured the pressure in the vacuum system to one micron as indicated on a meter manufactured by the National Research Corporation; both of these pieces of equipment for measuring pressure were on loan from Dr. Peterson.

The southern leg of the system was used to evacuate the *vacuum weighing bottles* described in Chapter VII. From the point at which the system branched on entering the box to the end of the southern branch, the system included a Hoke needle valve, a 2.5-ft. length of copper tubing, a short branch of copper tubing carrying another Hoke needle valve, and finally a Cenco fitting at the end of the leg. The first needle valve was used to connect the southern leg to the pump and the manifold of the barometer. The Cenco fitting was operated by firmly tightening an O-ring around the nozzle of the weighing bottle thus allowing evacuation of the bottle. The short branch of copper tubing carrying the second needle valve allowed restoration of atmospheric pressure in the southern leg and removal of the weighing bottle after its evacuation.

F. Gas Pipet

Because of the problems described in Chapter III concerning the reliability and calibration of the instruments for measuring relative humidity and because no attention had been paid to the variability of carbon dioxide in the atmosphere of laboratories and the effect of such changes on the density of air, a method was developed for a highly-accurate, gravimetric determination of each based on the use of a large, specially constructed gas pipet. The air being analyzed was drawn into the pipet, passing first through an absorption tube containing anhydrous magnesium perchlorate and then through an absorption tube containing Ascarite followed by anhydrous magnesium perchlorate. The absorption tubes were weighed, before and after the passage of the sample of air, to within 1 μg. (microbalance). The gas pipet was constructed so that the volume of the gas could be calculated from the lateral displacement of a piston and the internal diameter of the cylinder; thus, no calibration of the instrument involving a measurement of mass or of other gas volumes was involved. The uncertainty in a 3-liter volume of gas so measured was estimated to be less than 0.5 p.p.t. A photograph of the instrument is shown in Figure IV-9.

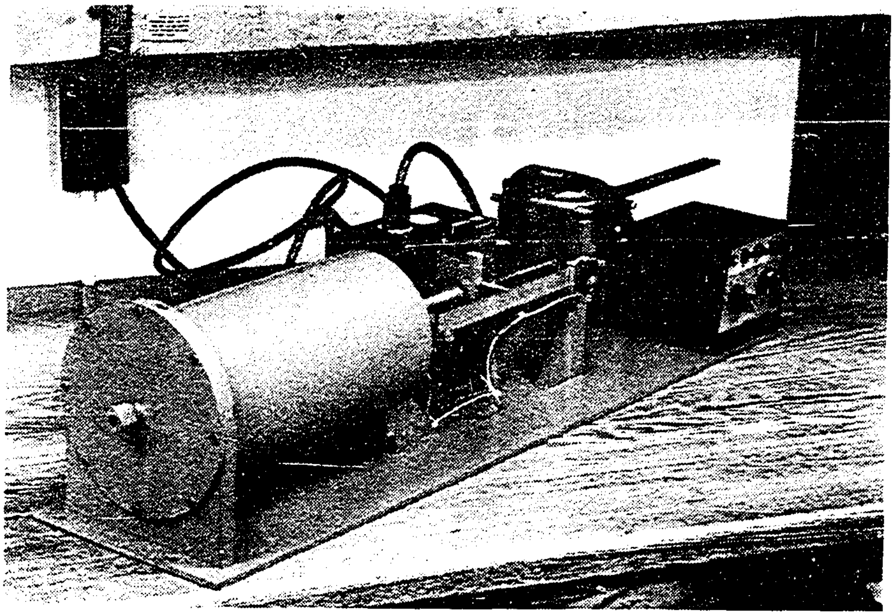


Figure IV-9. Gas pipet

The barrel of the gas pipet was a brass tube (A of Figure IV-10), outside diameter 5.5 in., length 10.5 in. This tube was bored with precision on a lathe and polished to give a cylinder of smooth and highly uniform internal diameter. The tube was soldered to brass supports (B). The piston (C) of the pipet consisted of a circular plate

Figure IV-10. Cross section showing the construction of the gas pipet

A. Brass tube forming barrel of pipet

B. Brass support

C. Piston

D. O-rings

E. Brass plate

F. Brass tube

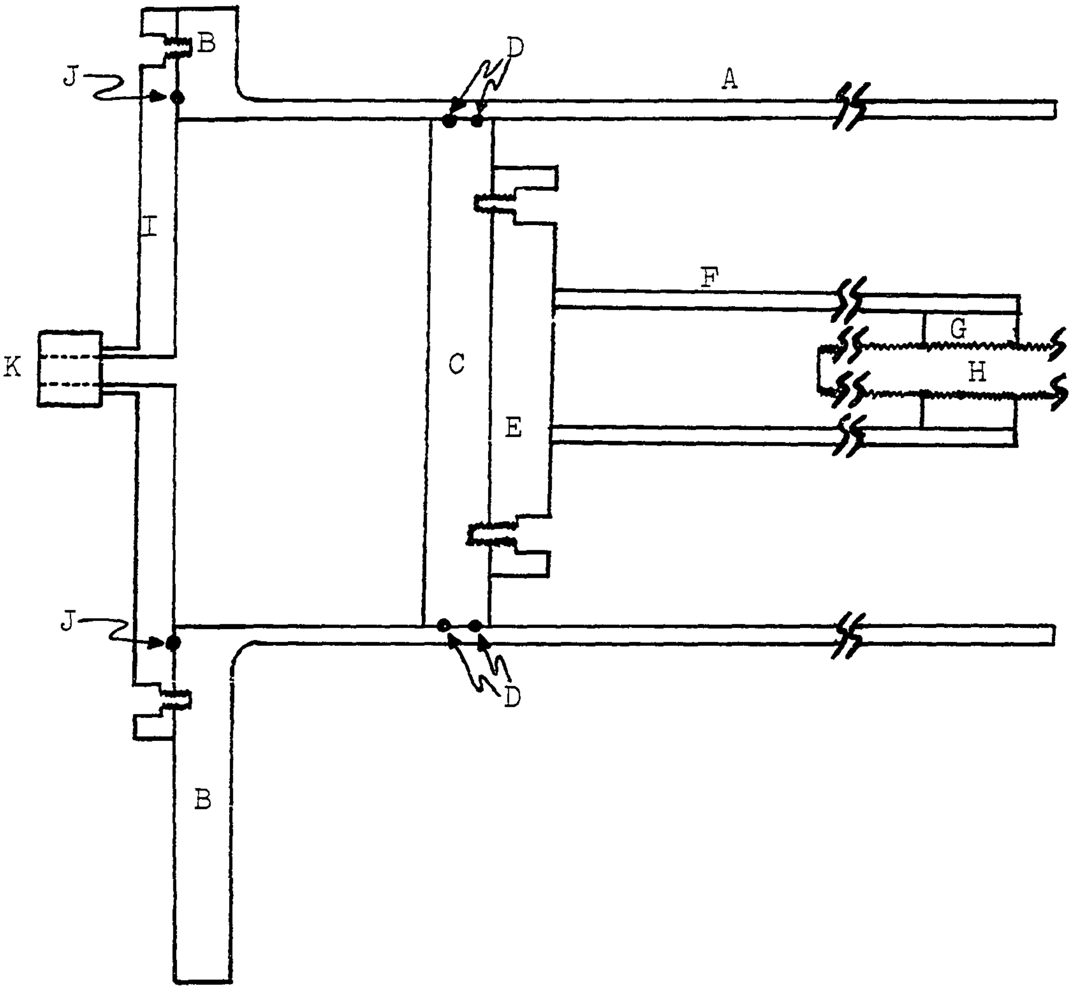
G. Brass nut

H. Brass rod driving piston

I. Front plate

J. O-ring

K. Cenco fitting


B
J
D
A
I
F
G
K
C
H
E
J
D
B

of aluminum, 5/8 in. thick, the diameter of which was nearly that of the interior of the tube. The piston was fitted with two O-rings (D) which insured an airtight seal between piston and cylinder. Attached by set screws to the outside surface of the piston was a brass plate (E), 0.5 in. thick and 4.0 in. in diameter, to which was silver-soldered a brass tube (F), 1.5 in. outside diameter, 10 in. long. This tube ended in a nut (G) through which the threaded driving rod (H) passed. The purpose of the great thickness of the piston, of the two O-rings, of the brass plate, and of the length of smaller brass tubing was to prevent any tilting of the piston from the normal to the axis of the cylinder as the piston moved.

A brass guide, carried in a slot in the smaller brass tube, prevented rotation of the piston and permitted lateral motion of the piston. The piston was moved by a variable-speed motor, Type NSH-12R, manufactured by the Bodine Electric Company of Chicago, Illinois, and a worm gear which turned the threaded driving rod (H). The distance travelled by the piston was measured by a dial caliper graduated to both 0.001 in. and 0.1 mm. The gauge of the dial caliper was secured to the rear support for the driving rod and one end of the movable scale of the caliper was secured to a brass plate attached to the rear of the brass tube and hence to the piston. By such an arrangement, the displacement of the piston could be measured by reading the gauge of the dial caliper before and after moving the piston. The displacement of the piston was limited by contact switches mounted on a strip of aluminum mounted between the supports for the driving rod; these switches were triggered by a horizontal post fixed on the brass plate carrying one end of the scale for the dial caliper.

The face of the gas pipet was a circular plate of brass (I), 3/8 in. thick, secured to the front support (B) by eight set screws and sealed airtight by an O-ring (J) mounted on the back side of the face. A Cenco fitting (K) was soldered around a hole (0.5 in. in diameter) drilled in the front plate and served as the port through which air was drawn into the gas pipet during operation of the pipet.

The internal diameter of the gas pipet was measured with an inside micrometer (L. S. Starrett, Athol, Massachusetts) graduated in 0.001 in. but readable to 0.000,2 in. The micrometer was carried on a brass fixture which had been carefully centered and mounted by a screw onto the face of the piston of the pipet. Such an arrangement allowed the measurement of the inside diameter of the pipet at different angular orientations of the micrometer by rotating the fixture carrying the micrometer and at different positions along the length of the pipet by advancing or withdrawing the piston.

The diameter of the gas pipet was measured at four angular orientations (0°, 45°, 90° and 135°; vertical orientation being 0°) for eleven positions along the length of the pipet. The micrometer was set in a particular orientation and then measurements were made in the eleven positions along the length of the tube. The piston was then withdrawn, the angular orientation of the micrometer was changed, and another series of eleven measurements were made at the new orientation. The measurements recorded are shown in Table IV-1. At 25.5°, the inside diameter of the gas pipet averaged 5.2865 in. (13.428 cm.) with a relative standard deviation of 2.1 parts in 10,000.

The atmospheric content of water vapor and carbon dioxide was determined by the increase in weight of absorption tubes filled with magnesium perchlorate (about 13 g., total weight) and with Ascarite followed by anhydrous magnesium perchlorate (13.6 g., total weight), respectively. Each absorption tube was capped at both ends by small rubber caps to prevent entry of air into the tubes between manipulations. Before initial use, each tube was painted with a 20 p.p.m. solution of cetylpyridinium bromide (Eastman Kodak Company) to lessen the adsorption of moisture on the surfaces. The determination of atmospheric water vapor and carbon dioxide began with the weighing of each absorption tube on an M5/SA microbalance, Serial Number

Table IV-1. Inside diameter of the gas pipet

Position Along Tube (inch)	Angular Orientation of Micrometer			
	0°[a]	45°	90°	135°
9.360[b]	5.2890	5.2855	5.2868	5.2855
8.500	5.2880	5.2850	5.2855	5.2850
7.650	5.2870	5.2860	5.2868	5.2860
6.800	5.2865	5.2865	5.2880	5.2865
5.950	5.2860	5.2865	5.2875	5.2865
5.100	5.2860	5.2860	5.2878	5.2860
4.250	5.2858	5.2860	5.2885	5.2860
3.400	5.2858	5.2858	5.2888	5.2858
2.500	5.2858	5.2860	5.2888	5.2860
1.700	5.2860	5.2855	5.2885	5.2855
0.8650[c]	5.2860	5.2855	5.2882	5.2855

---

[a] The angular orientation of the inside micrometer is given, in degrees, clockwise from the vertical orientation of the micrometer, 0°.

[b] Piston of pipet advanced to fullest extent as limited by front contact switch.

[c] Piston of pipet withdrawn to fullest extent as limited by rear contact switch.

52550. The caps were removed from the absorption tubes and the absorption tubes were connected to the gas pipet by glass and rubber tubing such that the air sampled passed first through the tube containing magnesium perchlorate and then through the tube containing Ascarite and magnesium perchlorate. After the sample passed through the tubes, the absorption tubes were recapped and reweighed. The volume of air sampled was calculated by multiplying the distance travelled by the piston, as measured by the dial caliper mounted on the movable assembly of the pipet and by the cross-sectional area of the interior of the pipet, 141.61 $cm.^2$. The entire determination took about 35 minutes: 16 minutes to weigh the two tubes allowing for dissipation of heat, three minutes to sample the air, and 16 minutes to reweigh the tubes.

The atmospheric content of water vapor was calculated by dividing the gain in weight of magnesium perchlorate (typically 32.5 mg.) by the molecular weight of water (44), 18.015,34 g./mole, to give n_{H_2O}, the number of moles of water in the sample taken. This quantity was substituted into equation (IV-6) derived from the gas law

$$P_w = \frac{760\ n_{H_2O}RT}{V} \qquad \text{(IV-6)}$$

in which P_w is the partial pressure of water vapor in mm. Hg; R is the gas constant, 82.0568 cm.·atm./mole·°K; T is the temperature within the box in Kelvin; and V is the volume of air drawn into the pipet in cm.^{3}. Substitution of equation (IV-6) into equation (III-4), used to calculate the density of air from the prevailing conditions, gives

$$d_a = \frac{0.001,292,3(P_{bp} - 0.378,02P_w)}{(1 + 0.003,660,99(t))\ (760)} \qquad \text{(IV-7)}$$

The increase in weight of the Ascarite was typically about 40 mg. The mole fraction of carbon dioxide, X_{CO_2}, in the air within the box was calculated by dividing the number of moles of carbon dioxide collected, n_{CO_2} (molecular weight of carbon dioxide, 44.009,95 g./mole) (44), by the number of moles of air in the volume sampled as given by the gas law

$$X_{CO_2} = \frac{n_{CO_2}}{(PV/RT)} \qquad \text{(IV-8)}$$

in which P is the barometric pressure within the box in atmospheres. The molecular weight of air was recalculated to take into account the deviation of the measured content of carbon dioxide from the value used by Harrison (44), $X_{CO_2} = 0.000,314$, in calculating the molecular weight of air.

The constant 0.001,292,3 in equation (IV-7) was obtained (see my M.S. thesis (Ref. 38, page 16)) by dividing the molecular weight of air, 28.964,5 g./mole dry air (Ref.

44, page 15), by 273.15 and the value of the gas constant, 82.056,8 cm.·atm./mole°K. By replacing the constant 0.001,292,3 with the terms from which it was derived and then simplifying, an equation for the density of air in terms of the barometric pressure, temperature, partial pressure of water, and the molecular weight of air is obtained

$$d_a = \frac{M_a(P_{bp} - 0.378{,}02P_w)}{1.703{,}450 \times 10^7(1 + 0.003{,}660{,}9(t))} \quad \text{(IV-9)}$$

G. Determination of the Acceleration of Gravity

The acceleration of gravity in Room 137A and on the pier carrying the balances in the constant temperature box was determined using a Worden Gravity Meter, Model 751, on loan from Mr. Jack Gilmore of the Iowa Geological Survey, Iowa City, Iowa. The range of this instrument was about 220 milligal, readable to 0.01 milligal. [1 cm./sec.^{2} = 1 gal. (after Galileo); the unit milligal is commonly used in the current literature.] The acceleration of gravity was measured relative to the value established by Gopfert in 1973 in Room 106, Town Engineering Building, Iowa State University, southeast corner of the Geodesy and Photogammetry Laboratory. The observed gravity at this location, designated ISU-85, was 980,294.91 ± 0.04 milligal and was tied to the Iowa Gravity Base Station Network through stations in Boone (IGS 8) and Des Moines (IGS 77); the network in Iowa is tied to the U. S. National Gravity Base Net at Station Minneapolis L (I.G.C. 15443L) (40,45). The value obtained by Gopfert was confirmed in October 1977 by Professor Diehl in a series of measurements made on a circuit comprised of stations in Des Moines (IGS 77; Des Moines Municipal Airport) and Marshalltown (IGS 64; Marshalltown Municipal Airport) and ISU-85. The station at the Boone Airport had been destroyed by new construction.

The acceleration of gravity at the bench mark in Room 137A (see Section H of this chapter) was measured by Professor Diehl and the author relative to the value at ISU-85 by a series of measurements made alternately in Room 137A and at ISU-85. In Room 137A, the gravity meter was mounted on a brass plate, 0.4 in. thick, resting on the bench mark and levelled by shims. Straight lines were fitted to the data obtained at each site, the difference in readings between the sites at different times was calculated, and the value of gravity at the bench mark was calculated. The acceleration of gravity at the bench mark in Room 137A was determined to be 980,293.38 milligal, the standard deviation in the measurements being 0.04 milligal. Students of the class in Geodetic Surveying taught by Dr. R. L. Hardy of the Department of Civil Engineering, Iowa State University, also determined the acceleration of gravity at the bench mark using the same instrument and ISU-85. The value obtained by the class, 980,293.59 ± 0.07 milligal, was viewed by Dr. Hardy with less than complete confidence owing to large differences between values obtained on two different days. The questioned value was viewed as a rough check of our work.

The acceleration of gravity was determined on the pier carrying the balances to be 980,292.96 milligal (standard deviation in the measurements, 0.08 milligal). This value was determined by a series of measurements done alternately at the bench mark and on the pier carrying the balances.

H. Determination of the Elevation of Room 137A and of the Balance Pier

Two bench marks were established in September 1977 in the Chemistry Hall, Iowa State University. These bench marks, made of stainless steel, were placed in the front lobby and in Room 137A. That in the front lobby (that is, the room just north of the south doors of the old building) is located between the middle and east, inner doors; that in Room 137A is just inside the door and is the east of two stainless steel markers so mounted. The elevation of these bench marks was determined by a first-order leveling run by an advanced class in geodetic surveying under the supervision of Professor R. L. Hardy of the Department of Civil Engineering. The elevations found were: Lobby, 291.527 m.; Room 137A, 291.533 m. These values were obtained using as a reference a bench mark about 20 ft. northeast of the northeast corner of Beardshear Hall, Iowa State University, established by the United States Coast and Geodetic Survey. The standard error in these values was estimated by Professor Hardy (42) to be 2 mm. The bench mark in the lobby of Chemistry Hall was marked "291.527 M ABOVE M.S.L."

The elevation of a steel rule, mounted on the east wall of the constant temperature box and behind and between the balances, was also determined by Professor Hardy's students. The elevation at the 16.00 in. mark in this rule was determined to be 293.170 m. above mean sea level. Professor Hardy advised that caution be exercised in using this value inasmuch as one of the two parties involved in the measurements did not have good results for this particular measurement and there was no check of the value of the other party.

The objective in having these elevations determined was to make possible a calculation of the acceleration of gravity from the latitude and altitude. Such a calculation, however, yields an inaccurate value for the acceleration of gravity in central Iowa owing to the Midcontinent Gravity Anomaly, a relatively narrow band running southwest to northeast, some of the most prominent features of which lie just a few miles west and north of Ames. Flanking the high gravity anomaly in parallel bands are low gravity regions. Ames is located on such a low-gravity region. For an exposition of the Midcontinent Gravity Anomaly and a discussion of the extraordinary gradients in the acceleration of gravity over short distances in central Iowa, see Carmichael (23).

V. MODIFICATION OF THE METTLER, SINGLE-PAN BALANCE

A. Introduction

Three single-pan balances, manufactured by the Mettler Instrument Corporation of Princeton, New Jersey, were used in the present work: a Mettler, Kilogram Balance, Model H315, having a capacity of 1000 g. and reading directly to 0.1 mg.; a Mettler Semimicrobalance, Model H51AR, having a capacity of 160 g. and reading directly to 0.01 mg.; and a Mettler Microbalance, Model M5/SA, having a capacity of 20 g. and reading directly to 1 μg. As with all single-pan balances, these balances operate on the substitution principle, that is, weights suspended from the beam are removed to equal the mass of the object being weighed. The weights suspended from the beam of the kilogram balance total 999 g.; the one-thousandth gram being obtained from the deflection of the beam as measured optically using the image of a reticule which is passed through a movable, readout device. The optical scale is divided into 10,000 divisions and the sensitivity of the balance is adjusted so that 10,000 divisions exactly equal 1 g. The optical scales in the semimicrobalance and the microbalance are divided into 12,500 and 20,000 divisions, respectively, and the sensitivity of both balances is adjusted so that 10,000 divisions exactly equal 0.1 g. and 0.01 g., respectively.

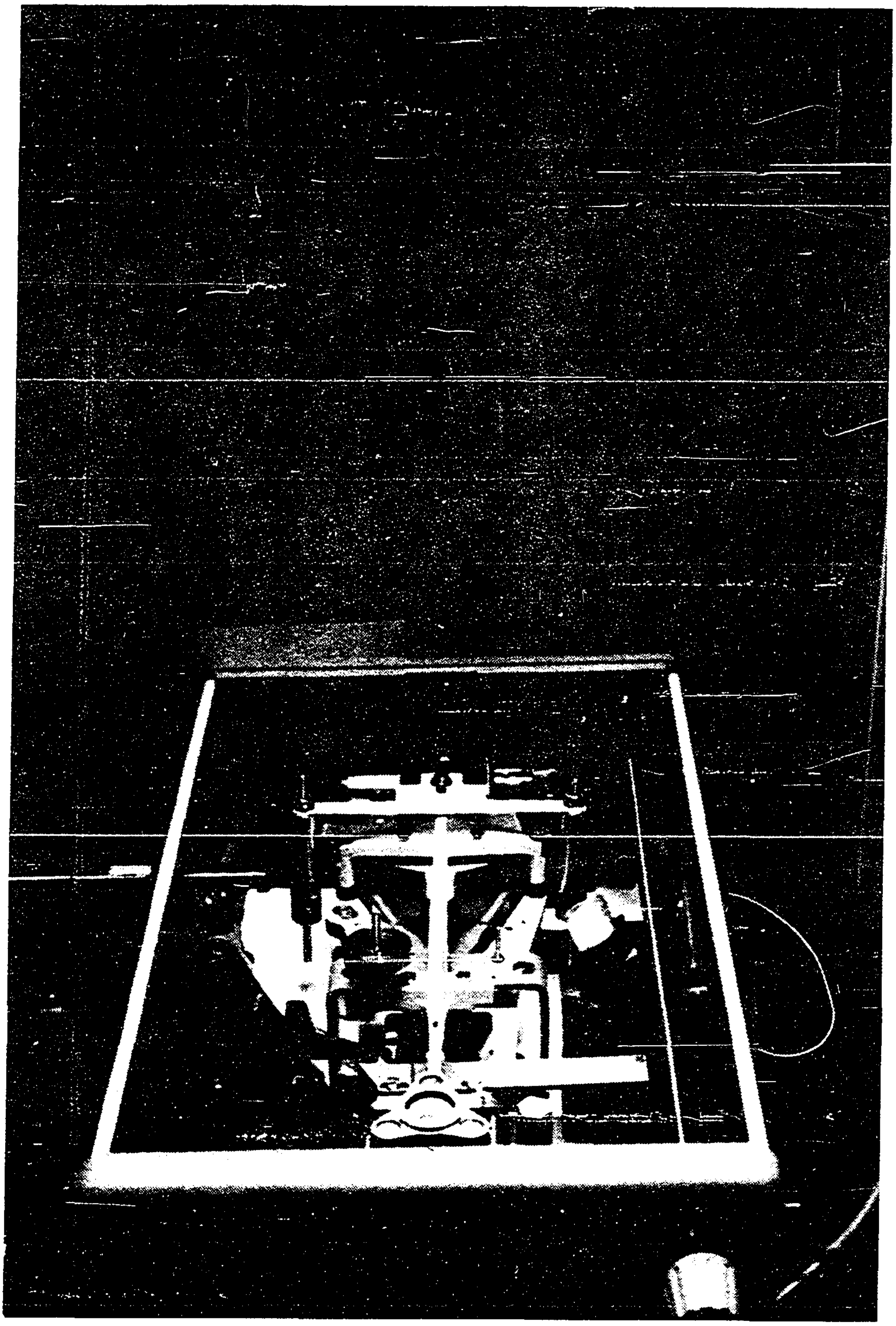
The Mettler Kilogram Balance, Serial Number 719830, used in the present work, was mounted in Room 145 Chemistry Hall and was the property of the Hach Chemical Company and on loan to Iowa State University; the Mettler Semimicrobalance, Serial Number 626447, and the Mettler Microbalance, Serial Number 525505, were the property of Iowa State University and were mounted in the constant temperature box in Room 137A Chemistry Hall. It was necessary for the present work to make a number of modifications to the kilogram balance and to the semimicrobalance, principally to increase capacity, to increase sensitivity, and to stabilize the zero-point. In making these changes, close attention was paid to temperature, to electrostatic effects, and to the retention of the requisite mechanical structure.

B. Increasing the Capacity of the Kilogram Balance

The use proposed for the kilogram balance was the weighing of masses (weights) up to one kilogram in the *vacuum weighing bottle* as described in Chapter X. The mass of the weighing bottle itself was 163.4846 g. so, it was necessary to increase the capacity of the balance to 1164 g. This was accomplished by increasing the mass of the counterweights on the long (back) arm of the balance. The added counterweights were in the form of two cylinders of stainless steel, bored and threaded axially. These new counterweights, each weighing 48 g., were carried on vertical screws projecting downward at the ends of a crosspiece bolted to the beam, Figure V-1. The counterweights could thus be moved up and down to adjust the sensitivity and the cross piece was slotted so that it could be moved along the beam after loosening the bolt. This assembly provided a rough adjustment of the zero-point, the final adjustment being made with the original "zero-point adjustment nut" of the balance. Actually, this crosspiece replaced a "rough zero-point adjustment weight" which was present on the balance when received; this rough adjustment weight and the new crosspiece which replaced it, were so grooved as to fit the beam; the pieces were thus confined to motion forward and backward along the beam.

The mass at the back end of the beam of the H315 balance consists mainly of the large mass of stainless steel visible between the new counterweights, Figure V-1, the piston operating within the cylinder (which provides air damping), and the rough zero-point adjustment weight. The mass needed for the new, additional counterweights was obtained by removing the original rough zero-point adjustment weight and making a weighing with the balance (pan empty); the mass of built-in weights lifted from the beam in this operation gave the effective mass of the rough zero-point adjustment weight.

Figure V-1. Additional counterweights added to the beam of the Mettler Single-Pan Kilogram Balance to increase the capacity



The ratio of this effective mass, 27.5810 g., to the mass of this rough adjustment weight, 16.5394 g., as determined on another balance, gave the ratio of the effective lengths of the arms of the balance:

$$\frac{\text{Rear arm}}{\text{Front arm}} = \frac{27.5810}{16.5394} = 1.6676$$

This ratio made it possible to calculate the total mass needed for the new crosspiece-counterweight assembly to just counterbalance the weighing bottle. Because of interference from other components of the balance, the new counterweight assembly could not be placed as far to the rear as was the original rough adjustment weight, and the final total mass of the assembly (crosspiece, two screws, four lock nuts and two cylindrical counterweights (all of stainless steel)) was some 25 g. more than the value calculated. The assembly was bolted to the beam, the position on the beam marked and the effective mass of the assembly determined by making a weighing. The assembly was then moved forward 3 mm. and the weighing repeated. With this data, it became easy to position the assembly so as to balance closely the 163.4846 g. of the weighing bottle. The final adjustment of the zero-point was then made with the original zero adjustment nut.

C. Increasing the Sensitivity of the Mettler Kilogram Balance and of the Mettler Semimicrobalance

The two large cylindrical counterweights added at the back end of the beam of the H315 kilogram balance, Figure V-1, were added to increase the capacity of the balance. These masses were made movable up and down on screws so that the essential, symmetric distribution of the masses on the beam was preserved. Some change in the sensitivity of the balance could be effected by raising and lowering these counterweights, but not a great deal, and primarily the positioning of them was to bring the zero-point into proper position.

A significant increase in the sensitivity of the balance was desired and this was achieved by replacing the original sensitivity nut with one considerably heavier. The masses of the original and the new nut were, respectively, 7.9405 g. and 24.5466 g. The bore of the new nut was centered as accurately as possible using a precision milling machine for boring and threading; a metric thread (3 mm. x 0.5 mm.) was used to conform with that in the balance as received. This heavier nut proved satisfactory. For the final work of this dissertation, the sensitivity was set at 6.5 μg. per optical scale division.

With this new sensitivity nut and setting, of course, it was necessary to obtain a new calibration of the optical scale. This was made during the course of each sequence of weighings by taking an arbitrary zero-point reading on the optical scale (usually somewhere in the middle of the scale), adding a "sensitivity weight", and obtaining a new reading. From the shift in equilibrium position, the sensitivity in µg. per optical scale division was calculated. Checks on this value were usually obtained at the same time by removing a similar sensitivity weight or by doubling it.

At this increased sensitivity of the kilogram balance, the full-scale deflection of the beam (10,000 divisions) was not 1 g. but about 65 mg., and the weights mounted within the balance were not sufficiently subdivided for operation at increased sensitivity. Fractional weights from a rhodium-plated set of weights, manufactured by Wm. Ainsworth and Sons of Denver, Colorado, and calibrated by the National Bureau of Standards, Test Number G37168, were placed on the pan of the balance when the balance was zeroed and were removed as needed during a weighing.

The sensitivity of the semimicrobalance was also increased by substituting the original sensitivity nut weighing 1.79 g. with a heavier nut made of brass and weighing 4.79 g. The sensitivity of the semimicrobalance was increased to 3 µg. per division. Despite the modifications described in this chapter, the zero-point of the semimicrobalance at increased sensitivity could never be stabilized sufficiently within the constant temperature box. The cause of the problem was traced to the periodic variation in relative humidity, up to 8 per cent, due to the operation of the air conditioner in Room 137A and the intermittent effect of the moisture exhaled by the operator within the box. These changes in relative humidity noticeably affected the zero-point of the balance at increased sensitivity by changing the density and the buoyancy of the air, an effect which was pronounced because of the highly asymmetric construction of the beam of the balance.

D. Removal of the Taring Mechanism

The Mettler Single-Pan, H315, Kilogram Balance and the Mettler H51AR, Semimicrobalance are delivered equipped with a taring mechanism by which an object on the pan of the balance, an empty vessel for example, is counterbalanced as the initial operation to a weighing. Experiment suggested that at the high sensitivity at which the balances in this study were operated, the taring mechanism was contributing to a nonreproducibility in the zero-point. The taring mechanism on both balances is a wire spring resembling the spring of the balance wheel of a watch and is mounted coaxially with the central knife edge. The central end of the spring is fastened to the beam so that the rotation of the beam winds and unwinds the spring as the beam oscillates. The taring force is applied to the outer end of the spring in such direction as to oppose the mass being tared. Fortunately, the taring mechanism was readily accessible; for the present work it was removed from both balances.

E. Eliminating the Effects of Static Electricity

By far the greatest trouble in stabilizing the balances so that reproducible values for the zero-point could be obtained derived from electrostatic effects. During early work, the zero-point was observed to drift, often steadily for two to three hours and then to reverse direction. The initial drift was not always in the same direction nor was the rate always the same. At least by superficial observation, the drift was not related to humidity. Just how serious the effects were was driven home by observations that persons within four feet of the balance caused the zero-point (on repeated lowering of the beam from partial arrest) to change slowly; by grounding such persons, and of course, the operator, the drift was eliminated. From these and other observations it became apparent that the balance was acting as a very sensitive electrometer.

By direct test it was found that the electrical components of the H315 balance were all grounded through the ground (green) wire of the 110 V.A.C. main. This was true also of the H51AR semimicrobalance (all of the following observations and statements apply equally to the H51AR). The beam of the balance and the pan-weight assembly carried on the stirrup were insulated from the structural components of the balance and from each other by the sapphire knife edges and plates; thus, no electrical pathways existed for electrostatic charges to be drained off except through the atmosphere. What appeared to be equally serious was that the construction of the balances quite possibly made them in effect variable electric condensers. The pan of the balance, some 13 cm. in diameter, moved up and down facing a thick glass plate, the floor of the weighing chamber, at a distance of only 1.5 cm. The cover of the balance, although of metal, was well coated with baked enamel and, as were the side walls, was electrically insulated from the structural members of the balance. Three walls of the weighing chamber were of glass. It is apparent that the whole assembly would act as an electrical capacitance and that the beam and weight-pan assembly served as the moving component of an electric indicating device.

There is a fair amount of literature, of course, on the erratic effects of electrostatics on balances and weighings.

The subject, in fact, goes back to Charles Augustine de Coulomb, who in 1785 (30) used a torsion balance in the experiments which led to his famous laws describing quantitatively the effects of electrostatic charges. The so-called "Attracted Disc Electrometer" constructed by Harris (43) and perfected by Thomson (98) to measure potential was essentially a single-pan balance. The perfected model consisted of two parallel plates, one of which was fixed horizontally and mounted on an insulating stem and the other of which was movable and attached to the longer end of an asymmetric balance beam by a stirrup and knife edge; this end of the beam was balanced by a large counterpoise attached to the other, shorter end of the beam. The distance between the plates was a measure of the difference in potential of the two objects being studied. Fundamentally, in design and response, the Mettler single-pan balances do not differ much from such an instrument.

Among the methods of overcoming electrostatic effects on the weighing process are two based on ionizing the air within the balance and permitting time for the ions to carry away the electrostatic charges; in one procedure a uranium compound is placed within the case, in the other a Tesla coil is operated in the neighborhood of the balance. In the present work both of these techniques were used, but principal reliance was placed on extensive grounding of the components of the balances and of the operating personnel, of shielding the balances from external forces by enclosing them in a shell of metal, and of installing sharp points on the moving parts.

1. Use of the Tesla coil

A Tesla coil, manufactured by the Fisher Scientific Company of Chicago, Illinois, was used to dissipate electrostatic charges within the kilogram balance by operating the Tesla coil in the neighborhood of the balance. A hole, about 1 in. in diameter, was drilled through the cover of the balance, just above the rear knife-edge, to allow diffusion of ionized air into the balance case; the hole was covered during the normal operation of the balance. The benefits of operating the Tesla coil in this manner were minimal and, for routine work, proved a nuisance. In a variation, the Tesla coil was operated within the balance case. The Tesla coil was mounted in a one-hole, Number 9, rubber stopper which was placed in a hole drilled in the cover of the balance, toward the rear of the beam. Even at the lowest setting of the coil, temperature effects from operating it disrupted the smooth operation of the balance and it was necessary to abandon this approach.

2. Radioactive material within the balance case

The idea of placing a uranium compound in the balance case to obviate the effects of static charge is found in several texts of the 1920's dealing with microanalysis. The practice has not been widespread of late, as bemoaned by Le Gallic (60) who revived it in work involving the weighing of microgram quantities. About the only literature found presenting concrete, experimental data on the validity of the procedure is the B.S. thesis of C. R. Chadwick (26), Iowa State University, 1940; Chadwick, working in the Department of Chemical Engineering, studied the effect of the uranium in carnotite on the static charge developed on a moving leather belt. Chadwick concluded that an effect was obtained only when the belt was enclosed with the carnotite in a box for an extended period; apparently the effect, which was a significant reduction in static charge, came about from the absorption by the belt of radon gas emitted by the carnotite.

In the present work, plastic test tubes of 6 $cm.^3$ capacity were filled with an uranium-bearing material and placed within the balances. One tube containing 20 g. of uranium metal turnings was placed in the weighing chamber of each balance; two tubes, each containing 25 g. of uranium tetrafluoride, were placed vertically in the upper chamber of each balance, one tube near the stirrup-weight assembly and the other near the rear knife edge. Each of the tubes was open at the top except for a plug of cotton. A qualitative check showed that the materials were radioactive and that the alpha-emission was sufficient to penetrate the plastic of the containing tubes.

3. Electrical grounding and shielding

By removal of enamel to expose bare metal to make electrical contact and by separate ground wires where necessary, every component of the kilogram balance (and of the semimicrobalance) was grounded electrically. The beam, weight-pan assembly, and stirrup could not, of course, be permanently grounded by an attached wire. To achieve the same effect, movable rods were installed through bushings in one wall. These rods carried, at the interior end, a fine wire at a right angle. The movable rod was grounded and by pushing the rod in so that the brush wire made contact with the beam, or the pan, static could be drawn off just before any weighing operation. By making the brush wire of very fine and flexible wire, the grounding contact was so light as to cause no disturbance to pan or beam.

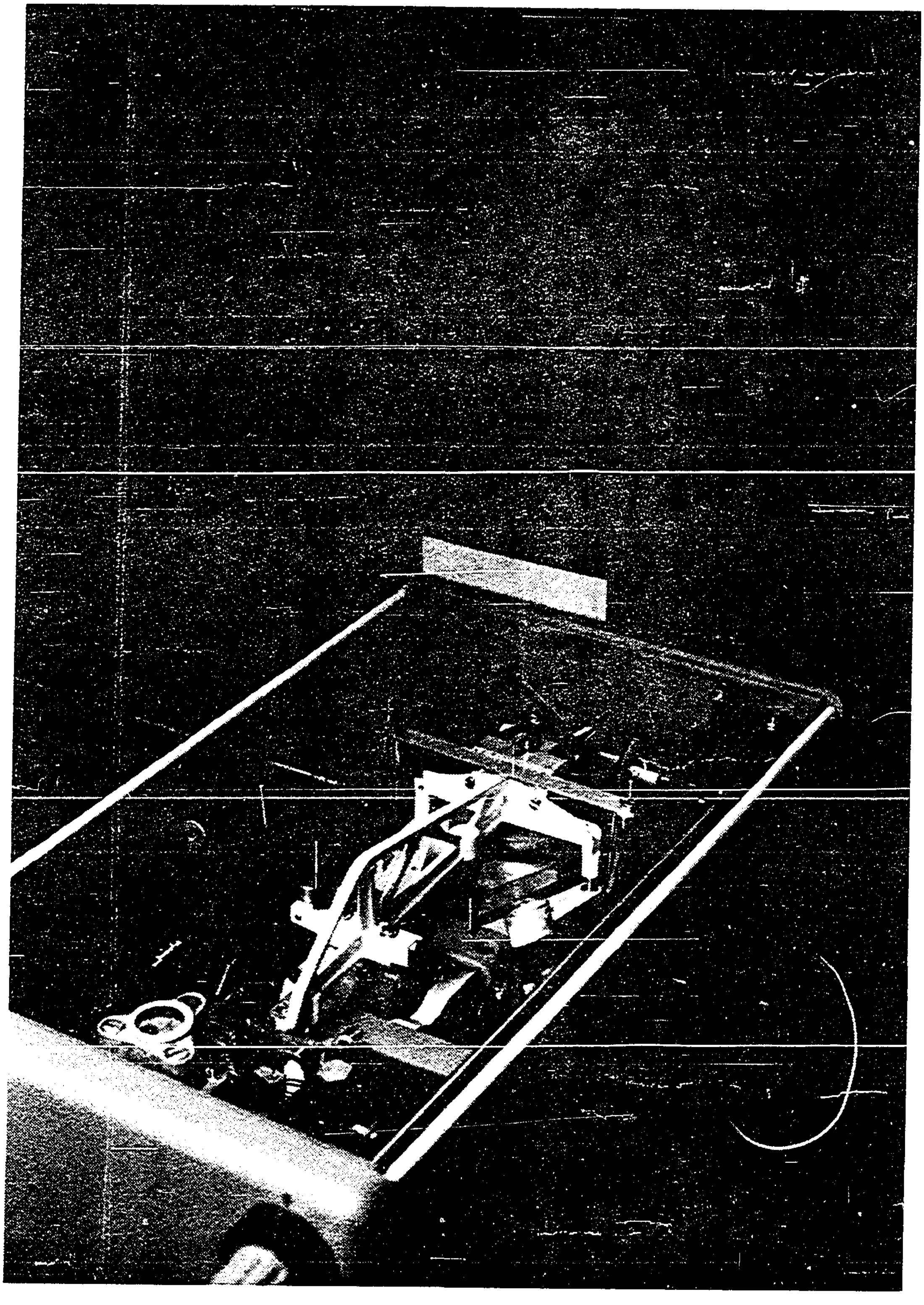
The large metal cover of the balance was also grounded and to the bottom side of it was fastened a sheet of bronze screen, the purpose being to destroy any capacitance between it and the moving beam. Similarly, sheets of screen were used to cover the glass windows. A sheet of thin aluminum was placed over the glass floor of the weighing chamber.

A grounded shell of aluminum sheet was built around the kilogram balance. The sheets of aluminum had previously been used as offset printing plate, were 0.008 in. thick, and were inexpensive and easily mounted. A grounded shell was provided the semimicrobalance by connecting and electrically grounding the layers of metallic foil covering the sheets of insulating material which made up the constant temperature box.

The operator and other persons in the balance room were grounded by contact of a ground wire with the skin, most conveniently by a bracelet.

Three fine rods ending in very sharp points (actually made from sewing needles) were mounted on the insulated, moving parts of the balance, one each on the beam, stirrup, and yoke (the latter being a component of the stirrup which is actually constructed of two pieces (insulated from each other and from the beam)). The theory of the fine point in concentrating the electrostatic charge on a conductor and of discharging it to the atmosphere is given in the text of S. W. Hockey (48) although the technique was first called to my attention by Professor C. A. Swenson. Another view of the interior of the kilogram balance is shown in Figure V-2; the sharp points, one of the tubes containing uranium tetrafluoride, and the rod carrying the brush wire are visible.

Figure V-2. Interior view of the Mettler Single-Pan Kilogram Balance as modified to obviate electrostatic effects. Note rod with brush wire, tube containing uranium tetrafluoride, and needle points



F. Partial Arrest Stop

From preliminary observations, it was concluded that one cause for the failure to obtain a reproducible zero-point was that the beam was being lowered into a slightly different position each time released. The tremendous forces exerted on a very small area of the plates by the mass concentrated on the knife edges must cause a depression in the plates into which the knife edges fit and move in an essentially rolling motion. Quite possibly the position of the depressions varies from one lowering of the beam to the next and better operation could be secured if the knife edges were never removed from the plates, that is the knife edges are kept partly loaded at all times. At least one of the large balances used in standards work, such as is being attempted in the present work, is constructed to operate in this manner. This is the so-called "Kilogram Comparator" of the National Bureau of Standards. This particular balance is used for one operation only, the comparison of kilogram masses, and the objects being weighed are moved on and off the pan mechanically. The Mettler H315 balance used in the present work is to be used to measure masses over the entire range 1 g. to 1 kg.; a mechanical weight transfer mechanism did not appear necessary, but the balance was modified so that the knife edges remained in contact with the plates through a sequence of weighings.

A stop was added to the front of the balance so that the arrestment lever could be stopped only part of the way to full arrestment (clockwise motion, about 90° for full arrestment). This partial arrestment was adjusted by closely observing the space between the knife edges and plates with a strong light properly located temporarily in the upper chamber of the balance.

G. Thermal Insulation of Balances

It was discovered during early experiments that the insulation on the kilogram balance and on the semimicrobalance as received from the manufacturer was inadequate for work at the increased sensitivity obtained by replacing the sensitivity nut with a heavier nut. This was true even when the balances were mounted in the constant temperature box within the constant temperature room; body heat and radiation from the operator were sufficient to affect the zero-point. For further thermal protection, the balances were covered with sheets of insulating foam, 1 in. thick; Figure V-3. The insulation used (the same as used for the constant temperature box), as manufactured, was covered on one side with metallic foil; the metal foils of the various pieces were connected electrically and grounded. A viewing port was provided, the cover of which could be lifted when it was necessary to see inside the weighing chamber.

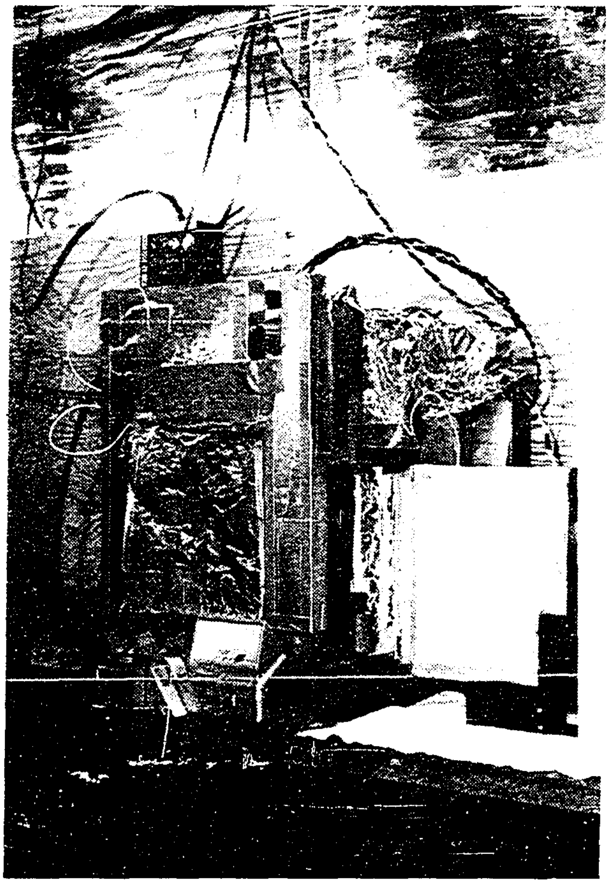


Figure V-3. Semimicrobalance mounted in constant temperature box and covered with thermal insulation. Right hand door to weighing chamber open

It also became apparent that the operation of the lamp which illuminated the optical reticule in the kilogram balance (and in the semimicrobalance; again, all the observations and changes reported here applied to both balances) had a disruptive effect on the zero-point, especially at the increased sensitivity. Continuous operation of the lamp led to the undesirable condition of a 0.5° difference in temperature between the front and rear of the balance as measured by 0.1° mercurial thermometers mounted at these positions through holes in the cover.

Temperature effects caused by the operation of the lamp were finally eliminated by modifying the electrical system of the balance and by rebuilding the housing assembly of the lamp. As delivered by the manufacturer, movement of the arrestment lever of the balance from full arrest turns on a 6-V lamp powered by a transformer located within the balance case. It was necessary to disconnect this transformer and power the lamp from another 6-V transformer, driven by an autotransformer, both located outside the balance case. The assembly carrying the lamp was removed from the mounting on the rear of the balance and remounted with shielding between the lamp and the balance. This shielding, progressively from the lamp to the balance case, consisted of (1) a Corning AKLO filter (Glass Number 3965, a glass which absorbs infrared but transmits the visible part of the spectrum), 2 mm. thick; (2) a sheet of black Bakelite, 12 mm. thick, with a 12 mm. hole; (3) a sheet of Plexiglass, 1 mm. thick; (4) a sheet of aluminum, 0.02 mm. thick, which extended out and back over the preceding shielding and covered the assembly; and finally (5) another sheet of black Bakelite. Optical alignment proved relatively easy and this source of temperature trouble was eliminated.

In preliminary experiments, the original lamp was replaced by a battery powered "Flexible Examination Light" manufactured by Hoyt Laboratories, Needham, Massachusetts; this is basically a flash light with the lamp in a long flexible probe; it is used primarily in dentistry and in rust-proofing work. This lamp projects an intense, highly directional beam and operates at essentially room temperature. This lamp performed satisfactorily but some difficulty was experienced in aligning the lamp and the assembly described above proved more convenient in practice.

VI. ABSOLUTE DENSITY CYLINDER FOR THE DETERMINATION OF THE DENSITY OF AIR

A. Introduction

Hollow, stainless steel spheres and cylinders were described in my M.S. thesis (38) for the rapid and convenient determination of the density of air. By weighing one of these hollow objects and its counterweight, the density of air could be calculated,

for the stainless steel spheres by

$$d_a = \frac{W_{cw,a} - W_{ss,a} + \alpha}{V_{ss} - V_{cw} + \frac{1}{d_W}(W_{cw,a} - W_{ss,a})} \qquad \text{(VI-1)}$$

or for the stainless steel cylinders by

$$d_a = \frac{W_{cw,a} - W_{cy,a} + \alpha}{V_{cy} - V_{cw} + \frac{1}{d_W}(W_{cw,a} - W_{cy,a})} \qquad \text{(VI-2)}$$

In these equations, α is the difference in mass of the hollow object and its counterweight in vacuum. Calibration of these objects, whether a hollow vessel or a counterweight, consisted in determining the external volume by hydrostatic weighing and the mass in vacuum from the mass in air by applying the correction for buoyancy. The density of air needed for the correction was calculated from the prevailing barometric pressure, temperature, and relative humidity. The mass observed in the hydrostatic weighing, that is, when the object was immersed in the water, was also corrected for the buoyancy of air (on the weights). Thus, a calculated density of air entered into the calibration of an object in two ways. Any value calculated later for the density of air using equation (VI-1) or equation (VI-2) was based on the density of air prevailing at the time the calibration of the hollow object and the counterweight was made, and thus, on the assumption made then that the formula used to calculate the density of air was correct. Pontius (86) questioned this assumption.

The way around this difficulty, that is, to make an "absolute" or "direct" measure of the density of air, one not involving or based on a known, prior density of air, is to either weigh the hollow vessel (and a counterweight) in an actual vacuum or to make the vessel (and a counterweight) in some regular geometric shape, measure the dimensions precisely, and calculate the volume. If either method alone is used, the absolute density could be obtained by a series of approximations. If both mass in vacuum and volume calculated from the dimensions could be obtained, the absolute value for the density could be obtained directly.

The volumes of the hollow, stainless steel objects described in my M.S. thesis could not be calculated from their dimensions. The diameter of the spheres was some 0.020 in. greater through the poles than through the equator and the approximation to a regular ellipsoid too poor to be useful. The ends of the hollow cylinders were re-entrant caps (see Ref. 38, Figure 7, p. 51) and too irregular to allow a calculation. For the work described in the present dissertation, a hollow stainless steel vessel in the form of a right cylinder and a counterweight in the form of a tube were constructed and calibrated. The volume of each object was calculated from the dimensions and also, as a check, determined by hydrostatic weighing. The actual mass in vacuum was obtained using the vacuum weighing bottle described in Chapter VII.

B. The Construction and Measurement of an "Absolute Density" Cylinder

A hollow, right cylinder of stainless steel, termed throughout the remainder of this dissertation as an "*absolute density cylinder*", was constructed from stainless steel tubing 1 in. outside diameter and 0.010 in. wall thickness. Three such cylinders were made. A cap, machined as shown in Figure VI-1, was fitted into each end of the tubing; the wall of the cap was 0.020 in. thick. An extension around the periphery of the cap fitted snuggly into the tubing and provided a heat sink which prevented the tubing from melting during the welding. The welding was done by the electron beam technique, which, being conducted

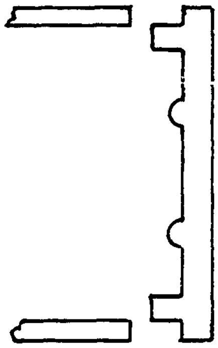


Figure VI-1. Cross section of cap closing the ends of the absolute density cylinder under vacuum, left the cylinders evacuated within. The welds were machined smooth and the surface of the cylinder was polished on the lathe with aluminum oxide and gentle pressure applied with the fingers. The polishing was continued until the cylinder was mirror bright. Each of the three cylinders made were about 2.45 in. long, weighed about 17 g., and had a density of about 0.5 g./cm.^{3}; see Figure VI-2.

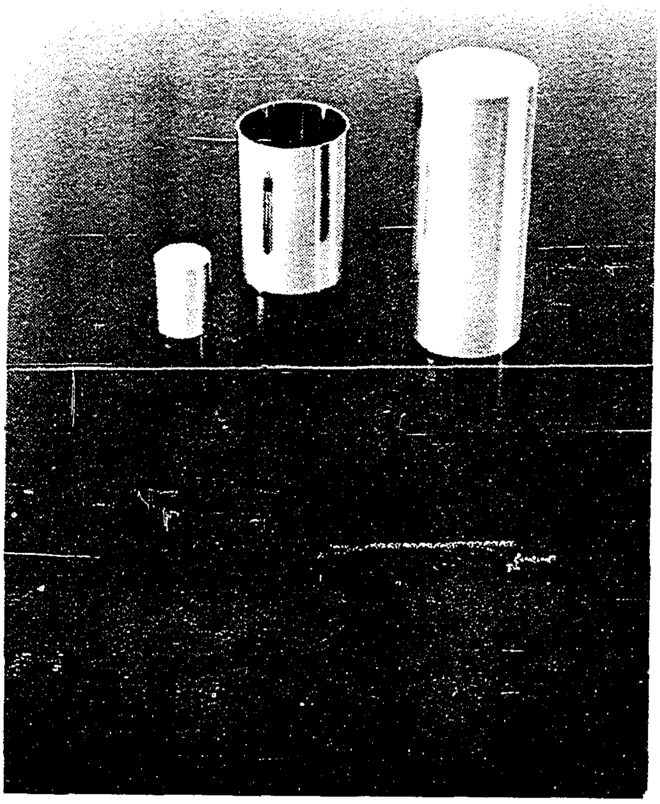


Figure VI-2. "Absolute density cylinder" with solid and tubular counterweights

The external volume of the absolute density cylinder was determined by making measurements of length (26 measurements) and diameter (56 measurements) using a Sheffield optical comparator (Sheffield Corporation, Dayton, Ohio), Model Number 1000, Serial Number 541621RS, calibrated with grade A gage blocks manufactured by the DoAll Company of Des Plaines, Illinois (Set 340R, Serial Number 2026, coefficient of expansion: 6.5×10^{-6}/°F). The optical comparator, which was graduated to 0.000,1 in. but readable to 0.000,02 in., and the gage blocks were the property of the Physics Machine Shop, Iowa State University, where the measurements were made. The temperature in the vicinity of the optical comparator was measured with a Matheson mercurial thermometer graduated to 0.1°. The cylinders were handled by gloved hands only.

The volume of the cylinder was calculated from the dimensions recorded using

$$V = \pi\left(\frac{D}{2}\right)^2 L \tag{VI-3}$$

The relative uncertainty in the calculated volume was calculated using

$$\frac{dV}{V} = \frac{2dD}{D} + \frac{dL}{L} \tag{VI-4}$$

an expression derived by differentiating equation (VI-3) and dividing the resulting equation by equation (VI-3).

For absolute density cylinder Number 1, the data obtained was

$t = 22.5°$

$L = 2.461,50$ in.

$\sigma_L = 0.000,32$ in.

$D = 1.001,41$ in.

$\sigma_D = 0.000,43$ in.

$V = 1.938,70$ in.^{3} (31.769,82 cm.^{3})

$dV/V = 0.990$ parts in 10^3

For absolute density cylinder Number 2, the data obtained was

$t = 22.5°$

$L = 2.453,10$ in.

$\sigma_L = 0.000,20$ in.

$D = 1.002,05$ in.

$\sigma_D = 0.000,57$ in.

$V = 1.934,57$ in.^{3} (31.701,98 cm.^{3})

$dV/V = 1.22$ parts in 10^3

For absolute density cylinder Number 3, the data obtained was

$t = 22.5°$

$L = 2.452,12$ in.

$\sigma_L = 0.000,16$ in.

$D = 1.001,40$ in.

$\sigma_D = 0.000,39$ in.

$$V = 1.931{,}27 \text{ in.}^3 \quad (31.647{,}88 \text{ cm.}^3)$$

$$dV/V = 0.844 \text{ parts in } 10^3$$

The relative uncertainty in the calculated volumes of the cylinders, about one part per thousand (1 p.p.t.) was about a half order of magnitude greater than required to determine the density of air to better than 1 p.p.t., and it was still considered unacceptably high. In the calculation, the uncertainty in the diameter is weighted more heavily than that in the length, equation (VI-4), but the uncertainty in the measurements themselves of the diameters were about twice that of the lengths. This uncertainty in the diameter reflected the quality of the stainless steel tubing used. This tubing was material which had been stored in the bins in the shops for some time, new commercial tubing of the specifications needed not being available from any mill or supplier. Although the lengths of tubing used were carefully selected, the tubing finally used was somewhat dented and scratched. Considerable effort was devoted to the possibility of improving the surface and geometric regularity of the cylinder by grinding. The experts in ten machine shops from Providence, Rhode Island, to Denver, Colorado, unanimously agreed that it was impossible to grind any thin-walled vessel successfully. Failing in this direction, a device was invented for lapping the cylinders with polishing compound.

C. Adjustable Lapping Block for Cylinders

An adjustable lapping block, Figure VI-3, for polishing the absolute density cylinders was fabricated from a block of brass 3.0 in. long, 1.5 in. wide and 2.4 in. high. A channel was milled in one of the narrow faces, 0.75 in. wide and 0.625 in. deep. A hole, 1 in. in diameter, was drilled through the block along the long dimension and honed smooth. A slot 0.16 in. wide was cut from the channel into the bore, this slot extending the entire length of channel and bore. Holes were drilled through the sides of the channel and threaded bolts passed through the holes. By turning the four nuts placed on each of the three bolts, the diameter of the bore could be varied easily, changes in the diameter of the bore being followed precisely by measuring the width of the slot with feeler gages.

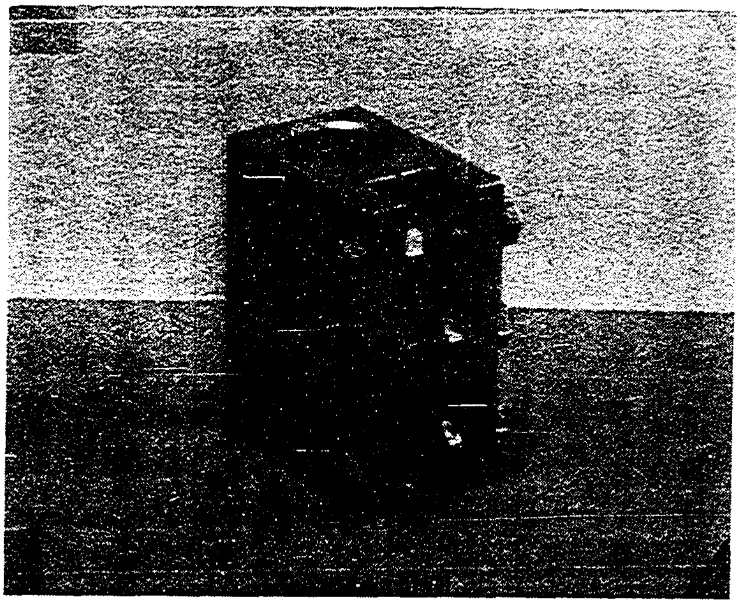


Figure VI-3. Adjustable lapping block

For lapping, a cylinder was mounted horizontally on a lathe, one end of the cylinder being attached to the end of a steel rod of slightly smaller diameter which was held in the chuck of the lathe. The end faces of the cylinder and rod were fastened together with Ridge-X, a lapidary wax manufactured by M. Argueso and Company of Momaroneck, New York. Early attempts at lapping involved the use of suspensions in water of Linde A (0.3 micron alumina) which was to be followed by lapping with Linde B (0.05 micron alumina); both grinding compounds are manufactured by Buehler Ltd. of Evanston, Illinois. During lapping, however, the water evaporated and the surface of the cylinder became scratched. The alumina was replaced with Grade 4-A, Clover Lapping and Grinding Compound, carborundum in an oil base manufactured by the Clover Manufacturing Company of Norwalk, Connecticut. The procedure for lapping included placing the lapping block around the mounted cylinder and tightening the block, adding the suspension of grinding compound, and turning the cylinder slowly on a lathe (39 r.p.m.); the lapping block was moved back and forth by hand along the length of the cylinder as the cylinder turned. The nuts on one side of the block were tightened at half hour intervals by about 0.002 in. to insure continued and uniform grinding. The removal of between 0.001 and 0.002 in. from the diameter of a cylinder took about eight hours of lapping. The lapping was concluded by polishing the cylinders by hand using polishing cloth (Buehler Microcloth) while the mounted cylinder was turned at about 350 r.p.m. on the lathe.

Cylinders Number 2 and Number 3 were polished in this manner. The lapping process was slow, about eight hours being required to eliminate the surface defects and obtain a high polish; the diameter of cylinder Number 2 was reduced during this time by 0.001,72 in. and that of cylinder Number 3 by 0.001,11 in. The dimensions of each cylinder were again measured, 26 measurements of length and 56 measurements of diameter, using the optical comparator. For cylinder Number 2, the data obtained were:

L = 2.453,79 in. t = 24.2°
σ_L = 0.000,14 in.
D = 1.000,36 in. t = 24.0°
σ_D = 0.000,26 in.
V = 1.928,66 in.^{3} (31.605,11 cm.^{3}) t = 24.1°
dV/V = 0.597 parts in 10^3

and the data obtained for absolute density cylinder Number 3 were

L = 2.452,51 in. t = 23.7°
σ_L = 0.000,12 in.
D = 1.000,29 in. t = 23.4°
σ_D = 0.000,17 in.

$V = 1.927{,}33$ cm.^{3} $(31.583{,}34$ cm.$^3)$ $t = 23.55°$

$dV/V = 0.389$ parts in 10^3

The volumes directly above are given at the average temperature prevailing in the vicinity of the optical comparator during the measurements of the dimensions of each cylinder and were calculated after correction of the length and diameter to that average temperature using the coefficient of expansion for Type 304 stainless steel, 9.6×10^{-6}/°F.

The results of the lapping are more readily seen if the dimensions of the cylinders after lapping are corrected to 22.5°, the temperature at which the measurements of the dimensions before lapping were made:

		Cylinder Number 2	Cylinder Number 3
Diameter (22.5°)			
before lapping,	D	1.002,05 in.	1.001,40 in.
	σ	0.000,57 in.	0.000,39 in.
after lapping,	D	1.000,33 in.	1.000,29 in.
	σ	0.000,26 in.	0.000,17 in.
difference, D		-0.001,72 in.	-0.001,11 in.
Length (22.5°)			
before lapping,	L	2.453,10 in.	2.452,12 in.
	σ	0.000,20 in.	0.000,16 in.
after lapping,	L	2.453,71 in.	2.452,51 in.
	σ	0.000,41 in.	0.000,12 in.
difference, L		+0.000,61 in.	+0.000,39 in.

The lapping reduced the uncertainty in the diameter of each cylinder to somewhat less than half of the earlier uncertainty, and of course, the uncertainty in the calculated volumes was correspondingly reduced. The length of each cylinder increased slightly during the lapping, for cylinder Number 2 by 2.52 parts in 10^4, and for cylinder Number 3 by 1.5 parts in 10^4; the uncertainty (standard deviation) in the measurements of the length was reduced.

During subsequent work with these cylinders, it was found that both had developed leaks during the lapping and had been made useless. Thus, although the lapping effected precisely the desired improvement in the characteristics of the cylinders, the work was for nothing.

Apparently, the stresses produced or relieved during the lapping caused the weld to crack. I recommend that hollow cylinders made in the future be fabricated by boring a rod of stainless steel leaving a bottom intact so that only one cap need be welded on and that the metal around the welding joint be made heavier.

D. Additional Measurement of the Dimensions of Absolute Density Cylinder Number 1

Because absolute density cylinders Number 2 and Number 3 were rendered useless by leaks developed during lapping, absolute density cylinder Number 1 was used for the work described subsequently. The uncertainty in the volume of cylinder Number 1, as calculated from the dimensions, 1 p.p.t., was unacceptably large, lapping to improve the characteristics of the cylinder appeared to be ruled out, and lacking any other approach, it appeared advisable to repeat the measurements of the dimensions. Actually, three additional measurements of the volume were made: another determination by direct measurement of the dimensions, a determination of the volume by hydrostatic weighing in water, and a determination of the volume by hydrostatic weighing in a fluorocarbon solvent.

The dimensions of cylinder Number 1 were measured by Mr. Clifford C. Hach in the shop of the Hach Chemical Company, Loveland, Colorado, using a Federal Electronic Gauge, Model EAS-1233, manufactured by the Federal Gauge Company of Providence, Rhode Island. This instrument was calibrated with a set of Grade A gage blocks, Set BEI-81-A, Serial Number 720026, manufactured by Mitutoyo. Thirty-three measurements of length and twenty-two measurements of diameter were made. The temperature at which the measurements were made was 20.1°. The data obtained for cylinder Number 1 by Mr. Hach was

$t = 20.1°$

$L = 2.462,38$ in.

$\sigma_L = 0.000,29$ in.

$$D = 1.001{,}40 \text{ in.}$$
$$\sigma_D = 0.000{,}43 \text{ in.}$$
$$V = 1.939{,}37 \text{ in.}^3 \quad (31.780{,}54 \text{ cm.}^3)$$
$$dV/V = 0.977 \text{ parts in } 10^3$$

The uncertainty in the calculated volume of cylinder Number 1 was almost identical for measurements made at Iowa State University and the Hach Chemical Company, as were the respective standard deviations in length and the respective standard deviations in diameter.

E. Determination of the Volume of Cylinder Number 1 by Hydrostatic Weighing in Water

The volume of absolute density cylinder Number 1 was determined by three hydrostatic weighings in water. The hydrostatic weighing method of determining the volume of such an object of density less than water involves three weighings: (1) the mass of the object in air (2) the mass of the immersion cage in water, and (3) the mass of the object and immersion cage in water.

The mass in vacuum of cylinder Number 1 was calculated from the mass of the cylinder in air. Cylinder Number 1 was weighed by double substitution in the constant temperature box using the Mettler Model H51AR Semimicrobalance and a set of Ainsworth, rhodium-plated brass, two-piece weights, Serial Number 9156, calibrated at the National Bureau of

Standards in 1944 and 1967 (Mass and Volume Section) and in 1974 (Electricity Division). The prevailing barometric pressure, temperature, and relative humidity were measured respectively with the Friez mercurial barometer mounted on the west wall of the box, platinum resistance thermometer Number 2 located in the balance case, and an Airguide, Model 113B, hygrometer; the density of air was calculated using equation (III-4).

The weighing of cylinder Number 1 by double substitution involved two weighings. First, the cylinder was weighed against the internal weights of the semimicrobalance. Adopting the symbolism developed in my M.S. thesis, the forces acting during this weighing are represented by

$$T_{cy} - d_a V_{cy} = T_{W,H51} - d_a V_{W,H51} + \beta_{cy} \qquad \text{(VI-5)}$$

in which the subscript W,H51 represents the weights remaining on the beam of the semimicrobalance and β_{cy} represents the reading on the optical scale recorded while weighing the cylinder and converted to mass by multiplication by the sensitivity of the balance. The optical scale was calibrated using the 50.00-mg. weight from the Ainsworth set. Next, the cylinder was replaced with weights from the set of calibrated, two-piece weights equivalent to the mass of the cylinder in air; the weights within the semimicrobalance were left undisturbed. The forces acting during this second weighing can be represented

$$W_{cy,a} - d_a V_W = T_{W,H51} - d_a V_{W,H51} + \beta_W \qquad \text{(VI-6)}$$

Equating equations (VI-5) and (VI-6) and solving for T_{cy}, the mass in vacuum of cylinder Number 1 is

$$T_{cy} = W_{cy,a} + (\beta_W - \beta_{cy}) + d_a(V_{cy} - V_W) \qquad \text{(VI-7)}$$

The mass in vacuum and the volume of the Ainsworth weights used were obtained using the data given on the calibration sheet supplied by the National Bureau of Standards (see Appendix II of my M.S. thesis). The volume of the Ainsworth weights was corrected to the temperature at which the weighings were made in the constant temperature box 29.36°, using the coefficient of cubical expansion for brass (85), $5.4 \times 10^{-5}/°$. The value used for the volume of cylinder Number 1 was an average of the values obtained from the dimensions at Iowa State University and the Hach Chemical Company and corrected to 29.36°. The data used for calculating the mass in vacuum of cylinder Number 1 were

$T_W = 17.012,436$ g.

$V_W = 2.028,537$ cm.^{3} at 29.36°

$V_{cy} = 31.786,5$ cm.^{3} at 29.36°

$\beta_W = 0.011,10$ g.

$\beta_{cy} = 0.012,08$ g.

for which $T_{cy} = 17.046,96$ g.

The weighing of cylinder Number 1 in water was performed in Room 137A using the Ainsworth TCX double-pan balance and supporting assembly described in detail and shown in Chapter V of my M.S. thesis. The immersion cage was equipped with a damping vane and was hung on a four-point monofilament fish line which attached through an S-shaped piece of chromel wire to the lower end of the gold chain hanging from the left stirrup of the balance. Deionized water was placed in a 4-liter beaker located in the lower chamber of the supporting assembly; the temperature of the water was measured using a Matheson, mercurial thermometer graduated in 0.1°. The density of the water was obtained from Table A-2 of Diehl's *Quantitative Analysis* (Ref. 34, page 411).

Measurements of temperature, barometric pressure, and relative humidity were made during each weighing of cylinder Number 1 in water and were used to calculate the density of air. The temperature of air was measured with a Matheson, mercurial thermometer graduated in 0.1° and positioned within the case of the double-pan balance. The relative humidity was measured to the nearest 0.5 per cent with the Airguide hygrometer. The barometric pressure was measured with the Friez, mercurial barometer mounted on the west wall of the constant temperature box; the door of the box was propped open while the weighings in water were performed so that the barometric pressure within the box and Room 137A were identical.

The weighings in water were made by substitution. The cage and vane were hung in the water and balanced with a tare placed on the right pan; actually the tare consisted of weights from another set of weights plus the weights added by the keyboard mechanism of the double-pan balance (less than 0.1 g.). The cylinder was then placed in the immersion cage and weights from the Ainsworth, rhodium-plated set were added to the left pan to return the center of swings nearly to the center of swings observed with the cage empty; the final adjustment was made by changing the weights on the keyboard. The weight added to the left pan less the change in the keyboard weights and any minor deviations from the center of swings observed with the cage empty was designated W_{cy,H_2O}. In this manner, the balance was operated at constant load and any difference in the length of the arms of the balance was cancelled The sensitivity of the balance during the weighings in water was 1.0 mg. per scale division.

The forces acting during the weighing of the empty cage can be represented by

$$T_c - d_{H_2O}V_c = T_{Tare} - d_a \frac{T_{Tare}}{d_{Tare}} \qquad \text{(VI-8)}$$

The forces acting during the weighing of the cylinder and cage in water can be represented by

$$T_{cy} - V_{cy}d_{H_2O} + T_c - d_{H_2O}V_c + W_{cy,H_2O} - \frac{d_a}{d_W} W_{cy,H_2O} = T_{Tare} - d_a \frac{T_{Tare}}{d_{Tare}} \qquad \text{(VI-9)}$$

Equating equations (VI-8) and (VI-9) and solving for V_{cy}, the volume of cylinder Number 1 was given by

$$V_{cy} = \frac{T_{cy} + W_{cy,H_2O} - \dfrac{d_a W_{cy,H_2O}}{d_W}}{d_{H_2O}} \qquad \text{(VI-10)}$$

Three sets of weighings in water were performed. The density of the weights was 8.4 g./cm ^{3}. For the first set of weighings in water, the data obtained were

W_{cy,H_2O} = 14.661,2 g.

d_a = 0.001,148,0 g./cm.^{3}

t_{H_2O} = 22.15°

d_{H_2O} = 0.997,764 g./cm.^{3}

for which V_{cy} = 31.777,2 cm.^{3}

For the second set of weighings in water, the data obtained were

W_{cy,H_2O} = 14.662,6 g.

d_a = 0.001,147,1 g./cm.^{3}

t_{H_2O} = 22.3°

d_{H_2O} = 0.997,724 g./cm.^{3}

for which V_{cy} = 31.779,9 cm.^{3}

For the third set of weighings in water, the data obtained were

W_{cy,H_2O} = 14.660,7 g.
d_a = 0.001,148,1 g./cm.^{3}
t_{H_2O} = 22.3°
d_{H_2O} = 0.997,724 g./cm.^{3}
for which V_{cy} = 31.777,9 cm.^{3}

The average volume of cylinder Number 1 as determined by hydrostatic weighings in water was 31.778,3 cm.^{3} at 22.3°, the relative standard deviation in the volume being 4.4 parts in 10^5.

F. Determination of the Volume of Cylinder Number 1 by Hydrostatic Weighing in FC-75

The volume of absolute density cylinder Number 1 was determined by four hydrostatic weighings in FC-75. FC-75 is the electronic grade of FC-80, a completely fluorinated liquid composed largely of perfluorobutyltetrahydrofuran and its isomers; at least eight peaks have been recorded for FC-80 by gas chromatography (71). Bowman, Schoonover, and Carroll used FC-75 (8) at the National Bureau of Standards for hydrostatic weighings performed to determine the density of four pieces of single-crystal silicon subsequently used as density standards. Bowman, Schoonover and Carroll cited three advantages gained by substituting FC-75 for water during hydrostatic weighings. First, the density of FC-75, about 1.77 g./cm.^{3}, is almost twice that of water so the precision for weighings in FC-75 can be almost double that realized when water is used. Secondly, problems arising due to the large and variable surface tension of water are lessened as the surface tension of FC-75 is one-fifth that of water (15 dyn./cm. for FC-75, 75 dyn./cm. for water). The third advantage of FC-75, the one I consider the most important, is the vast ability of FC-75 to dissolve gases. For example, the solubility of oxygen in FC-75 is about 17 times greater than in water at 25°, the solubility of oxygen being 2.9 ml. O_2/100 ml. water but 48.8 ml. O_2/100 ml. FC-75 (93). During my work with FC-75, I noticed none of the small bubbles of air that cling to objects in water and plague hydrostatic weighings in water; in fact, these tiny bubbles never formed on the cylinder while it was in FC-75.

Each weighing of cylinder Number 1 in FC-75 was bracketed by two determinations of the density of FC-75. The density of FC-75 was determined by weighing in FC-75 a cube of single-crystal silicon obtained from the National Bureau of Standards.

The mass in vacuum of the silicon cube, T_{Si}, was calculated from data obtained by weighing the cube by double substitution in the constant temperature box using the

Mettler, Model M5, Microbalance and the 20 g. weight from the set of Ainsworth, rhodium-plated brass weights. The prevailing temperature, barometric pressure, and relative humidity were measured with the same instruments used while weighing cylinder Number 1 by substitution in the constant temperature box; the density of air was again calculated using equation (III-4). The mass in vacuum of the cube was calculated using an expression derived in the same manner as equation (VI-7)

$$T_{Si} = \frac{W_{Si,a} - d_a V_W}{1 - \frac{d_a}{d_{Si}}} \qquad \text{(VI-11)}$$

The density of the silicon cube was calculated by correcting the average density of the four pieces of single-crystal silicon used by Bowman, Schoonover and Carroll (8) in their work, 2.329,120,5 g./cm.^{3} at 20°, to the temperature at which the mass in air of the cube was determined, 26.74°, the coefficient of linear expansion for silicon being 2.56×10^{-6}/°C; the density of the silicon cube at 26.74° was 2.329,000 g./cm.^{3}. The volume of the Ainsworth weight was also corrected to 26.74°. The mass in vacuum of the silicon cube was calculated to be 20.010,875 g.

The silicon cube was weighed by substitution in FC-75. Again, two weighings were involved but, since the silicon cube was denser than FC-75, the order of the weighings was reversed from that used in weighing the cylinder in water; first the immersion cage was loaded and weighed

$$T_{Si} - d_{FC}\left(\frac{T_{Si}}{d_{Si}}\right) + T_c - d_{FC}\left(\frac{T_c}{d_c}\right) = T_{Tare} - d_a\left(\frac{T_{Tare}}{d_{Tare}}\right) \qquad \text{(VI-12)}$$

and then the cage was weighed empty

$$W_{Si,FC} - d_a\left(\frac{W_{Si,FC}}{d_W}\right) + T_c - d_a\left(\frac{T_c}{d_c}\right) = T_{Tare} - d_a\left(\frac{T_{Tare}}{d_{Tare}}\right) \qquad \text{(VI-13)}$$

Equating equations (VI-12) and (VI-13) and solving for d_{FC},

$$d_{FC} = \frac{T_{Si} - W_{Si,FC} + d_a \dfrac{W_{Si,FC}}{d_W}}{\dfrac{T_{Si}}{d_{Si}}} \qquad \text{(VI-14)}$$

The density of the silicon cube was corrected to the average temperature at which the cylinder was weighed in FC-75, 23.95°, the density of the cube being 2.329,050 g./cm.^{3} at this temperature. The density of air was calculated from the prevailing temperature, barometric pressure, and relative humidity for all weighings in FC-75 from measurements made with the same instruments used to measure the prevailing conditions during the weighings in water. The sensitivity of the balance during the weighings in FC-75 was 0.28 mg. per scale division.

The volume of cylinder Number 1 was determined by hydrostatic weighings done by substitution in FC-75. The equation used to calculate the volume of the cylinder, derived in the same manner as equation (VI-10), was

$$V_{cy} = \frac{T_{cy} + W_{cy,FC} - \dfrac{d_a W_{cy,FC}}{d_W}}{d_{FC}} \tag{VI-15}$$

For the first set of weighings in FC-75, the data obtained were

$W_{cy,FC} = 39.127{,}51$ g.
$d_a = 0.001{,}140{,}0$ g./cm.^{3}
$t_{FC} = 23.9°$
$d_{FC} = 1.767{,}45$ g./cm.^{3}
for which $V_{cy} = 31.779{,}8$ cm.^{3}

For the second set of weighings in FC-75, the data obtained were

$W_{cy,FC} = 39.123{,}92$ g.
$d_a = 0.001{,}141{,}5$ g./cm.^{3}
$t_{FC} = 23.9°$
$d_{FC} = 1.767{,}32$ g./cm.^{3}
for which $V_{cy} = 31.780{,}0$ cm.^{3}

For the third set of weighings in FC-75, the data obtained were

$W_{cy,FC} = 39.122{,}5$ g.
$d_a = 0.001{,}140{,}5$ g./cm.^{3}

t_{FC} = 23.95°

d_{FC} = 1.767,28 g./cm.^{3}

for which V_{cy} = 31.780,0 cm.^{3}

For the fourth set of weighings in FC-75, the data obtained were

$W_{cy,FC}$ = 31.120,9 g.

d_a = 0.001,138,2 g./cm.^{3}

t_{FC} = 24.0°

d_{FC} = 1.767,16 g./cm.^{3}

for which V_{cy} = 31.781,1 cm.^{3}

The average volume calculated for absolute density cylinder Number 1 from the hydrostatic weighings in FC-75 was 31.780,2 cm.^{3} at 23.95°, the relative standard deviation in the volume being 1.6 parts in 10^5.

G. Comparison of the Results Obtained for the Volume of Cylinder Number 1

A summary is given in Table VI-1 of the values obtained for the volume of cylinder Number 1, corrected to 22.5°, as determined in the four determinations described above: (1) measurement of the dimensions at Iowa State University, (2) measurement of the dimensions at the Hach Chemical Company, (3) hydrostatic weighing in water, and (4) hydrostatic weighing in FC-75. The average of all four values for the volume of the cylinder at 22.5° was 31.777,7 cm.^{3}.

Table VI-1. The volume of cylinder Number 1 determined by several methods[a]

a. Calculation from Measurements of the Dimensions

Site of Experiment	Volume, $cm.^3$	Uncertainty in the Calculated Volume, parts per 10^5
Iowa State University	31.769,8	99.3
Hach Chemical Company	31.784,4	97.7
difference	0.014,6 $cm.^3$	
mean	31.777,1 $cm.^3$	

b. Hydrostatic Weighing

Immersion Liquid	Volume, $cm.^3$	Relative Standard Deviation, parts per 10^5
Water	31.778,6	4.4[b]
FC-75	31.777,8	1.6[c]
difference	0.000,8 $cm.^3$	
mean	31.778,2 cm^3	

---

[a] All volumes given have been corrected from the temperature at which the volume was determined to 22.5°; linear coefficient of expansion, 9.6×10^{-6}/°F.

[b] Three determinations.

[c] Four determinations.

The standard deviation in the volume obtained by averaging all four values was 0.006,0 $cm.^3$ or, on a relative basis, 1.9 parts in 10^4.

The agreement between the mean values for the volume of cylinder Number 1 obtained from the measurements of the dimensions and that obtained from the two hydrostatic weighings, the difference being only 0.001,2 $cm.^3$, is remarkably good. Clearly, however, the results obtained by the hydrostatic weighings are far more precise, the uncertainties (relative standard deviations) being 4.6 (water) and 1.6 (FC-75) parts in 100,000 compared to 98 parts per 100,000 for that from the dimensions. Clearly, the hydrostatic weighing using the fluorinated hydrocarbon FC-75 as the transfer liquid gave results superior to those using water.

The entire experience simply followed, and took advantage of, the work at the National Bureau of Standards which culminated the high-precision evaluation of the Avogadro constant (32), probably the finest piece of experimental work ever done in North America. That work, which involved the high-precision determination of the density of elemental silicon involved also, as a transfer solid, the determination of the mass of a steel object of regular geometry. A sphere was chosen as the geometric configuration from which the volume could be calculated from the dimensions, and the problem was, in this respect, easier than mine because the sphere was a solid and could be machined precisely by grinding using the manufacturing techniques developed and highly perfected for making ball bearings. The measurements of the diameter of the steel sphere were made by the interference method (32,58) and the final uncertainty was less than 1 p.p.m. The choice of the fluorocarbon liquid as the transfer liquid (8), after the use of water and the unsurmountable difficulties in its use had been thoroughly explored (9), was brilliant, and the confirmation I offer here was hardly necessary. In retrospect, then, perhaps it was not even necessary to make a cylinder of perfect geometry. And in retrospect, the volume obtained through FC-75 against elemental silicon, 31.777,8 cm.^{3}, may be the best of the values reported in the table above, although I am uncertain as to the origin of the elemental silicon used other than that it came from a lot which was part of the stock at the NBS.

I consider 31.778,2 cm.^{3} at 22.5°, the volume obtained by averaging the results of the hydrostatic weighings, to be the volume of cylinder Number 1. Although this value for the volume is almost identical to the value obtained by averaging the results calculated from the dimensions and to the value obtained by averaging the results of all four dimensions, the results obtained from the hydrostatic weighings are an order of magnitude more precise than those obtained from the dimensions and certainly more reliable than any value which included the results obtained from the dimensions. Further, the hydrostatic weighings were performed under conditions in which better monitoring and control of temperature could be exercised than those existing during measurement of the dimensions.

H. Construction and Determination of the Volume of Tubular Counterweight for Cylinder Number 1

A tubular counterweight was constructed for use with absolute density cylinder Number 1 in determining the density of air. The density of air could be determined by weighing the cylinder and then the counterweight using the microbalance and applying equation (VI-2). The tubular design was chosen so that both mass and surface area of the counterweight could be made as close to the mass and surface area of the cylinder as possible. By matching cylinder and counterweight in surface area, it was hoped to obviate effects of changes in the amount of adsorbed moisture resulting from changes in humidity.

The tubular counterweight was constructed from Carpenter 20CB3, a stainless steel which is highly resistant to corrosion; see Chapter X. The dimensions of the counterweight were chosen such that: (1) the mass of the counterweight was within 1 mg. of that of the cylinder (cylinder Number 1) in air, (2) the surface area of the counterweight was approximately equal to that of the cylinder, and (3) the outer diameter of the counterweight was such that the tubular counterweight would fit into the weighing bottle. The first and second requirements are described mathematically by

$$A_{cy} = A_{cw} = 2\pi R_e^2 H + 2\pi R_i^2 H + 2\pi(R_e^2 - R_i^2) \qquad \text{(VI-16)}$$

and

$$W_{cy} = W_{cw} = d_{cw} V_{cw} = d_{cw} \pi H(R_e^2 - R_i^2) \qquad \text{(VI-17)}$$

in which R_e and R_i are the external and internal radii of the tube, respectively, and H is the height. Solving both equations for H, equating the resulting expressions, and solving for R_i, an equation for the internal radius of the tube was obtained

$$R_i = \frac{\dfrac{d_{cw} R_e^2 A_{cy}}{2W_{cy}} - R_e^2 - 2\pi R_e^2}{1 - 2 + \dfrac{d_{cw} A_{cy}}{2W_{cy}}} \qquad \text{(VI-18)}$$

An appropriate value for R_e was chosen and a rod of the stainless steel was cut on the lathe to the chosen external diameter. The internal radius was then calculated and the rod was bored and honed to an internal diameter which was slightly smaller than twice the value calculated using equation (VI-18). The tube was weighed and material was removed from the inner wall of the tube by honing until the masses in air of the cylinder and tubular counterweight were within several milligrams. The counterweight was polished with Linde B and pressure applied with the fingers; the final mass of the counterweight was adjusted to within one milligram of the cylinder by carefully polishing one end of the counterweight with 600-grit emery cloth.

The volume of the tubular counterweight was determined from the dimensions measured using equipment at Iowa State University and the Hach Chemical Company and from hydrostatic weighings in water and FC-75. The volume of the counterweight was calculated from the dimensions using

$$V = \pi H\left[\left(\frac{D_e}{2}\right)^2 - \left(\frac{D_i}{2}\right)^2\right] \qquad \text{(VI-19)}$$

in which D_e and D_i are the external and internal diameters of the tube, respectively. An expression for the uncertainty in the volume of the tube was derived by differentiating equation (VI-19) with respect to D_e, D_i, and H and dividing the resulting expression by equation (VI-19) to give

$$\frac{dV}{V} = \frac{2dD_e}{D_e\left(1 - \frac{D_i^2}{D_e^2}\right)} - \frac{2dD_i}{D_i\left(\frac{D_e^2}{D_i^2} - 1\right)} - \frac{dH}{H} \qquad \text{(VI-20)}$$

Thirty-six measurements of the outer diameter and sixteen measurements of the height of the tubular counterweight were made at Iowa State University using the optical comparator calibrated with gage blocks. The internal diameter of the tube was determined by forty measurements made with a Scherr-Tumico snap gage (Scherr-Tumico Company, St. James, Minnesota) and the optical comparator. The internal diameter was measured by inserting the snap gage into the tube, allowing the probe of the snap gage to expand to the internal diameter of the tube, locking the snap gage, and removing the snap gage from the tube for measurement using the optical comparator. The data obtained at Iowa State University for the tubular counterweight were

$D_i = 0.944{,}92$ in. $t = 22.25°$

$\sigma_{D_i} = 0.000{,}29$ in.

$D_e = 1.000{,}28$ in. $t = 27.2°$

$\sigma_{D_e} = 0.000{,}14$ in.

$H = 1.511{,}35$ in. $t = 27.4°$

$\sigma_H = 0.000{,}13$ in.

for which at 22.25°

$V = 0.127{,}811 \text{ in.}^3$ $(2.091{,}10 \text{ cm.}^3)$

$dV/V = 2.27$ parts in 10^3

The external diameter and height of the tube were corrected to 22.25° using the coefficient of linear expansion of 304 stainless steel, $9.6 \times 10^{-6}/°\text{F}$.

Twenty-eight measurements of the external diameter and twenty-seven measurements of the height of the tubular counterweight were made by Mr. C. C. Hach in the shop of the Hach Chemical Company using the Federal Electronic Gauge calibrated with gage blocks. Mr. Hach also made twelve measurements of the internal diameter of the tube using a Boyce Acra-cord CMM, Model C-301, Serial Number XY0579-497, connected to a Hewlett-Packard 9815A calculator. The data obtained by Mr. Hach for the tubular counterweight were

$$t = 20.1°$$

$$D_i = 0.945{,}04 \text{ in.}$$

$$\sigma_{D_i} = 0.000{,}17 \text{ in.}$$

$$D_e = 1.000{,}33 \text{ in.}$$

$$\sigma_{D_e} = 0.000{,}19 \text{ in.}$$

$$H = 1.511{,}37 \text{ in.}$$

$$\sigma_H = 0.000{,}20 \text{ in.}$$

for which at 22.25°

$$V = 0.127{,}690 \text{ in.}^3 \quad (2.092{,}47 \text{ cm.}^3)$$

$$dV/V = 0.633 \text{ parts in } 10^3$$

The average, measured internal diameter, external diameter, and height of the counterweight at 22.25° were obtained by correcting the measurements made in both shops to 22.25° and averaging the appropriate values to give, at 22.25°

D_i = 2.400,30 cm.
D_e = 1.270,36 cm.
H = 3.838,75 cm.

The surface area of the counterweight was calculated to be 60.677,3 cm.^{2} using equation (VI-16). The surface area of cylinder Number 1 was calculated to be 60.134,9 cm.^{2}, the averaged, measured height and diameter of the cylinder being 6.253,45 cm. and 2.543,63 cm., respectively, at 22.25°. Therefore, the surface area of the counterweight was only 0.902 per cent larger than that of the cylinder.

The volume of the tubular counterweight was determined by four hydrostatic weighings in water and three hydrostatic weighings in FC-75. The mass of the counterweight in vacuum was calculated from data obtained by weighing the counterweight by double substitution using the semimicrobalance and the Ainsworth weights in the constant temperature box; the mass in vacuum was calculated using an equation derived in identical fashion as equation (VI-7). The volume of the counterweight (an average of the values obtained from the dimensions) and the volume of the weights were corrected to the temperature at which the comparison was made, 29.36°. The mass of the counterweight in vacuum was calculated to be 17.013,95 g. All the hydrostatic weighings of the counterweight were made by substitution.

The volume of the counterweight was calculated from the data obtained during the hydrostatic weighings in water using

$$V_{cw} = \frac{T_{cw} - W_{cw,H_2O} + \frac{d_a}{d_W}(W_{cw,H_2O})}{d_{H_2O}} \qquad \text{(VI-21)}$$

Equation (VI-21) was derived by analyzing the forces acting during both weighings made in water for each hydrostatic weighing and solving for V_{cw} in the same manner as equation (VI-10) was derived for the volume of cylinder Number 1. The sensitivity of the balance for the hydrostatic weighings in water was 1.0 mg. per scale division.

Three hydrostatic weighings were made in water. For the first set of weighings in water, the data obtained were

W_{cw,H_2O} = 14.918,8 g.
d_a = 0.001,147,1 g./cm.^{3}
t_{H_2O} = 22.35°
d_{H_2O} = 0.997,719 g./cm.^{3}
V_{cw} = 2.102,0 cm.^{3}

For the second set of weighings in water, the data obtained were

W_{cw,H_2O} = 14.917,3 g.
d_a = 0.001,147,0 g./cm.^{3}
t_{H_2O} = 22.40°

d_{H_2O} = 0.997,706 g./cm.^{3}
V_{cw} = 2.103,5 cm.^{3}

For the third set of weighings in water, the data obtained were

W_{cw,H_2O} = 14.919,0 g.
d_a = 0.001,148,9 g./cm.^{3}
t_{H_2O} = 22.35°
d_{H_2O} = 0.997,712 g./cm.^{3}
V_{cw} = 2.101,8 cm.^{3}

For the fourth set of weighings in water, the data obtained were

W_{cw,H_2O} = 14.918,5 g.
d_a = 0.001,149,8 g./cm.^{3}
t_{H_2O} = 22.45°
d_{H_2O} = 0.997,695 g./cm.^{3}
V_{cw} = 2.102,3 cm.^{3}

The average volume of the tubular counterweight as determined by hydrostatic weighings in water and corrected to 22.25° was 2.102,4 cm.^{3}, the relative standard deviation in the volume being 3.6 parts in 10^4.

The volume of the counterweight was calculated from the data obtained from the hydrostatic weighings in FC-75 using

$$V_{cw} = \frac{T_{cw} - W_{cw,FC} + \frac{d_a}{d_W}(W_{cw,FC})}{d_{FC}} \qquad \text{(VI-22)}$$

which is identical in form to equation (VI-21). Again, the density of the fluorocarbon solvent was determined by the hydrostatic weighing of a cube of silicon before and after the hydrostatic weighing of the counterweight; the density of the silicon cube was calculated to be 2.329,066 g./cm.^{3} at the average temperature at which the weighings were made in FC-75, 23.05°. The sensitivity of the balance for the weighings in FC-75 was 0.3 mg. per scale division.

Three hydrostatic weighings of the counterweight were made in FC-75. For the first set of weighings, the data obtained were

$W_{cw,FC}$ = 13.298,58 g.
d_a = 0.001,151,7 g./cm.^{3}
t_{FC} = 22.95°
d_{FC} = 1.768,44 g./cm.^{3}
V_{cw} = 2.101,9 cm.^{3}

For the second set of weighings in FC-75, the data obtained were

$W_{cw,FC}$ = 13.298,82 g.
d_a = 0.001,150,0 g./cm.^{3}
t_{FC} = 23.05°
d_{FC} = 1.768,25 g./cm.^{3}
V_{cw} = 2.102,0 cm.^{3}

For the third set of weighings in FC-75, the data obtained were

$$W_{cw,FC} = 13.299,31 \text{ g.}$$
$$d_a = 0.001,149,1 \text{ g./cm.}^3$$
$$t_{FC} = 23.15°$$
$$d_{FC} = 1.768,08 \text{ g./cm.}^3$$
$$V_{cw} = 2.101,9 \text{ cm.}^3$$

The average volume of the tubular counterweight as determined by hydrostatic weighing in FC-75 and corrected to 22.25° was 2.101,9 cm.^3, the relative standard deviation in the volume being 2.8 parts in 10^5.

I. Comparison of the Results Obtained for the Volume of the Tubular Counterweight

A summary is given in Table VI-2 of the values obtained for the volume of the tubular counterweight as determined by the methods described in the preceding section and corrected to 22.25°. The average of all four values for the volume is 2.096,9 cm.^3; the standard deviation in the volume obtained by averaging all four values was 0.006,1 cm.^3 or, on a relative basis, 2.9 parts in 10^3. The values obtained by averaging the results obtained from the dimensions and hydrostatic weighings, respectively, differ by 0.001,0 cm.^3 or 5.0 parts in 10^3.

Table VI-2. The volume of tubular counterweight determined by several methods[a]

a. Calculation from Measurements of the Dimensions

Site of Experiment	Volume, cm.^{3}	Uncertainty in the Calculated Volume, parts per 10^5
Iowa State University	2.090,91	227
Hach Chemical Company	2.092,47	63
difference	0.001,56 cm.^{3}	
mean	2.091,69 cm.^{3}	

b. Hydrostatic Weighing

Immersion Liquid	Volume, cm.^{3}	Relative Standard Deviation, parts per 10^5
Water	2.102,4	36[b]
FC-75	2.101,9	2.8[c]
difference	0.000,5 cm.^{3}	
mean	2.102,2 cm.^{3}	

---

[a] All volumes given have been corrected from the temperature at which the volume was determined to 22.25°; linear coefficient of expansion, 9.6×10^{-6}/°F.

[b] Four determinations.

[c] Three determinations.

I have less confidence in the values of the volume obtained from the dimensions than those obtained from the hydrostatic weighings for several reasons. First, both determinations of the volume from the dimensions had large uncertainties associated with them. This fact is not surprising since to determine the volume of the tubular counterweight, the diameters of two "cylinders" had to be determined: the external diameter and internal diameter of the tube. Secondly, since the average value of the counterweight as obtained from the dimensions was smaller than that obtained from the hydrostatic weighings, it appears that the internal diameter of the counterweight may actually be smaller than that obtained by physical measurements. In order to precisely measure the internal diameter of a tube, the probe of the measuring device must be exactly parallel to the ends of the tube. An inclination of the probe resulting in a measured diameter which is 0.000,05 in. larger than the actual diameter would lead to the calculated volume of the counterweight being larger by approximately one part in 10^3. While care was taken at Iowa State University to measure the internal diameter of the counterweight with the snap gage being kept parallel to the ends of the tube, it cannot be guaranteed that this was the case; the same problem probably existed for the measurements made by Mr. Hach. Thirdly, it was found from the measurements of the internal diameter made at Iowa State University that the bore of the counterweight was not perfectly round nor was it uniform. For example, the average internal diameter of the counterweight at one end, the middle, and the other end were, respectively, 0.946,11 in., 0.945,68 in., and 0.945,81 in. While the idea of constructing a tubular counterweight having the same surface area as the cylinder with which it is used was a good one, it is doubtful that the volume of such a tubular counterweight can be obtained from the dimensions unless the counterweight is of nearly perfect geometric configuration and a more reliable method is obtained to measure the internal diameter. It is also advisable that gage blocks of higher quality (Grade AA, Grade AAA) be used in future work when measuring the dimensions.

I consider the volume of the tubular counterweight to be 2.102,2 cm.^3, the value obtained by averaging the results from the hydrostatic weighings.

VII. VACUUM WEIGHING BOTTLE FOR THE DETERMINATION OF MASS

A. Introduction

The correction for the buoyant effect of air on an object being weighed is often referred to as the "correction to weight in vacuum". The claim of Pontius that the density of air cannot be obtained by calculation from measurements of the prevailing conditions of atmospheric pressure, temperature and humidity with the accuracy necessary to make this correction with any degree of confidence dictates that high-precision weighings be made in an actual vacuum. Making such weighings is hardly new. There is, in fact, a journal devoted to papers on the subject: *Vacuum Balance Techniques* (Library of Congress call number: QC107, V139). Invariably, these papers are devoted to applications involving changes in weight brought about by some reaction between a solid phase suspended from one arm of the balance and a gas phase introduced into the chamber: rate of evaporation or deposition, adsorption on the surface of the solid, changes in density of the gas phase because of chemical reaction, and so on. A search through this and related literature, however, failed to uncover any work attacking the more fundamental problem of making absolute measurements of mass in a vacuum.

Attempts were made at Iowa State University during 1975 to make weighings in an actual vacuum. A vacuum balance designed and built by Professor David Peterson of the Department of Material Science and Engineering for the measurement of the vapor pressure of metallic calcium at high temperature was modified for the purpose. This device consisted of an Ainsworth microbalance, Model FDJ, removed from the original case, mounted on a brass plate, and covered with a glass bell jar. The brass plate was milled with a circular groove which carried a gasket on which rested the specially ground, flat, bottom edge of the bell jar. The brass plate was penetrated by openings for (a) a vacuum line, (b) electrical connections, and (c) a vertical rod which passed up through a metal bellows seal and through the brass plate; this rod was used to manipulate the fractional weights on the right stirrup of the FDJ balance.

In initial work with the vacuum balance, it was found that the zero-point of the balance changed as the air was pumped from the bell jar. The FDJ balance, although an equal-arm balance, was not symmetric in construction; the stirrup on the right side was larger than the stirrup on the left because of the "keyboard" by which fractional (less than 1 g.), wire weights were added and removed. In addition, the pans were not the same size owing to modifications necessary to accommodate the mechanism for manipulating the keyboard weights which was brought in through the brass plate. Because the volumes of metal on the opposing sides of the balance were unequal, the buoyancy effect of air was unequal and a shift in the zero-point occurred on pumping out the air.

This shift in zero-point on passing from atmospheric pressure to vacuum was only the beginning of the troubles. The zero-point continued to shift with time of pumping after the pressure in the bell jar had been reduced to 50 µm. (micron) Hg. Temperature changes resulting from pumping the air from the bell jar accounted for only part of the drift because sufficient time was given for such effects to be dissipated. It became apparent from alternate admission of dry air and evacuation that surface films, presumably of moisture, oil from the pump, and possibly volatile materials from stopcock grease and the atmosphere of the laboratory, were involved. Even more disturbing were the effects of electrostatic charges generated by the flow of air in and out of the bell jar and by the very oscillation of the beam of the balance on the agate knife edges and plates; these effects produced large and erratic variations in the normal, evenly damped oscillations of the beam. Ultimately, after serious effort involving an inordinate expenditure of time, the project was abandoned.

The problem of making weighings in a vacuum was solved by Professor Diehl and myself in April of 1976 by the invention of a *vacuum weighing bottle*. This weighing bottle, Figure VII-1, was of such a design that the bottle could be first evacuated and weighed, then opened and an object inserted, and the weighing bottle then closed, evacuated and again weighed. The buoyancy of air on the weighing bottle is the same in both operations so that the increase in weight is the mass ("true mass" or "weight in vacuum") of the object. Two such weighing bottles were constructed. The first, shown in Figure VII-1, and again, disassembled, in Figure VII-2, was constructed of stainless steel and was of a size to accommodate the absolute density cylinder and its counterweight. A larger weighing bottle, shown in Figures VII-3 and VII-4, was constructed from stainless steel Carpenter 20CB3 for use in the calibration of weights in the form of cylinders and of mass up to 1 kg. (Chapter X).

B. Design of the Weighing Bottles

The weighing bottles were tubes of stainless steel or Carpenter 20CB3 closed at one end. The open end carried a flange grooved to accommodate an O-ring which extended slightly above the groove. A flat cover of stainless steel, carrying a stainless steel vacuum valve, rested on the O-ring;

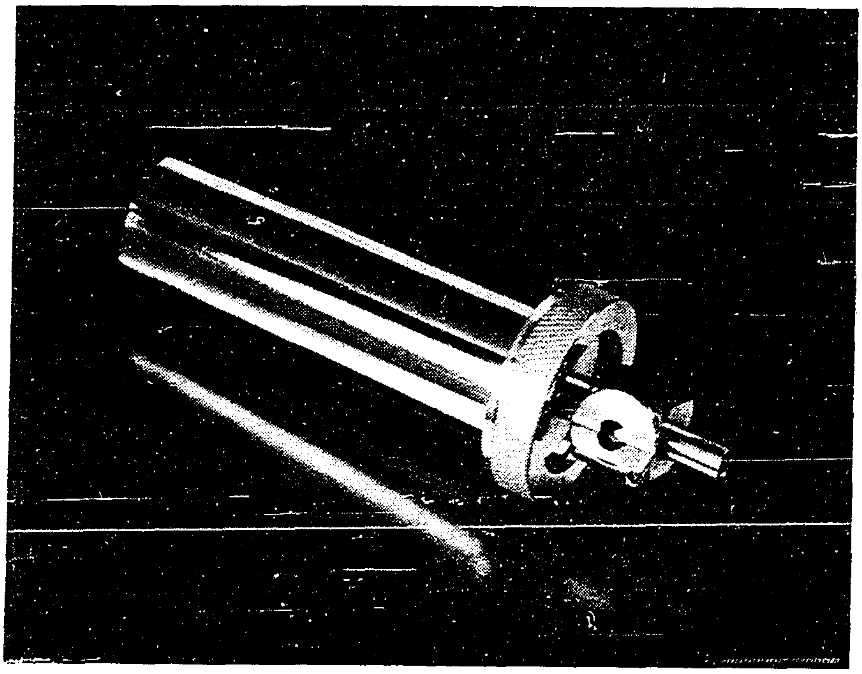


Figure VII-1. Smaller weighing bottle evacuated and with retaining rings in place

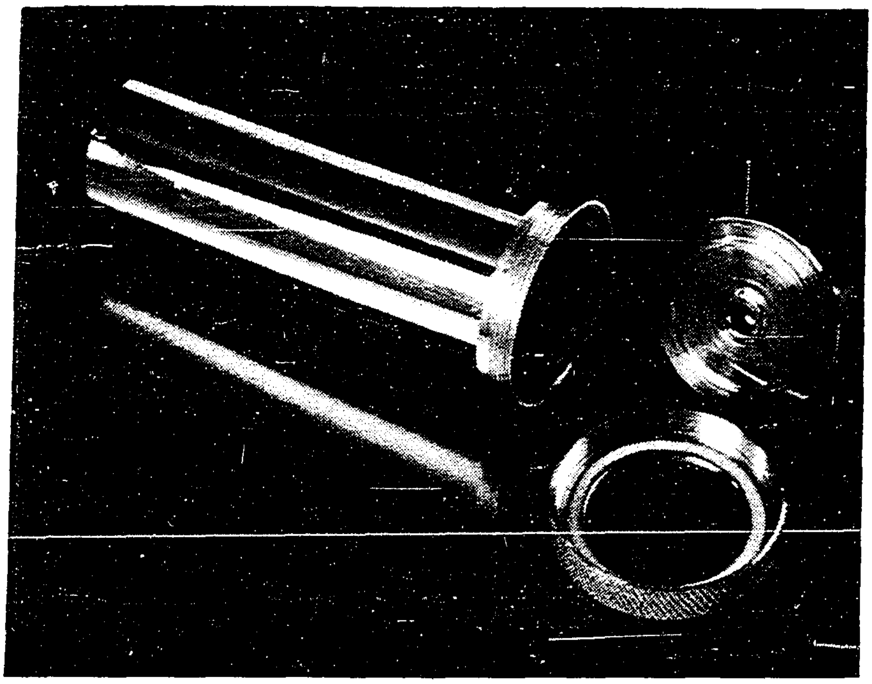


Figure VII-2. Smaller weighing bottle disassembled. The lower retaining ring is still in place

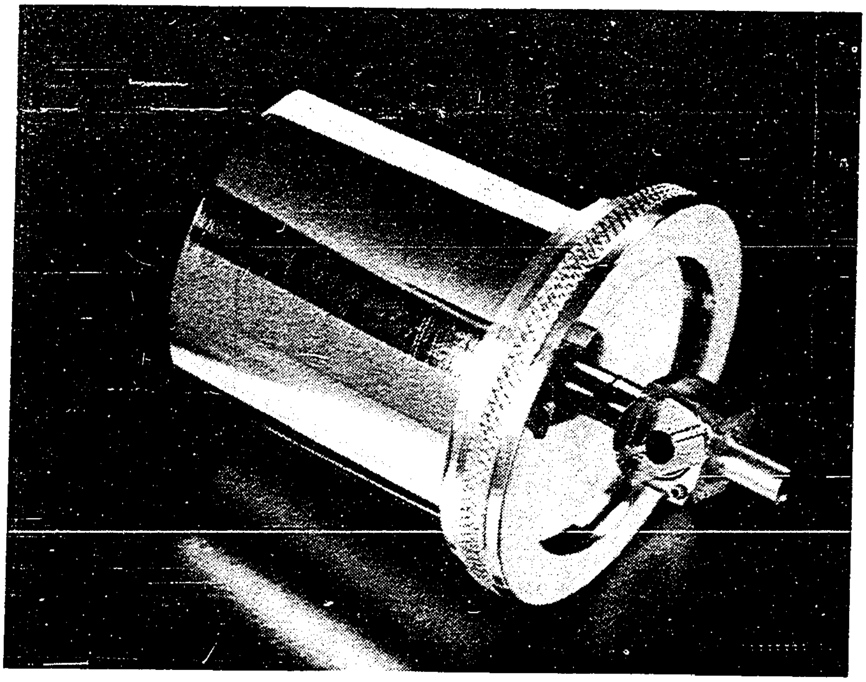


Figure VII-3. Larger weighing bottle with retaining rings in place

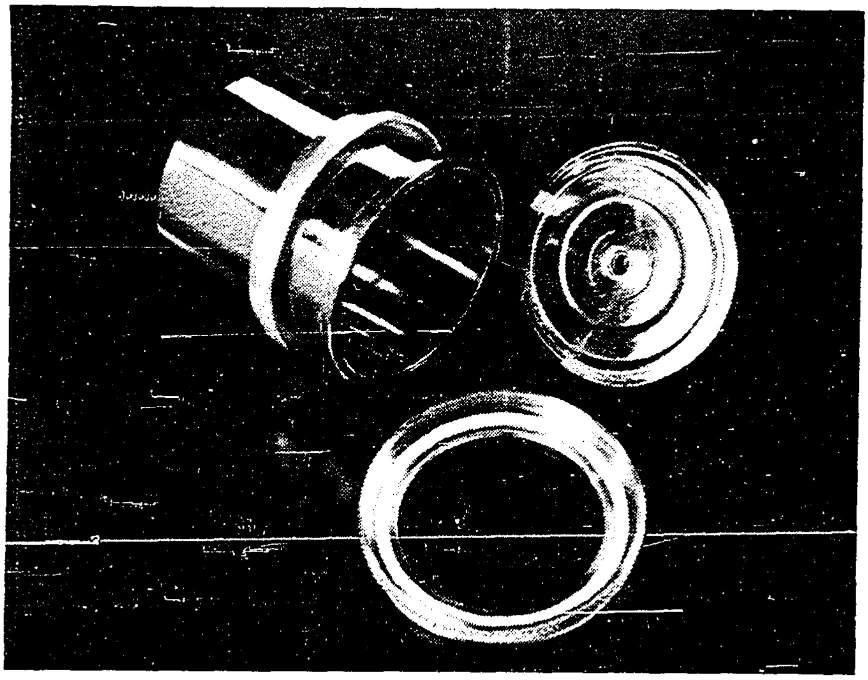


Figure VII-4. Larger weighing bottle disassembled. The lower retaining ring has been pushed down the bottle to reveal the flange carrying the O-ring a circular land on the inside of the cover kept the cover centered on the flange. To the vacuum valve was welded a stainless steel tube (6.4 mm. outside diameter) which served to connect the weighing bottle to the vacuum line, the connection being secured by a Cenco quick-connecting fitting carrying another O-ring. The vacuum valve was a commercial valve (Circle Seal Plug Shutoff Valve, Circle Seal Products Co., Inc., Anaheim, California) from which a good deal of unnecessary metal was removed to reduce the mass. The vacuum valve was manipulated with a small strip of aluminum which fitted snuggly into a slot in the end of the plug of the valve.

The principal dimensions of the smaller weighing bottle were: length, bottom of flange, 87 mm.; inside diameter, 27 mm.; outside diameter, 28 mm.; outside diameter of flange and lid, 34 mm.; overall length, 119 mm.

The principal dimensions of the larger weighing bottle were: length, bottom to flange, 64 mm.; inside diameter, 57 mm.; outside diameter, 59 mm.; outside diameter of flange and lid, 63 mm.; overall length, 99 mm.

It was found during early applications that the seal between the lid and the flange could be momentarily weakened during the act of removing the weighing bottle from the vacuum line after evacuation of the bottle. This problem was circumvented by fitting both weighing bottles with retaining rings made of aluminum, shown in Figures VII-2 and VII-4. A lower ring, lined with Teflon on the inside and threaded on the outside, was brought in from the bottom of the bottle and seated around and level with the flange carrying the O-ring. A second ring, threaded on the inside and carrying a Teflon gasket which insulated the upper ring from the top of the lid, was placed over the lid and lightly tightened onto the lower ring. The upper ring carried a knurled strip which stretched around the periphery of the upper ring. The two weighing bottles weighed 86.58 g. and 209.86 g., respectively, when empty and with their respective retaining rings in place.

C. Measurement of the Mass (in an Actual Vacuum) of Cylinder Number 1 and of Its Counterweight

A sequence of weighings was made using the smaller weighing bottle to establish the difference in the mass in vacuum of absolute cylinder Number 1 and its tubular counterweight; this difference is the term α in equation (VI-2). The weighing bottle was pumped down several times to a pressure of one micron on the day preceding the study and stored overnight while evacuated. The sequence of weighings was begun by inserting the cylinder into the weighing bottle and pumping the weighing bottle down to a pressure of 1 µm. (one micron). The valve was then closed and the bottle disconnected from the vacuum line. After ten minutes the bottle was weighed on the Mettler, Model H51AR, Semimicrobalance using the weights inside the balance. A "sensitivity" weight, made of Carpenter 20CB3 and weighing 20.000,2 mg. in air (20.003,0 mg. in vacuum), was added and the weighing repeated; this step served as a check on the functioning of the balance and to calibrate the optical scale. The bottle was then opened and the operation repeated with the tubular counterweight (that is, the counterweight having essentially the same mass and surface area). This sequence of weighings of the two objects was repeated five times. Each of the successive weighings required about twenty minutes.

The results obtained from this sequence of weighings are given in Table VII-1. The term α, the difference between the mass in vacuum of cylinder Number 1 and its counterweight, was calculated for weighings numbers two to nine by averaging the results of the weighing immediately preceding and following the weighing under consideration and then subtracting, in the proper order, the averaged weight of the weighing bottle plus one of the objects and the weight of the weighing bottle plus the other object as obtained by the weighing under consideration. By using this method of calculation, a drift experienced in the weight of

Table VII-1. Successive weighings of weighing bottle containing cylinder Number 1 and alternately counterweight Number 1

Weighing Number[a]	Barometric Pressure, mm. Hg	Bottle plus Cylinder, g.	Bottle plus Counterweight, g.	α g.[b]
1	735.82	103.533,50		
2	735.82		103.500,31	0.033,19
3	735.84	103.533,50		0.033,19
4	735.88		103.500,31	0.033,18
5	735.86	103.533,48		0.033,18
6	735.88		103.500,29	0.033,18
7	735.78	103.533,45		0.033,20
8	736.41		103.500,21	0.033,20
9	736.54	103.533,36		0.033,17
10	736.78		103.500,17	
			mean	0.033,19
			standard deviation	0.000,01

---

[a] Weighing made in sequence at interval of 20 minutes.

[b] Difference between mass in vacuum of cylinder Number 1 and its tubular counterweight; see equation (VI-2).

the loaded weighing bottle, resulting from a variable drift in the density of air, was taken into account. The difference between the mass in vacuum of cylinder Number 1 and its tubular counterweight was found to be 0.033,19 g., the standard deviation in the result being 10 µg.

VIII. DETERMINATION OF THE DENSITY OF AIR USING CYLINDER NUMBER 1

A. Equation Used to Calculate Results

In this chapter, I report the results of a series of measurements of the density of air made with absolute density cylinder Number 1. The physical characteristics and the fabrication of the cylinder and its counterweight are described in Chapter VI. The determination of the respective volumes of these two objects is also described in Chapter VI. The determination of the difference between the mass in vacuum of the cylinder and its counterweight is described in Chapter VII as is the construction of the vacuum weighing bottle which was used in measuring this quantity.

An equation was derived for calculating the density of air from weighings of absolute density cylinder Number 1 and its tubular counterweight by substituting the pertinent values into equation (VI-2). The value for the difference between the mass in vacuum of cylinder Number 1 and its counterweight, α, was found to be 0.033,19 g. as discussed in Chapter VII. The volumes of the cylinder and the counterweight, 31.778,2 cm.^{3} (22.50°) and 2.102,2 cm.^{3} (22.25°), respectively, were corrected to 28.0°, The average temperature within the constant temperature box. The equation for calculating the density of air from data collected using cylinder Number 1 and its counterweight was therefore

$$d_a = \frac{W_{cw,a} - W_{cy,a} + 0.033{,}19 \text{ g.}}{29.684{,}5 \text{ cm.}^3} \qquad \text{(VIII-1)}$$

As was the case with the stainless steel cylinders described in my M.S. thesis (38), the term $(1/d_W)(W_{cw,a} - W_{cy,a})$, which is analogous to a similar term in the denominator of equation (VI-2), was so small with respect to the difference in volume between the cylinder and counterweight that this term involving the density of the weights was neglected in equation (VIII-1); the difference between the mass of the counterweight and cylinder in air was typically about 900 μg. or less.

The uncertainty in the density of air as determined using cylinder Number 1 and its counterweight was set at 3 parts in 10^4, the relative uncertainty in the measurement of the difference between the mass in vacuum of the cylinder and the counterweight; the uncertainty in this term was the largest for the terms appearing in equation (VIII-1). The uncertainty in the difference in volume of the cylinder and counterweight was an order of magnitude smaller having been assessed at 2.7 parts in 10^5. The uncertainty associated with weighing the cylinder or counterweight in air with the microbalance was 1 μg. or 2.97 parts in 10^5.

B. Apparatus and Procedure

Several determinations of the density of air were made using cylinder Number 1 and its counterweight and applying equation (VIII-1). The results of these determinations were compared to values calculated from the prevailing conditions using equation (III-4). The cylinder and the counterweight were weighed on the Mettler, Model M5/SA, Microbalance in the constant temperature box. The commercially available pan of the microbalance was not large enough to accommodate conveniently the cylinder so the pan and hanger of the microbalance were replaced with a stainless steel hanger in the form of a wire cage which carried the cylinder or counterweight during a weighing. The sensitivity of the microbalance was determined using a "sensitivity" weight of Carpenter 20CB3 weighing 8.034 mg. in air. This sensitivity weight, in the form of a hook, was added to the hanger and another weighing was made. The sensitivity of the balance in µg. per scale division was found by dividing the mass of the sensitivity weight by the difference in the optical readout before and after addition of the weight.

The barometric pressure was determined using the barometer and cathetometer described in Chapter IV; the three corrections listed in Chapter IV were made to each reading. The temperature within the microbalance was recorded using platinum resistance thermometer Number 2 which was placed in the chamber housing the beam of the microbalance.

The relative humidity was measured for all the determinations using the Airguide, Model 113B, hygrometer. A determination of the atmospheric content of water and of carbon dioxide was made using the gas pipet for the two final determinations of the series. The density of air was calculated for the two final determinations using equation (IV-9) into which was substituted the molecular weight of air recalculated for the actual atmospheric content of carbon dioxide.

The density of air was determined by weighing first the cylinder and then the tubular counterweight on the microbalance. About seven minutes was allowed between weighings for the dissipation of heat. The two objects were weighed by substitution and the mass of the objects in air was determined from the optical readout of the microbalance. The difference in the mass of the two objects in air was calculated by multiplying the difference in the optical readouts by the sensitivity of the microbalance.

C. Results and Discussion

The results of the determination of the density of air using cylinder Number 1 and its counterweight and the results for the density of air calculated from the prevailing conditions are given in Table VIII-1. The values of the density of air calculated from the prevailing conditions were calculated for all dates listed using equation (III-4) in the interest of showing the trend in the results. More reliable values for the density of air calculated using equation (IV-9) are given for August 21 and 22, dates on which the water and carbon dioxide contents of the atmosphere were determined gravimetrically (absorption tubes and gas pipet). The values obtained on these dates for the atmospheric contents of carbon dioxide (expressed as mole fraction) and of water (expressed in mm. Hg) and the relative humidity calculated from the gravimetric determination of water content and measured with the Airguide hygrometer were

August 21

X_{CO_2} = 0.000,859
P_{H_2O} = 11.65 mm. Hg
Rel. Hum.,grav. = 42.42 per cent
Rel. Hum.,hygr. = 46.0 per cent

and

August 22

X_{CO_2} = 0.000,680
P_{H_2O} = 10.71 mm. Hg
Rel. Hum.,grav. = 39.00 per cent
Rel. Hum.,hygr. = 45.0 per cent

Table VIII-1. Density of air by measurement with absolute density cylinder Number 1 and tubular counterweight and calculated from the prevailing conditions

		Density of air, g./liter		Difference	
Date (time)		Found[a]	Calculated[b]	g./liter[c]	p.p.t.[c]
Aug. 6, 1979	(11:26 a.m.)	1.133,5	1.130,7	0.002,8	2.47
Aug. 7, 1979	(8:54 a.m.)	1.129,2	1.126,1	0.003,1	2.75
	(11:28 a.m.)	1.130,7	1.128,2	0.002,5	2.22
	(1:34 p.m.)	1.130,0	1.127,4	0.002,6	2.31
Aug. 8, 1979	(9:16 a.m.)	1.131,6	1.128,5	0.003,1	2.74
	(11:24 a.m.)	1.132,0	1.129,4	0.002,6	2.30
Aug. 14, 1979	(1:54 p.m.)	1.148,5	1.144,7	0.003,8	3.32
Aug. 21, 1979	(8:38 a.m.)	1.132,3	1.127,8 (1.128,5)[d]	0.004,5 (0.003,8)[d]	3.99 (3.37)[d]
Aug. 22, 1979	(8:33 a.m.)	1.129,2	1.124,2 (1.125,3)[d]	0.005,0 (0.003,9)[d]	4.45 (3.46)[d]
Jan. 18, 1980	(9:05 a.m.)	1.145,8	1.142,4	0.003,4	2.98

[a] From weighing absolute density cylinder Number 1 and tubular counterweight and applying equation (VIII-1).

[b] From barometric pressure, temperature, and relative humidity and application of equation (III-4).

[c] Value of "Found" minus "Calculated".

[d] From barometric pressure, temperature, and gravimetric determinations of the water and carbon dioxide content of the atmosphere and application of equation (IV-9).

The density of air determined with the cylinder and counterweight was higher than that calculated from the prevailing conditions for all nine determinations done over a two week period during August, 1979. The relative difference between the density of air determined using the cylinder and that calculated from the prevailing conditions increased linearly over this period. The increase in the relative difference between the "found" and calculated values for the density of air with time, in days, was analyzed by the least-squares method using a Texas Instruments, Model TI-55, calculator. To simplify the calculations, the date on which the difference in mass between the cylinder and counterweight in vacuum was determined, August 5, was designated as "day zero", August 6 as "day one" and so on. By handling the data in this manner, a straight line was plotted for the data having

slope = 0.122 p.p.t. per day
intercept = 2.202 p.p.t.
correlation = 0.966,2

Another determination of the density of air was made on January 18, 1980, after vapor degreasing both cylinder and counterweight with 1,1,1-trichloroethane; the density of air was found to be 1.145,8 g./liter. The density of air was also calculated from the prevailing conditions using equation (III-4) and the value 1.142,4 g./liter obtained.

The difference between these values for the density of air was 0.003,4 g./liter or 2.98 parts in 10^3. Apparently the upward trend in the relative difference between the "found" and calculated values for the density of air with time stopped sometime between late August and mid-January. The difference in mass between the cylinder and the counterweight in vacuum was also checked using the weighing bottle on January 18, 1980; the value obtained for the difference in mass for the two objects in vacuum was identical with that obtained on August 5, 1979.

As recorded in Table VIII-1, the density of air obtained by measurement of the cylinder is some 3.4 p.p.t. greater than that obtained by calculation from the prevailing conditions. As stated above, the uncertainty in the density as determined by the cylinder is placed at 0.3 p.p.t., an order of magnitude less than the difference found.

The drift in the difference found between the two densities may be connected with the measurement of humidity and/or the failure to measure the carbon dioxide in the atmosphere of the balance. On the two days that the accurate, gravimetric determination of the water and carbon dioxide were made the difference between the found and calculated values was essentially the same (0.0038 g./liter). The drift in the difference of the two densities is not correlated with the density, which actually went down, then up and again down during the eleven-day period.

The difference of 3.4 p.p.t. between the values for the density of air as obtained from the absolute density cylinder and from calculation from the prevailing conditions of barometric pressure and temperature and the gravimetric determinations of the water and carbon dioxide content is baffling. The method using the cylinder is simple in principle and the checks obtained on the volumes and masses of the cylinder and counterweight make the method appear correct and accurate. The values for the volumes were derived from four independent measurements (two of the dimensions, two by hydrostatic weighing (water as the standard in one, elemental silicon in the other)); the masses were measured in the actual vacuum of the vacuum weighing bottle. Surface effects were eliminated by simultaneous measurements of a counterweight of equal mass and area. The measurements of the prevailing conditions appear also to have been made accurately; the barometric pressure was measured with the specially constructed mercurial barometer and the Wild Heerbrugg cathetometer and all of the appropriate corrections were applied; the temperature was measured with a carefully calibrated platinum resistance thermometer; the gravimetric measurements of water and carbon dioxide were made on a very large sample taken from within the balance case and measured accurately; the absorbents for water and carbon dioxide were the best known and the handling and weighing of the absorption tubes followed all the carefully prescribed techniques evolved over the years in the field of microchemical analysis; the environment of the balances was monitored constant within 0.10°. All these considerations would seem to put the uncertainty in each well below 0.5 to at the most 0.7 p.p.t. The difference must lie, therefore, in the method of calculation from the prevailing conditions: nonconformity of moist air to the gas laws; an error in the gas constant; an error in the molecular weight assumed for air, in turn dependent on the constancy of the composition of the atmosphere, in particular of the oxygen content.

In a detail theoretical treatment of the density of air, Jones (59) evaluated the departure of a mixture of carbon dioxide-free air and water vapor from the ideal gas laws using the second and third virial coefficients of carbon dioxide-free air and of water, and compiled a table of "compressibility factors" as functions of temperature, pressure and relative humidity. This compressibility factor, applied as a correction term in the numerator of the final equation for calculating the density, has the value, for example, at 750 mm. Hg, 25.0° and 50 per cent relative humidity, of 0.99964. Nor are the values over the ranges 19° to 26°, 525 mm. Hg to 825 mm. Hg, and 0 to 100 per cent relative humidity, much different, being in all cases between 0.99955 and 0.99973. Thus, the departure from the gas laws is too small to explain the difference observed.

It is unlikely that the source of the difference found in the two values for the density of air is derived from an error in the gas constant. Although the currently accepted value for the gas constant is based on experimental work dating from the period 1924 to 1952, in the most recent critical review of the value, that by Cohen and Taylor (Ref. 28, p. 700, and Table 33.1, p. 719), the value accepted and the uncertainty are

$$R = 82.0568\ (\text{cm.}^3)(\text{atm.})/(\text{mole})(°\text{K}) \qquad (31\ \text{p.p.m.})$$

An excellent historical and critical review of the subject of the gram molecular volume and the gas constant is that of Batuecas (Ref. 1, p. 139). As Quinn (Ref. 87, p. 529) has pointed out, however, the current value is based on only one method, a measurement of the gas density of oxygen, by Baxter and Starkweather (4,5) as refined by Moles (72), Moles, Toral and Escribano (73), and by Batuecas and Garcia Malde (2) and Casado and Batuecas (25). Quinn et al. proposed and carried through (87,88,89) a determination of of the gas constant by a measurement of the velocity of sound in argon; this value was subjected (92) to a correction bringing the value down to the current density of oxygen-value and within the uncertainty in the latter. Thus, it appears necessary to look elsewhere for a source of the difference in the two values for the density of air found by the two methods.

The molecular weight of air used in calculating the density of air from the prevailing conditions is calculated from the volume per cent of the molecular weights of the gases present; the assumption is made that the composition, except for the moisture content, is constant. Jones (59), for example, uses for the volume per cent of oxygen 20.946 and places the uncertainty (possible variation) at 0.001 per cent oxygen. Even refusing to accept the almost universally held concept that the oxygen content of the atmosphere is a constant (to 0.001 per cent oxygen, in most opinions), the variation in the oxygen content necessary to explain the 3.4 p.p.t. difference reported above must be almost 2 per cent oxygen, far greater than might be found. This comes about because the molecular weights of oxygen (31.9988 g./mole) and nitrogen (28.0134 g./mole) are not very different and a large change in the composition of a mixture of the two is necessary to effect a small change in the molecular weight (density) of the mixture.

At the time of this writing (January 1980), I must attribute the difference between the density of air found using the cylinder and that calculated from the prevailing conditions to a deviation in the local composition of the atmosphere from the "standard" composition given in the literature. Furthermore, there appears to be a variability in the local composition of the atmosphere with time. Inasmuch as the gravimetric determinations of water and carbon dioxide eliminate these components of the atmosphere from responsibility for the observed difference of some 3 p.p.t. in the density of air and assuming the value for the gas constant to be correct, the obvious variable is the oxygen content even though a large increase in the oxygen content would be necessary to explain the results above. A survey of the literature concerning the determination of atmospheric oxygen is given in Chapter IX as well as a proposal for an improved method of determining oxygen.

Having just asserted, as did Pontius, that the density of air cannot be calculated from the prevailing conditions with sufficient accuracy to enable the correction for buoyancy to be made with accuracy, it is incumbent to offer a practical solution to the worker wishing to obtain an accurate value for the density of air. The answer is simple: Make a weighing of a hollow cylinder such as the one just described. If the cylinder is properly calibrated, the correct density of air will be obtained and troublesome measurements (measurements usually not made with sufficient accuracy anyways) of barometric pressure, temperature, and relative humidity are avoided and any questions about the local composition of the atmosphere are circumvented.

IX. SURVEY OF THE LITERATURE ON THE CONTENT AND THE DETERMINATION OF OXYGEN IN THE ATMOSPHERE

A. Survey of the Literature

The finding, reported in the preceding chapter, of a large difference, some 3.4 parts per thousand, between the values for the density of air found by the hollow, stainless steel cylinder and calculated from the prevailing conditions of barometric pressure and temperature and the content of water and carbon dioxide as determined gravimetrically, prompted an extensive review of every phase of the work. One possible source of the trouble is that an error exists in the value for the oxygen content of the atmosphere used in calculating the density from the ambient conditions, or perhaps that the oxygen content is not fixed but variable on a daily or seasonal basis. In the present chapter, I present a survey of the literature dealing with the oxygen content of the atmosphere and the methods of determining this quantity. At the end of the chapter, I propose a new method for a high-precision, gravimetric determination of the oxygen in the atmosphere.

On pursuing the literature in this field, the reader quickly encounters an almost universally held belief that the percentage of oxygen in the gases composing the atmosphere is a fixed quantity, as fixed and unvarying as the international meter bar or the speed of light. And, this belief is backed up by apparently incontrovertible experimental evidence. The critical reader, however, arrives at the conclusion that a good deal more faith has been placed in the accuracy of the findings reported over the years than is justified by the inherent accuracy of the analytical methods used.

Currently, the accepted value for the oxygen content of the atmosphere is 20.946 per cent by volume, and this number has been built into a large volume of theoretical and practical work in the physics of the atmosphere, meteorology, and the chemical engineering of the handling of air and of air conditioning (44,47,53,59,74). The value is needed for calculating the molecular weight of air, in turn needed in applying the gas laws to air. The 20.946 value has been used since 1951 when Glueckauf (39) recommended it following a survey of the literature. In an earlier survey of essentially the same literature and data, Paneth (83) had recommended 20.95 per cent oxygen, a value he advanced with the admonition "to remember that the second decimal is not certain", a realistic assessment of the likely uncertainty for which he was later severely criticized. Apparently because results were reported to 0.001 per cent, others found it comforting to believe the figures were reliable to this extent and went blithely about building up on them a considerable theoretical structure.

Even the Paneth value is a considerable advance over the values, "one-fifth", of Boyle and of Mayow of the 1665 to 1680 period, obtained by burning a candle to exhaustion or leaving a mouse until collapse in air in a closed container (for an account of these experiments see Partington (Ref. 84, pp. 75, 80)). The Boyle work has a curiously modern ring for he made extensive experiments with phosphorus, using it to deprive air completely of what is now referred to as oxygen, a procedure used in the very latest work (56) on the oxygen content of the atmosphere. Priestley, a hundred years after Boyle and Mayow, did a good deal better, adapting Mayow's reaction of oxygen with nitric oxide to form red, water-soluble nitrogen dioxide to a reasonably quantitative method. A history of the Priestley nitric oxide eudiometer is found in Conant (29) and Benedict (6).

Skipping over work of the early nineteenth century on the development of procedures for handling and analyzing gases, I pass to the work of Regnault (90) and Regnault and Reiset (91). Regnault organized and carried through an extensive, international study of the composition of the atmosphere. Samples were collected, with the cooperation of foreign scientists and "travelers", at Paris and other parts of France, at Berlin, at Madrid, in Switzerland, on the Mediterranean Sea, on the Atlantic Ocean, in Ecuador, in Algeria, on the Indian Ocean, on the Arctic Ocean, and on the Pacific Ocean. The samples were analyzed in Paris by explosion with hydrogen using an apparatus designed by Regnault and Reiset for studying the respiration of animals. As a result of his study, Regnault concluded that variations in the composition of the atmosphere were very small, the oxygen content generally varying only from 20.9 to 21.0 per cent. In certain cases, usually in warm countries, Regnault found that the oxygen content was as low as 20.3 per cent. Regnault also concluded that the oxygen content at Paris in 1848 was 20.96 per cent, the error in the method used being assessed at 0.02 per cent oxygen.

The Regnault work is truly astonishing. Although done in the period 1847 to 1952, it is the best work on the oxygen content of the atmosphere to date. Regnault and Reiset knew about, studied, and rejected various liquid absorbents and phosphorus as absorbents for oxygen, identifying the errors of incomplete absorption, solubility loss into reagents, introduction into the gas of components of the reagents, and the difficulties of readjusting the vapor pressure of water in the gas and of restoring the temperature of the gas for the final measurement. In one brilliant stroke, they eliminated all these problems by perfecting the hydrogen eudiometer and measuring manometrically the contraction which occurs when hydrogen and oxygen interact (touched off in the eudiometer by an electric spark). Every aspect of the procedure was developed in meticulous detail, and this included illustrated, detailed instructions to travelers gathering the samples. Six analyses made with the hydrogen eudiometer on the same air gave values falling between 20.932 and 29.960, average 29.943 per cent oxygen, standard deviation 0.009,8 per cent oxygen. Not only was the analytical work superb but the application was a great example of international cooperation (actually done in part during a time of war).

The most outstanding work of this century on the composition of the atmosphere is that of Benedict (6). His study was volumetric in method and based on the absorption of oxygen in alkaline pyrogallate after previously absorbing carbon dioxide in a solution of potassium hydroxide. The measuring pipet in which the decrease in volume of the sample was measured was designed to read directly in per cent oxygen; the smallest graduation on this pipet was 0.01 per cent oxygen but the pipet was readable, according to Benedict, to 0.001 per cent. The standard deviation in the results obtained by Benedict on any day for the analysis of a cylinder of air (20.877 per cent oxygen) was 0.004 per cent oxygen. Benedict concluded, after analyzing 212 samples of air collected outside his laboratory in Boston, that there was no material fluctuation in the oxygen content during the period of the study, April 15, 1911 to January 30, 1912, despite a great variety of weather conditions. Benedict found the oxygen content during this period averaged 20.952 per cent. Benedict also analyzed samples collected on the ocean between Montreal and Liverpool, on the ocean between Genoa and Boston, and on the summit of Pike's Peak; the average results obtained for these samples were, respectively, 20.950 per cent, 20.946 per cent, and 20.941 per cent. Machta and Hughes (70) raised some doubts concerning the flasks that Benedict used to collect and transport his samples.

Carpenter (24), using essentially identical procedure and apparatus of Benedict, analyzed 75 samples collected at Durham, New Hampshire, 790 samples collected at Baltimore, and 291 samples collected at Boston. The grant average of the results of all 1156 analyses was 20.929 per cent, the standard deviation being about 0.003 per cent.

Using a completely different method, Stock, Ramser, and Eyber (95) made measurements of the oxygen content of the atmosphere, and simultaneously also of the density of the atmosphere and of the barometric pressure, in all some 18 sets of measurements, during 1931 and 1932. They were unable to find any correlation among these three quantities although there was considerable variation in each. The oxygen was measured in a closed vessel by absorption on copper at 500° and measurement of the reduction in pressure. Three analyses on a test sample of air gave 20.82, 20.78, and 20.77 per cent oxygen, and four analyses on the same air to which about 0.15 per cent oxygen had been added gave 20.98, 20.98, 20.98, and 20.95 per cent oxygen; this is really excellent precision and indicative that the procedure was working very well. The 18 values found for the oxygen content of the atmosphere ranged from 20.77 to 20.87 per cent oxygen. The average of these results is significantly lower, by some 0.15 per cent oxygen, than the earlier values. Although Stock, Ramser, and Eyber knew about the work of Regnault and of Benedict, they made no attempt to resolve the difference or actually to comment on it, and, unfortunately, did not perform a check by analysis of a synthetic mixture of pure gases or a comparison with some other method.

Lockhart and Court (62) made a study of the oxygen content of the atmosphere during 1940 and 1941 at Little America III on the Ross Ice Shelf of Antarctica. The oxygen content was determined volumetrically by absorption of oxygen in alkaline pyrogallate after previously determining carbon dioxide by absorption with potassium hydroxide. Lockhart and

Court found a deficiency in the oxygen content of the Antarctic atmosphere and furthermore found a seasonal variation in the oxygen content: 20.50 per cent oxygen by volume in the summer (December and January) and 20.80 per cent in the winter (July and August); the uncertainty in the oxygen content was assessed as 0.04 per cent oxygen. Lockhart and Court pointed out that no determination was made of "standard" air from the middle latitudes during their work because the program to analyze Antarctic air was not planned until the expedition was in the Antarctic. Glueckauf (39) and Machta and Hughes (70) discount the findings of Lockhart and Court for just this reason despite claims that the apparatus, method, and chemicals used at Antarctica had been used at Harvard University for years with reliable results.

According to Machta and Hughes (70), in 1935 M. Shepherd of the National Bureau of Standards made six analyses of a single large sample of air collected west of Washington, D.C.; Machta and Hughes cite Shepherd's *U.S. Army Stratosphere Flight of 1935 in the Balloon Explorer II* as their source. Shepherd obtained results ranging from 20.935 to 20.950 per cent oxygen by volume, the average being 20.946 per cent. Presumably, the determinations were made by absorption of oxygen by alkaline pyrogallate.

Machta and Hughes (70) determined the oxygen content of 78 samples of air collected by two oceanographic vessels over the continental shelf and the open ocean and ten samples of air collected over land in western Maryland. The oxygen content of these samples was determined using a "modified" Beckman oxygen analyzer calibrated by comparison with a standard air. They reported the oxygen content of air collected over the ocean to be: "...20.946 per cent by volume relative to a standard with an accuracy of ±0.006 per cent by volume. The precision or geographic variability, or both, is ±0.005." The oxygen content of the ten samples collected over land was found to be 20.946 per cent with an uncertainty of 0.0018 per cent. Although the results of Machta and Hughes appear highly precise, the results must be viewed with a little skepticism. The Beckman (Pauling) oxygen analyzer operates by measuring the paramagnetism of the oxygen molecule. Precision better then 0.1 per cent had never been claimed for it previously and the nature of the modifications made by Machta and Hughes have never been described. The instrument was calibrated with a standard air, 20.959 per cent oxygen, prepared and analyzed by a gravimetric, dry-reagent method developed by Hughes (56).

In the Hughes (56) gravimetric procedure, a 200-cm.^{3} flask containing white phosphorus is evacuated, closed (by stopcock) and weighed. The sample of water-free air is then admitted, and after the reaction of oxygen and phosphorus has taken place, the flask is again evacuated and again weighed (actually against an identical flask used as counterpoise). Because of the significant vapor pressure of phosphorus (0.07 mm. Hg at room temperature), to avoid loss of phosphorus, it is necessary to cool the flask in liquid nitrogen during the pumping operations. In a modification of the procedure, the phosphorus is replaced by a sodium-potassium alloy; it is necessary then to either correct for the carbon dioxide present or to remove it by passage over Ascarite. The standard deviation in results on the compressed air from a cylinder by the phosphorus method was 0.064 per cent oxygen, by the sodium-potassium alloy procedure 0.038 per cent oxygen. Hughes placed the over-all uncertainty of the method at 0.1 per cent oxygen. Inasmuch as the Hughes and Machta results on the air taken from over the ocean and obtained with the Beckman oxygen analyzer are referred to compressed air analyzed by the Hughes procedure, it seems rather unreasonable if not ridiculous, to report the results of the analyses to 0.000,1 per cent oxygen and indeed to put the uncertainty in the results much below 0.05 per cent.

Paneth (83), in his 1937 review of work on the composition of the atmosphere, was probably correct in recommending 20.95 per cent as the oxygen content of the atmosphere and in placing the uncertainty in the second decimal point. He was roundly criticized for this in a later review by Glueckauf (39) in 1953, who placed greater reliance on the results of the statistical treatment of a very large number of analyses than on a Paneth-style, dispassionate examination of the errors inherent to the method. Glueckhauf apparently did not know of the work of Stock, Ramser and Eyber and in quite arbitrary fashion he rejected all of the Regnault findings on samples from the Mediterranean and Indian Ocean, apparently because they were low. Similarly, he rejected the results of Lockhart and Court from the Antarctic on the sole basis that they had not been checked. The Glueckauf review antedates the Machta and Hughes work but as I have implied in paragraphs above, I have severe reservations about the numerous Machta and Hughes results with the Beckman oxygen analyzer. And I assess the accuracy and the precision of the Hughes gravimetric-phosphorus and sodium-potassium alloy results at about the same level as those of Regnault and Benedict.

Statistically, perhaps, for the air of the middle latitudes, which appears to be continually very well mixed by the winds of the frequent cyclonic storms, the oxygen content is possibly the 20.946 per cent value. As an analytical method, simple in concept and inherently free from the numerous errors which afflict the liquid absorbent methods, the Regnault method is clearly superior. It is fortunate that the Regnault and Benedict methods yield the same value for the oxygen content of air, and while withholding still some reservation that Stock, Ramser and Eyber may be right, I would place the oxygen content of the atmosphere at the Paneth value of 20.95 per cent with the uncertainty possibly as low as 0.02 per cent. As for the natural variation, I see no reason for rejecting either the low values of Regnault from the warm, tropical regions or the very low values of Lockhart and Court from the Antarctic and I feel that the Stock, Ramser and Eyber variation of 0.1 per cent oxygen may well have been real.

Because the carbon dioxide content of the atmosphere (0.029 per cent in 1890; 0.034 per cent currently) has received a great deal of attention in recent years, prompted principally by the potentially serious "greenhouse effect" on the climate, it might be wondered that similar attention has not been given the oxygen content. The answer lies in the nature of the problem and the difficulty of effecting the analysis with the requisite degree of accuracy. For the determination of carbon dioxide, the entire amount present in the sample of the atmosphere is measured and procedures are at hand for measuring this amount with an uncertainty of less than 1 p.p.t. The measurement of oxygen called for, in studies of the natural variation in the oxygen content and the consequence on it of the combustion of coal and petroleum hydrocarbons and of the photosynthesis and the respiration of the biomass, is a change equivalent to the change in the carbon dioxide, that is, for a change in the carbon dioxide of 1 p.p.t., (0.001)(0.034) = 0.000,034 per cent carbon dioxide, the equivalent change is 0.000,034 per cent oxygen. For an atmosphere 21 per cent oxygen, this means a change of one part per million. Currently, our methods for oxygen do not approach this by even two orders of magnitude and on the basis of absolute accuracy by probably three orders of magnitude. A possible start in the right direction, a by-product of the present work, a method for the high-precision determination of large amounts of oxygen, is offered in the following section.

B. Proposal of a Method for the High-Precision Determination of the Oxygen Content of the Atmosphere

Variability in the oxygen content of the atmosphere, occurring in nature as discussed in the preceding paragraphs and postulated in Chapter VIII as an explanation for the high value for the density of air obtained by measurement with the absolute density cylinder, can really only be confirmed or refuted by experiment, an experiment which calls for a method of chemical analysis of a degree of accuracy not currently known. As a result of the present work, however, there is now available for such a chemical analysis, a suitable sample of the atmosphere, three liters in size, very accurately measured, dry and free of carbon dioxide, and ready for delivery; this is the gas left over from the gravimetric determinations of water and carbon dioxide described earlier. The problem is to effect the determination in such a way as to avoid the numerous pitfalls of the usual methods of gas analysis.

Certainly, if the uncertainty in the determination of the oxygen content of the atmosphere is to be less than 0.001 per cent oxygen, aqueous retaining liquids and liquid absorbents must be proscribed. Solubility losses, despite the various tricks and cares which have been exercised to circumvent or correct them, are simply too uncertain to be risked. The vapor pressure problem, both the adjustment and the correction, is never solved with any degree of assurance and must be avoided. And the inherent troubles which plague the various liquid absorbents for oxygen, the release of carbon monoxide from alkaline pyrogallol, for example, lend an intolerable uncertainty to any absorption process involving liquids. Very clearly, then, the method must be gravimetric in nature, be perferably a one-pass-through operation, and involve only dry chemistry. A possible method is proposed in the next paragraph.

The dry and carbon dioxide-free sample in the 3-liter, precision gas pipet is passed over metallic copper at 375°, the oxygen being absorbed by the reaction

$$O_2 + Cu^o = CuO\ (+\ Cu_2O).$$

The exit gas is discarded. The gas in the manifold between the pipet and the hot copper tube is swept on through the hot copper by a stream of oxygen-free nitrogen. Hydrogen gas is then passed through the hot copper tube converting the copper oxides to copper and the oxygen to water

$$CuO + H_2 = Cu^o + H_2O.$$

The water is collected on anhydrous magnesium perchlorate. The hydrogen is swept from the copper tube and the absorption tube by a stream of nitrogen. Finally, the absorption tube containing the anhydrous magnesium perchlorate (filled with nitrogen before and after the absorption of the water) is weighed.

A survey of the literature has uncovered no evidence that such a procedure has ever been used for the determination of oxygen. But, the component reactions have been studied and used in various other connections and the procedure is almost certain to work.

X. THE DISSEMINATION OF MASS. THE CONSTRUCTION OF A SET OF STAINLESS STEEL WEIGHTS

A. General Considerations

The standard of mass is the *International Kilogram* kept at the International Bureau of Weights and Measures (BIPM), Sevres, France. It is one of some forty kilograms fabricated about 1885 of an alloy approximately 90 per cent platinum and 10 per cent iridium. The particular kilogram mass selected for the International Kilogram was that closest in mass to an earlier standard kilogram, the *Kilogram of the Archives*. Five other of the forty kilograms are also preserved at BIPM and are used as secondary, working standards. The other of the forty platinum-iridium kilograms have been distributed to the national laboratories of various countries. The two at the National Bureau of Standards, Gaithersburg, Maryland, constituting the mass standards for the United States, are Numbers 20 and 4. Such history and other facts of a general nature about the standards of mass will be found in: (a) the chapter on mass in *The International Bureau of Weights and Measures*, edited by C. H. Page and P. Vigoureux (75), specifically pages 43 to 63; and (b) *Mass and Mass Values* by P. E. Pontius (85).

The measurement of mass, perhaps more than any other measurement and perhaps because of the apparent ease and simplicity of the measurement, is one that seems inherently to invoke implicit trust. This is, of course, a matter of the level of accuracy at which a given consideration is pitched but, even among scientific workers, implicit trust is usually accorded work on mass in the national standards laboratories. Thus, it came as an unpleasant surprise to Professor Diehl that the values of two of the weights he and his co-workers used in their faraday work were significantly in error. These weights, which had been used by Knoeck and Diehl (64,65) in early work at Iowa State University (ISU) on high-precision coulometry and by Koch, Hoyle and Diehl (68) in determining a value for the faraday, had been calibrated by the Mass Section of the National Bureau of Standards (NBS) in 1966 and at that time Professor Diehl had been given assurance by the members of the Mass Section responsible for the work that the best possible job would be done in calibrating the weights. The errors were uncovered in January 1975 by Mr. V. E. Bower, at that time working in the Electricity Division of NBS on the value of the faraday; Mr. Bower knew exactly how the error had been made in the Mass Section, having had an identical experience with a set of weights he was using. Fortunately, the recalibration of the ISU weights came in time to permit a recalculation of the results, a recalculation which actually was made during the publication (55,67,68) process.

Determining mass with an error less than 5 p.p.m. at the present time is difficult and perhaps not possible. For an even less generous assessment of the uncertainty, see Diehl (33) who puts the figure at 10 p.p.m. The difficulties begin at the very top, and indeed were recognized there, see Page and Vigoureux (Ref. 75, p. 44); see also Swindells (96) for a history of the casting of the platinum-iridium alloys used for the prototype kilograms and meter bars. A lower density was obtained than expected for the alloy owing to contamination by iron and ruthenium and cracking of the metal was experienced. The density of the International Kilogram is not accurately known (Ref. 75, p. 44) and, although this may be immaterial when comparing the International Kilogram with the secondary platinum-iridium kilograms at BIPM and with the various national kilograms cast at the same time, it is a very serious matter in establishing the weights of the national working standards, which are usually of stainless steel. In the United States, the standards are the platinum-iridium Kilogram 20 and Kilogram 4 and the working standards are the nichrome Kilograms N1 and N2. No comparison of the U. S. standards with the International Kilogram has been made for over thirty-five years. Moreover, when the comparison is made, the first operation is a steam cleaning. In view of our present knowledge of platinum surfaces and the formation and decomposition of platinum oxide on platinum surfaces, derived from the extensive studies of the polarographers over the past three decades, such a treatment is disastrous indeed at the current level at which mass measurements are now desired.

The review of the standard of mass problem and the measurement problems of Page and Vigoureux includes a discussion of the problems of measuring the density of air (Ref. 75, p. 50). I feel that the absolute density, hollow, stainless steel cylinder described in preceding chapters of this dissertation now offers a solution to this problem; the simple weighing of this cylinder and the counterweight will give the density of air with sufficient accuracy to make the correction for buoyancy with an uncertainty less than 1 p.p.m. and the difficult measurements of the prevailing temperature, barometric pressure, and composition of the atmosphere are obviated.

One problem which Page and Vigoureux do not discuss is the question of the gases adsorbed on the surface of the weights and how such adsorption varies with changes in the prevailing conditions of temperature, barometric pressure, and water, carbon dioxide, and oxygen content of the atmosphere. Yoshimori and co-workers (103) have shown by direct chemical analysis that the moisture adsorbed on stainless steel is of the order of 1 µg. per cm.^{2};

presumably this varies with the relative humidity. In the course of extensive reading of the literature on weights and weighing, I have not found an estimate of the mass of carbon dioxide, oxygen, or nitrogen adsorbed on steel or other metal surfaces. Yet such adsorption would certainly depend on the prevailing conditions and the treatment given the surface. Moreover, in a set of weights, the ratio of surface to mass increases greatly on passing to the smaller weights. Thus, for cylindrical weights of density 8.0 g./cm.^{3} and whose height equals their diameter:

Mass	1 kg.	1 g.
Area	138.4 cm.^{2}	1.384 cm.^{2}
Area/mass	0.1384 cm.^{2}/g.	1.384 cm.^{2}/g.

Assuming the adsorption effect involves only water and using the Yoshimori finding, the effect on the kilogram weight is 138 µg. or 0.138 p.p.m. and on the 1-g. weight 1.38 µg. or 1.38 p.p.m. This is at the very level aimed for in the current work on the faraday and is serious and merits close scrutiny inasmuch as the adsorption may be greater than this, may be variable, and may well affect the reproducibility of the surface on cleaning.

The problem of cleaning weights was solved by Mr. R. Schoonover (94) of NBS working with the NBS working standards N1 and N2. Schoonover found that N1 and N2 during daily use gained in weight owing to the pick-up of dust and oil from the atmosphere of the laboratory but that the weights returned to initial mass (as determined by comparison with Kilogram 20 (only occasionally taken from under cover)) when given a vapor degreasing with 1,1,1-trichlorethane. Mr. Schoonover has probably wrought better than he knew. Professor David Peterson of ISU, when told of the Schoonover cleaning technique, stated he felt that a chemical union occurs between the 1,1,1-trichlorethane and the surface of the steel, probably with a chromium oxide in the surface. Stainless steel once vapor degreased is impossible to weld and the coating, he reported, is difficult to remove short of sandpapering. In confirmation of this, a very preliminary study of samples of stainless steel I submitted for ESCA analysis gave definite indication of significant changes in the character of the surface. Presumably, the union of the three chlorine atoms of the 1,1,1-trichlorethane with the chromium on the surface leaves the methyl groups pointing away from the surface and the surface polar in character. I found, too, that stainless steel, once vapor degreased, comes to constant weight in the vacuum weighing bottle readily.

Because of the surface problem, the reluctance of platinum to come to constant weight in the vacuum weighing bottle (presumably because of the slow release of gases dissolved in the metal), and the uncertainties in the transfer of mass from the International Kilogram to the daily working weights of stainless steel, it became worthwhile to attempt a new approach to the entire problem. A start on this has been made in the present dissertation, as reported in this and the following chapter.

The overall objective was to fabricate the weights of a stainless steel having the greatest possible resistance to corrosion, give the weights a high polish at the same time bringing the mass of each as close to the integral (nominal) value as reasonably possible, give the weights a surface treatment, calibrate the set internally performing the experimental work (weighings) in the vacuum weighing bottle, relate one of the 1000-g. weights to the International Kilogram, and then finally to recalculate the calibration data to this absolute mass scale.

A stainless steel, Carpenter 20CB3, was selected and fabrication of the set begun. For reasons given in the next chapter, the set of weights was arranged on the basis of the Fibonacci series rather than on the conventional pattern. The set thus consisted of the twenty-one weights:

Name	F_{-1}	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	F_{11}	F_{12}	F_{13}	F_{14}	F_{15}
Nominal mass	1	0	1	1	2	3	5	8	13	21	34	55	89	144	233	377	610

F_{16}	ISU-1	ISU-2	ISU-3	ISU-4
987	1000	1000	1000	1000

As this dissertation was being written, the fabrication of this set of weights was well under way; the undertaking to date (January 1980) is described in the following sections of this chapter and a theory for the calibration of a set of Fibonacci weights is given in the next chapter.

B. Selection of Stainless Steel Carpenter 20CB3 for Weights

Consultation with members of the Department of Materials Science and Engineering of Iowa State University and of the Metallurgy Section of the Ames Laboratory of the Department of Energy and with the chemical engineers of the Hach Chemical Company, Loveland, Colorado, narrowed the selection of the particular stainless steel to be used to two varieties: (1) a niobium-stabilized, chromium-nickel alloy designated 309SCB, and (2) Hastelloy C, an alloy of nickel (54 per cent), molybdenum (17 per cent), chromium (15 per cent), iron (9.5 per cent), and tungsten (4 per cent). Experience with both steels as pipes and containers for hydrogen chloride, hydrochloric acid, and other corrosive chemicals on a large scale and as crucibles for high temperature use showed these alloys to have extraordinary resistance to chemical attack.

The final selection was based on density, availability, and cost. The density of Hastelloy C is 9.84 g./cm.^{3}; it was available at $27.50 per kg. Stainless steel 309SCB proved to be no longer available commercially, but a slight modification of it, Carpenter 20CB3, was available at $8.50 per kg.; the density of this alloy is 8.11 g./cm.^{3}. Carpenter 20CB3 was selected, the final choice being determined principally because the density is close to those of the stainless steel weights currently in use and to the U. S. (National Bureau of Standards) working standards of mass, N1 and N2, weights which are made of chromel, density 8.3456 g./cm.^{3}.

The nominal composition of Carpenter 20CB3 was obtained from Professor R. Schmidt of the Department of Materials Science:

C max.	0.07 per cent
Mn max.	2.0 per cent
Si max.	1.0 per cent
S max.	0.035 per cent
Cr	19 - 21 per cent
Ni	30 - 39 per cent
Mo	2 - 3 per cent
Cu	3 - 4 per cent
Nb + Ta	8 times the carbon concentration (min.) or max. of 1 per cent Nb+Ta

The source of this specification was not stated, but the compositions of the various lots of the material subsequently obtained conformed to these specifications; see Table X-2.

The purpose of the niobium (the metallurgists continue to refer to this element as *columbium* (Cb)) in the alloy is to prevent the deposition of chromium carbide in grain boundaries. Such deposits of chromium carbide are presumably the sites at which corrosion and chemical attack begin. The niobium acts by precipitating carbon as niobium carbide, which is apparently innocuous, and lowers the concentration of carbon sufficiently to prevent the precipitation of chromium carbide and the depletion of chromium in the grain boundaries.

Rods of appropriate diameters of Carpenter 20CB3 were purchased from Carpenter Technology Corporation, Reading, Pennsylvania 19603:

Diameter in in.	Weight in pounds
0.5	8.60
1.0	5.95
1.5	10.65
2.0	8.15
2.5	24.2

and a later purchase

Diameter in in.	Weight in pounds
2.5	39.0

Total weight 96.55 pounds.

The density of each rod and the chemical composition of each is given below.

C. Density of Various Lots of Carpenter 20CB3

The rods of Carpenter 20CB3 were cleaned with methylisobutylketone to remove grease, markings and residual gum from shipping tape. A circular disc, approximately 0.150 in. thick, was cut from each of the rods 1.0, 1.5, 2.0 and 2.5 in. diameter. These discs were lightly buffed with emery paper. A hole, 0.25 in. in diameter, was drilled through each disc near the edge for attaching the suspending cord. The holes were made large to eliminate any possibility of entrapment of air when immersed in water. The edges of the hole were chamfered deeply to further prevent the entrapment of air. The cutting from the 0.5-in. rod was prepared by first removing 0.005 in. from the surface of the rod by lathe and then cutting off a 1-in. length; this piece was polished on the lathe with fine emery cloth until tool marks were barely discernible. The dimensions of this piece were: diameter 0.494 in., length 1.00 in. No hole was drilled in this piece and the hydrostatic weighing was made by placing it in a wire basket.

All three of the weighings required for the determination of density by this method were made on an Ainsworth

Model 28N, single-pan balance, sensitivity 0.1 mg. The determination of the density of the disc was made by measuring the weight of the disc in air, $W_{o,a}$, the weight of the disc and monofilament line, $W_{o+1,a}$, and the weight of the disc and line immersed in water, W_{o+1,H_2O}. The temperature of the water was measured with a mercury thermometer graduated to 0.1° and the density of water at the temperature observed was obtained from tables (Diehl, Ref. 34, p. 411). The volume and density of the disc were calculated using equations (X-1) and (X-2):

$$V_o = \frac{W_{o+1,a} - W_{o+1,w}}{d_{H_2O}} \qquad \text{(X-1)}$$

$$d_o = \frac{W_{o,a}}{V_o} \qquad \text{(X-2)}$$

No corrections for the buoyancy of air were made. The results are tabulated in Table X-1.

The density of the piece cut from the 0.5-in. rod was determined in a similar manner, a wire basket being used to carry the steel piece when immersed in water (see my M.S. thesis (38). The results were calculated by equations (X-1) and (X-2), the symbol 1 then representing the weight of basket and supporting line.

Table X-1. Density of rods of Carpenter 20CB3

Diameter of Rod in. (cm.)	Diameter of Disc in. (cm.)	Thickness of Disc in. (cm.)	Weight of Disc g.	Volume of Disc cm.^{3}	Density of Disc g./cm.^{3}	Average Density of Disc g./cm.^{3}
0.5 (1.27)	0.494 (1.25)	1.006	25.4070	3.1373	8.0983	
		(2.555)	25.4069	3.1373	8.0984	8.0894
1.0 (2.54)	1.0 (2.54)	0.1525	15.6165	1.9245	8.1146	
		(0.3874)	15.6165	1.9248	8.1134	8.1140
1.5 (3.81)	1.5 (3.81)	0.1500	34.5894	4.2663	8.1076	
		(0.381)	34.5895	4.2676	8.1052	8.1064
2.0 (5.08)	2.0 (5.08)	0.1525	63.1522	7.7847	8.1123	
		(0.387)	62.2922[a]	7.6779	8.1141	8.1132
2.5(1)[b](6.36)	2.5 (6.35)	0.128	81.9319	10.1037	8.1091	
		(0.325)	81.9316	10.1060	8.1072	8.1082
2.5(2)[c](6.35)	2.49 (6.33)	0.126	81.5859	10.0667	8.1046	
		(0.321)	81.5860	10.0670	8.1043	8.1045

[a] After hole was enlarged.

[b] First lot purchased.

[c] Second lot purchased.

Table X-2. Composition and properties of rods of stainless steel Carpenter 20CB3

Diameter, in.	0.5	1.0	1.5	2.0	2.5(1)[a]	2.5(2)[b]
Heat number	826452	826906	10790	19795	826672	837597
Composition						
C	0.025	0.021	0.016	0.019	0.04	0.019
Mn	.29	.32	.35	.35	.30	.31
Si	.36	.28	.45	.31	.39	.32
P	.020	.023	.019	.024	.023	.017
S	.001	.002	.002	.004	.001	.002
Cr	19.32	19.15	19.63	19.29	19.42	19.64
Ni	33.43	33.09	33.23	33.08	34.27	33.45
Mo	2.18	2.20	2.20	2.13	2.17	2.08
Cu	3.21	3.59	3.27	3.17	3.32	3.22
Nb+Ta	0.49	0.56	0.83	0.90	0.82	0.52

---

[a] First lot purchased.

[b] Second lot purchased.

Table X-2. (Continued)

Diameter, in.	0.5	1.0	1.5	2.0	2.5(1)	2.5(2)
Yield strength, (0.20 per cent), KSI	97.0	54.0	48.5	40.3	47.5	45.0
Tensile strength, KSI	---	94.5	93.5	89.0	86.0	87.5
Elongation in 2 in., per cent	---	41.3	42.0	42.0	41.0	42.0
Reduction of area, per cent	---	67.0	69.0	67.0	67.0	70.0
Hardness, Brinell	---	187.0	---	---	174.0	---
Intragranular corrosion test	P[c]	P	P	P	P	P

[c] Capable of passing test.

D. Fabrication of Weights

The major part of the machine work to be described in this chapter was performed in the machine shop of the Department of Chemistry, Iowa State University, by Mr. Eldon Ness, shop foreman, and Mr. George Steininger. Certain special operations, principally metal rolling and wire drawing were performed in the Metallurgy Section of the Ames Laboratory of the Department of Energy by Mr. Ardis Johnson under the direction of Professor David Peterson of the Department of Materials Science and Engineering. Advice and direct assistance on preliminary work on polishing metals and on the use of the vibrating polisher was obtained from Mr. Harlan Baker of the Ames Laboratory and Professor Peterson. Practically all of the metal polishing was done in Room 138 Chemistry Hall, using apparatus purchased or designed and built for the work of the present dissertation.

Weights F_{-1}, F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8 and F_9, that is, the weights 1 g. through 34 g. were made in the form of rectangular flat pieces of the Carpenter 20CB3. The weights F_{10} (55 g.) through F_{16} (987 g.) and the four 1-kilogram weights were fabricated in the shape of right cylinders. The choice of metal flats for the smaller weights was dictated by the cylindrical shape and the dimensions of the vacuum weighing bottle, it being necessary during the calibration operation to place up to fifteen of the weights in the vacuum weighing bottle at once.

The flat pieces of Carpenter 20CB3 from which the smaller, flat weights were cut were prepared in the following manner. The rod of Carpenter 20CB3 was mounted in a lathe and enough of the surface was removed by turning so that oxides and any imperfections lodged in the surface were eliminated. Discs of the rods were then cut off with a thin, cut-off grinding wheel and the flat surfaces then turned on a lathe. The discs, usually 0.2 to 0.24 in. thick, were then rolled to a desired thickness. The final plates were elliptical in shape because the repeated rolling was done in the same direction. The thinnest piece obtained was a strip some 30 in. long, 2.28 in. wide, and 0.007 in. thick.

Blanks for the small, flat weights were cut from these plates (thickness varying from 0.025 in. (the 1-g. weights) to 0.232 in. (the 34-g. weights)) with a cut-off wheel. The edges of the plates were made smooth and parallel on the power grinder, three plates, identical in size and mounted in a bundle, usually being worked up at once. The mounting on the power grinder was a precision device and the grinder adjustable to 0.000,1 in. The grinding wheel used was the "soft", "white" wheel of the Norton Company, Worchester, Massachusetts, Number 32A (aluminum oxide)-60 (medium grain size)-H (soft)-12 (open density)-VBEF (vitrified, resin bonded); this wheel proved ideal for putting a fine finish on the relatively soft Carpenter 20CB3. One end of the blank was then trued on the power grinder and, calculating from the mass, density and dimensions of the plate, the necessary length cut such that the mass obtained was about 1 g. higher than the nominal value at which was aimed. The plate was then polished on the Syntron Lapping-Polishing Machine; see below.

The heavier weights, in the form of right cylinders, were all cut from the rods of Carpenter 20CB3 2.5 in. in diameter. The diameter was reduced on the lathe to 2.1 to 2.2 in. (so that the final weight would fit comfortably into the large vacuum weighing bottle (internal diameter 2.244 in.)). The final cuts on the lathe were made very shallow and with slow feed so that no striations were visible and the final finish unusually smooth. The requisite lengths were then cut from the rod and the ends of the blank trued on the lathe. One end was then ground flat and smooth on the power grinder, the final cuts across the face being very shallow, about 0.000,2 in. in depth. This end face was then polished on the Syntron Lapping-Polishing Machine; see below. The cylindrical face was then polished on the cylindrical-surface polishing machine described below. The second end face was then ground flat on the power grinder, as much metal being removed by successive passes of the wheel as necessary to reduce the mass to about 0.1 g. greater than the nominal value aimed for. Finally, the second end was polished on the Syntron Lapping-Polishing Machine and the weight brought as close as feasible to the nominal value.

1. Aluminum oxide polishing powders

The polishing powders used in the operations described below with the vibrating Syntron Lapping-Polishing Machine and with the cylindrical-surface polishing machine were the three grades of aluminum oxide obtained from Buehler Ltd., 2021 Greenwood Street, Evanston, Illinois 60204:

Buehler Micropolish No. 40-6310-080
Linde C 1.0 Micron Alpha Aluminum
Buehler Micropolish No. 40-6305-016
Linde A 0.3 Micron Alpha Alumina
Buehler Micropolish No. 40-6301-016
Linde B 0.05 Micron Gamma Alumina

Little use was made of Linde C, experience indicating that it was too coarse and generally caused deterioration of the surface as left by fine lathe or power grinder work. By far the major polishing was done with Linde A, the surfaces being brought to mirror finish, the operation sometimes requiring periods as long as 75 hours. The very final super-mirror finish was obtained with Linde B but it was found that the period of polishing must never exceed a very few minutes or the surface deterioration resulted, pits being produced ("orange peel effect").

The suspension of these aluminum oxides in water used for the polishing operation was prepared by mixing about 30 g. of the oxide, about 3 g. of a dry detergent (Dreft), and about 750 ml. of water. The water used was distilled water taken from the house supply and filtered first through a fine fritted-glass filtering funnel and then through a Gelman Metricel Membrane Filter, 0.45 μm., Gelman Instrument Company, Ann Arbor, Michigan. Usually some additional alumina, Dreft, and, of course, water were added during the polishing operation.

The major part of the polishing, with Linde A, was done on a wax surface prepared by melting in the bowl of the Syntron polishing machine a mixture of Buehler wax and Apiezon sealing wax (as hardener). When solidified, the surface was scraped flat and scored lightly with a razor blade. The final polishing with Linde A and with Linde B was done on Buehler micropolishing cloth stretched over the bottom of the bowl of the Syntron polishing machine. Care was taken to maintain a high state of cleanliness and, as far as possible, a dust-free atmosphere in the polishing room (Room 138 Chemistry Hall). A special grade of paper towel, Kaydry Disposable Towels, manufactured by Kimberly-Clark Corporation, Neenah, Wisconsin 54956, having a "super soft cellulose surface" prepared especially for buffing and polishing work, was used for all wiping and storage of polished surfaces.

2. Syntron vibrating polishing machine. Polishing the flat surfaces of weights

All of the faces of the flat, smaller weights (34 g. and smaller) and the flat ends of the cylindrical, larger weights (55 g. and heavier) were polished on a commercial vibrating polisher, a Syntron Lapping-Polishing Machine, manufactured by the FMC Corporation, Materials Handling Equipment Division, Homer City, Pennsylvania 15748, Catalog description: Type LP 014D, Style CC; Figure X-1. The Syntron Lapping-Polishing Machine was the property of the Hach Chemical Company, Loveland, Colorado, and was on loan to Iowa State University for this specific project.

The very heavy weights, the 1000-g. weights and F_{16} (987 g.), were wrapped with electric tape to protect the cylindrical face and placed directly on the polisher. Weights F_{10} (55 g.) through F_{15} (610 g.) were fastened to cylindrical, steel carrying slugs of somewhat smaller diameter and sufficiently heavy to bring the total mass to 950 g. to 1000 g. Attachment was made with adhesive tape having adhesive on both surfaces (Permacel Corporation, New Brunswick, New Jersey). The flat weights were similarly attached to a carrying slug, two or three such weights being

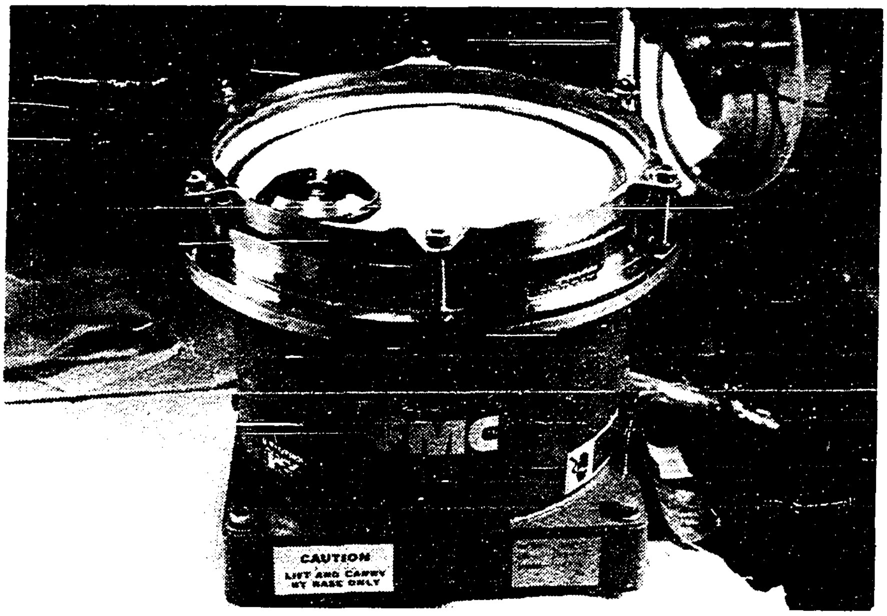


Figure X-1. Syntron Lapping-Polishing Machine, showing cylindrical, steel carrying slug (flat weights being polished fastened to bottom) and circular guard ring of weighted rubber tubing, in a suspension of alumina in water

fastened to the slug and polished simultaneously; these slugs were 3 in. in diameter and by arranging two flat weights as far apart as feasible or three flat weights in the configuration of a triangle, the slug was maintained upright during the polishing and the faces of the flats were maintained flat and parallel to the opposite face. Some of the weights and carrying slugs were shown in Figure X-2.

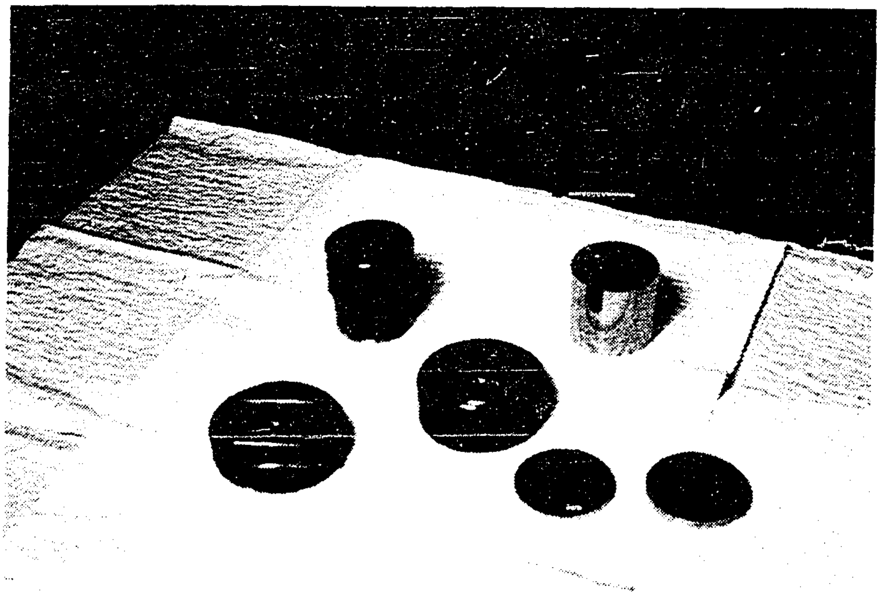


Figure X-2. Blanks of Carpenter 20CB3 for weights and carbon steel "carrying slugs". Upper left, weight F_{15} (610 g.) fastened to carrying slug and both wrapped with electric tape; polished surface of F_{15} uppermost. Upper right, F_{16} (987 g.), cylinder wall and flat face exposed already polished. Lower left, 3-in. carrying slug with two flat weights attached. Center, 3-in. carrying slug. Lower right, blanks for F_{10} (55 g.) and F_{11} (89 g.) with one face (up) already polished.

For polishing the edges of the small, flat weights, a holder was made from a piece of stainless steel rod 3 in. in diameter and 0.75 in. thick, cut into three segments and a central triangular piece, Figures X-3 and X-4. The central, triangular piece was bored to reduce the weight (final weight of four pieces and clamping ring, 515 g.).

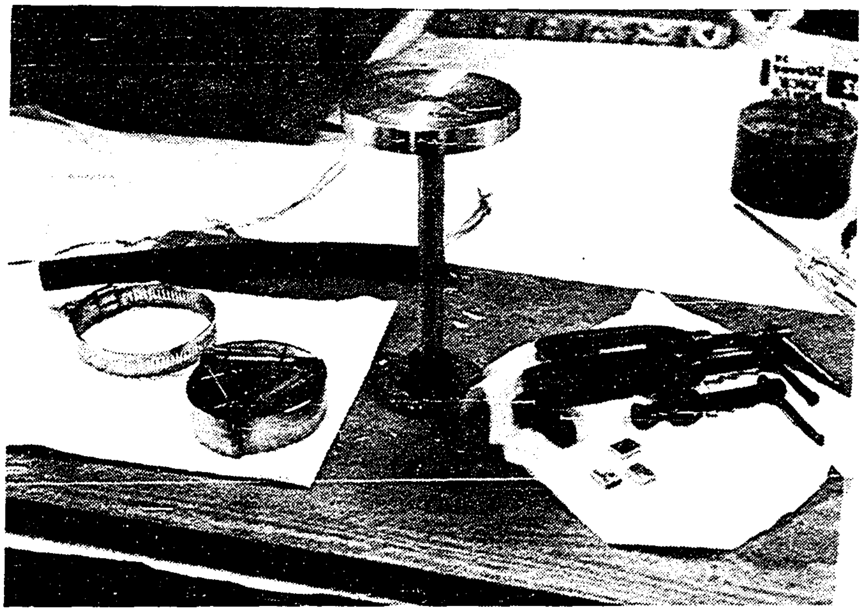


Figure X-3. Four-piece holder for polishing edges of flat weights, with upper spacing pieces, mounting plate, temporary clamps, and clamping ring

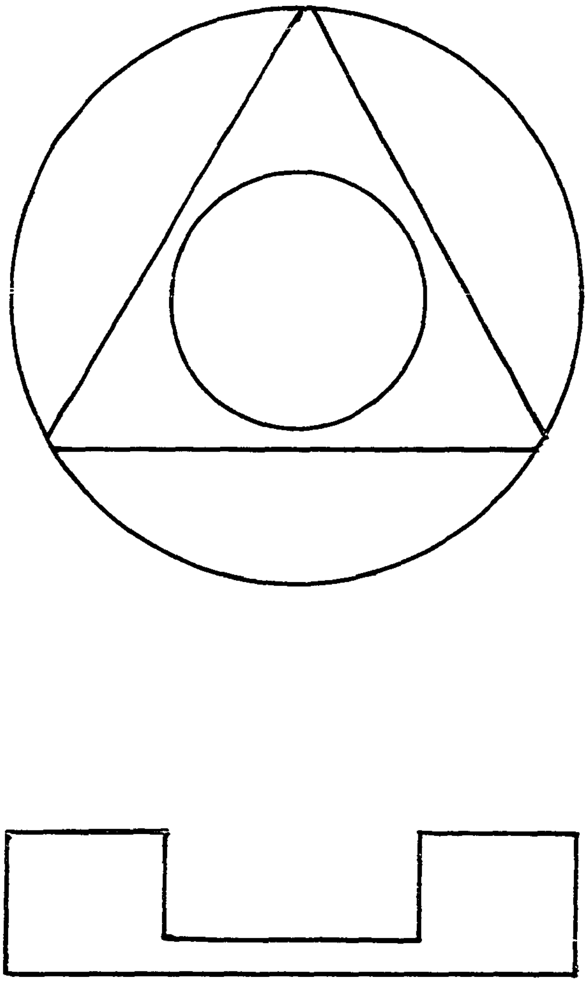


Figure X-4. Holder for polishing edges of flat weights, top view and cross section

Three weights were polished at once, each placed between a segment and the central triangular piece, and the assembly drawn up tight with a flexible, hose-clamping ring. The lower edge of the flat piece, that to be polished, projected below the holder 0.004 in.; this was arranged by covering the bottom faces of the three segments and the triangular piece with electric tape before assembly (on the flat mounting plate, Figure X-3) and stripping off the tape after assembly.

3. Cylindrical-surface polishing machine

The polishing of the vertical walls of the cylindrical large weights presented a much greater problem than polishing the flat surfaces. An extensive search failed to uncover a commercial machine which would effect the polishing of a cylindrical surface. Considerable effort was also expended trying to polish the large weights by anodic polishing; the results were consistently bad. The final surfaces were uneven and marred by irregularities and grooves. The problems arose principally from failure to develop a satisfactory method of making electrical contact with the cylinder. Attention was then directed to making a machine for the purpose. Such a machine was designed and built and, although it went through numerous modifications, in the end, a machine was perfected which did the job well; Figure X-5. Many of the basic features, the construction

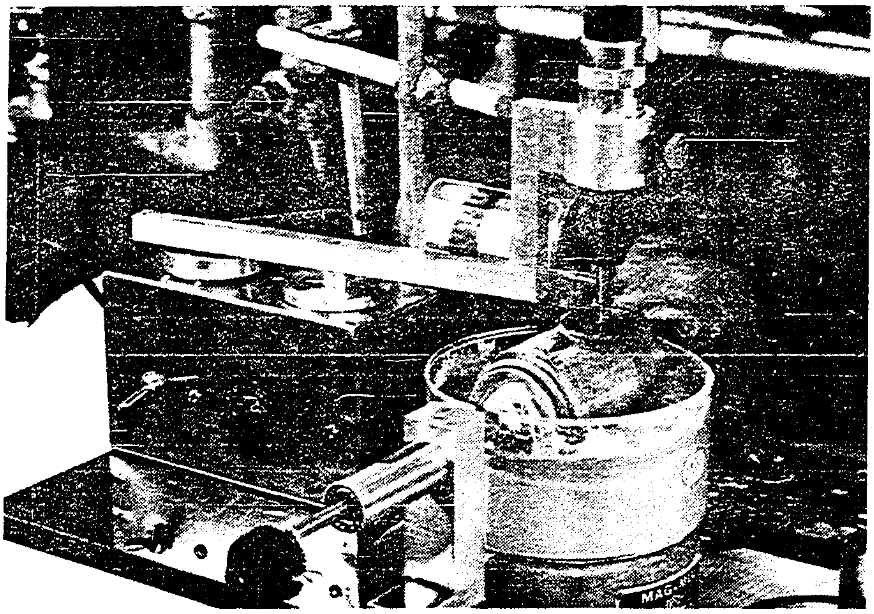


Figure X-5. Cylindrical-surface polishing machine

of the machine, and the modifications in structure were the work of Mr. Eldon Ness, foreman of the machine shop of the Department of Chemistry.

The cylinder to be polished was mounted on a horizontal axis so that it could be rotated while partly submerged in a suspension of aluminum oxide polishing powder. The suspension was carried up on the rotating cylinder and wetted a rotating buffing wheel which traveled back and forth across the cylinder. The buffing wheel was faced with

Buehler micropolishing cloth so that the dual motion of it and the motion of the rotating cylinder acting with the suspension of aluminum oxide did the polishing.

The rate of rotation of the cylinder was variable, the power being supplied by a variable speed A. C. motor with gear reducer manufactured by the Dayton Electric Company, Chicago, Illinois 60648, their Gearmotor, Model 22803. The direction of rotation could be changed by throwing a switch. The output of the gear reducing unit was normal to the shaft of the motor. At the end of the output shaft was placed a circular mounting plate to which was fastened the cylinder to be polished, the fastening being made with tape with adhesive on both faces. The other end of the cylinder was supported by a spring-loaded plate carried on a freely rotating shaft; contact of plate and cylinder was made through a flat rubber ring carried in a circular groove on the plate. The driving plate was made easily removable from the drive shaft and thus mounting and dismounting the cylinder was the relatively simple operation of pressing back on the rubber ring and plate against the spring and sliding the cylinder and drive plate off the drive shaft. It was necessary to center the drive plate exactly on the axis of the cylinder; this centering was done on the precision boring machine in the shop of the Department of Chemistry.

As will be seen in Figure X-5, the suspension of aluminum oxide was held in a crystalline dish 5 in. in diameter, slotted to accommodate the shafts on which the cylinder rotated.

The buffing wheel was rotated by a flexible shaft coming down vertically for 3 ft., Figure X-6. The motor driving this shaft, visible at the top of Figure X-6 on a sheet of plastic foam on a shelf, was variable, depending on the A. C. voltage delivered from an autotransformer (lower right). The arm carrying the buffing wheel was pivoted on the control box and driven by an eccentric, a pin on a rotating plate, the pin moving in a slot in the arm. The rotating plate carrying the pin was mounted on the vertical shaft of a motor placed in the control box. The sweep of the arm was adjustable by changing the radius of the circle through which the eccentric pin rotated. The arm was spring-loaded to eliminate chattering at the ends of the sweep.

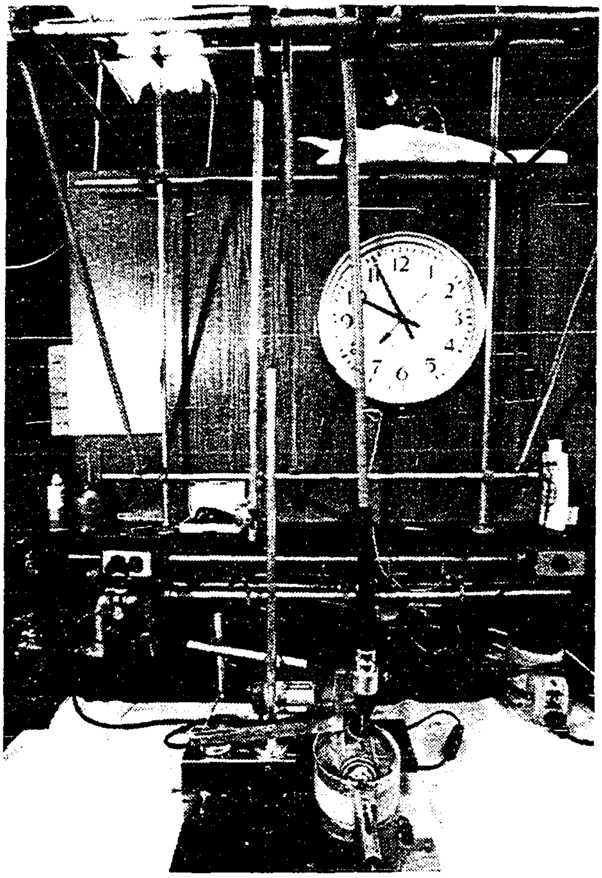


Figure X-6. Cylindrical-surface polishing machine, showing mounting and the vertical drive shaft to buffing wheel

XI. THEORY OF THE CALIBRATION OF A SET OF WEIGHTS BASED ON THE FIBONACCI SEQUENCE

A. The Composition of a Set of Weights

Basically, a set of weights should be so composed that every integral number within the range covered can be made up by some combination of the weights in the set. For convenience and simplicity in manipulation, the number of weights in the set should be kept to a minimum although other factors must also be considered: the ease with which the arithmetic involved can be performed, minimizing the mechanical contrivances for adding and removing weights in direct-reading balances, and (a very important consideration in the present work) opportunity for suitable and effective cross checks during calibration.

Of various sequences of numbers which have the property that some combination of the numbers will add up to every integral number, five sequences are of interest: (1) the conventional sequence used in sets of weights, 1, 2, 2, 5, 10, 20, 20, 50, ..., or some variation on it; (2) the geometric sequence, 1, 2, 4, 8, 16, 32, 64, ...; (3) the geometric sequence, 1, 3, 9, 27, 81, ...; (4) the sequence of prime numbers, 1, 2, 3, 5, 7, 11, 13, 19, 23, 31, 37, 41, 43, 47, ...; (5) the Fibonacci sequence, 1, 1, 2, 3, 5, 8, 13, 34, 55, 89, ..., .

Of these sequences of numbers, the Fibonacci sequence is by far the most interesting for the present purpose in that it provides numerous cross checks for the calibration operation. Fortunately, the Fibonacci sequence has been extensively studied, both as a branch of pure mathematics and for its appearance in numerous places in geometry and in the physical and living worlds. In fact, there exists a well-developed branch of mathematics devoted to the subject, complete with its own society and journal. And, addressing the very problem under consideration, there exists a considerable number of mathematical investigations, both already reported and currently under way. The pertinent investigations fall into three branches of the Fibonacci mathematics, known respectively as *identity*, *summation*, and *representation*. Among the numbers comprising the Fibonacci sequence, numerous algebraic relations exist; these relations are analogous to the identities of trigonometry and they provide the basis for the proposed application to the problem of the dissemination of a standard mass. The sums obtained by combining various of the Fibonacci numbers in certain ways are other Fibonacci numbers and the generalization of such relations lead to so-called *summation formulas*, highly useful for the present purpose. The term *representation* is used technically in this field to describe how combinations of the numbers of a sequence can be made to total given integral values; a sequence of numbers is said to be *complete* if some combination of the numbers will add up to every integral value. The Fibonacci sequence, and the closely associated Lucas sequence, are complete, that is, provide complete representation.

In the following review of each of the five sequences mentioned above, the discussion covers the range 1 to 1000 inasmuch as the problem addressed in the present dissertation is the subdivision of the kilogram. Inasmuch as weights on the metric system are under study, the expressions 1-g. weight, 2-g. weight, as so on, will be used when convenient.

1. The conventional sequence of sets of weights

The conventional sequence, 1, 2, 2', 5, 10, 20, 20', 100, 200, 200', 500, and in some sets of weights a variation employing 1, 2, 3, 5, 10, 20, 30, 50, 100, 200, 300, 500, has the merit that the arithmetic of adding up various combinations of the weights (on the decimal system) is almost automatic. Eleven weights are required to cover the range 1 to 1110 (1210 in the variation). An additional 1-g. weight is required for the calibration. Checks are provided for the calibration operation, although the number of these is distinctly limited in contrast to the cross checks possible in the Fibonacci sequence. Thus, using the additional 1-g. weight, 1', the calibration operations involve the comparisons

1 vs. 1'
1 + 1' vs. 2
1 + 1' vs. 2'
1 + 2 + 2' vs. 5
1 + 2 + 2' + 5 vs. 10
1 + 2 + 2' + 5 + 10 vs. 20
1 + 2 + 2' + 5 + 10 vs. 20'
10 + 20 + 20' vs. 50
1 + 2 + 2' + 5 + 20 + 20' vs. 50
and so on.

2. The geometric sequence, 2^k $(k = 0, 1, \dots n)$

Powers of two, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, are complete, that is, provide representation for every integer over the range 1 to 1023, and only ten weights are required. An additional 1-g. weight is required for calibration. No cross checks are provided, the sum of weights $k = 0$ to n being $2^{n+1} - 1$. The arithmetic in the use of such a set of weights could be simplified by a table prepared in advance. Although the small number of weights would appear to demand a minimum of cams and levers for the mechanical manipulation of such weights in a direct-reading balance, no commercial balance makes use of such a set.

3. The geometric sequence, 3^k $(k = 0, 1, 2, \dots n)$

This sequence, consisting of the powers of three, 1, 3, 9, 27, 81, 243, 729, is complete but requires that subtraction as well as addition be used. The range covered is 1 to 1093 and only seven weights are required; a second 1-g. weight is required for the calibration. Physically, the subtraction operation can be accomplished with an equal-arm balance by placing the weights on both pans. The manipulation of weights between the two pans and the arithmetic appear cumbersome and confusing. Where such a set appears to offer advantage is in the direct-reading, single-pan balances, which operate at constant sensitivity obtained by maintaining constant load. In such a constant-load balance, the object being weighed plus all of the weights are normally carried on the pan and only those necessary to equal the object are removed. With only seven weights to be removed, the mechanism would appear to offer a minimum of complication. No commercial, single-pan balance operates with such a set of weights however, some modification of the conventional sequence always being used.

4. The sequence of prime numbers

The sequence of prime numbers obviously offers representation but the prime numbers are so numerous there is an excessive redundancy and the sequence would hardly be considered for a set of weights.

5. The Fibonacci sequence

In the Fibonacci sequence, 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, 233, 377, 610, 987, each member of the sequence is obtained by adding together the two preceding members. Fifteen weights are required to cover the range 1 to 1596, although for the present purpose of the subdivision of a kilogram, inclusion of the sixteenth weight, 987, offers certain advantages. There are numerous mathematical relations between the members of the Fibonacci sequence which offer opportunities for independent cross checks during a calibration operation. The Fibonacci sequence was adopted in the present work and in the next few sections of this dissertation there is presented sufficient Fibonacci mathematics for the problem at hand and for the development of a theory for the propagation of the experimental uncertainties inherent to an actual calibration operation.

B. Fibonacci Mathematics. General Survey, Nomenclature, and Symbolism

The Fibonacci sequence of numbers is treated in that branch of mathematics called *number theory*. The Fibonacci mathematics, in which currently a great deal of research is in progress, is essentially pure mathematics, but there is associated with it some surprising applications to such diverse fields as physics, astronomy, botany, communications, data handling, architecture, and esthetics. The theoretical developments of recent years have been so numerous that a more or less standardized nomenclature and symbolism have been adopted. For the beginner, there is an excellent introductory literature: (1) Verner E. Hoggatt, Jr., *Fibonacci and Lucas Numbers* (50); (2) Brother U. Alfred, *An Introduction to Fibonacci Discovery* (12); Marjorie Bicknell and Verner E. Hoggatt, Jr., *A Primer for the Fibonacci Numbers* (7); (4) Brother Alfred Brousseau, *Linear Recursion and Fibonacci Sequences* (13); (5) H. E. Huntley, *The Divine Proportion* (57).

Hoggatt's *Fibonacci and Lucas Numbers* is exceptionally well written and is an easy introduction to some surprisingly sophisticated mathematics. It also has short but excellent introductions to certain applied areas, particularly to representations (as defined above and again below), phyllotaxis, and geometry. This book is quoted frequently in the current literature. The two publications of Brother Alfred Brousseau (Brother U. Alfred) are also skillfully presented introductions to the mathematics of number theory. The *Primer for the Fibonacci Numbers* is a reproduction of some twenty-four papers, mostly by Hoggatt and Bicknell, published in *The Fibonacci Quarterly* between 1963 and 1973; these papers were originally written for the advanced beginner and are pitched expertly for the serious novice. *The Devine Proportion* by Huntley is of entirely different character; while bringing in the Fibonacci mathematics where necessary, it deals primarily with the so-called *Golden*

Ratio, with the importance of this number in art and architecture, with the connection of it with the Fibonacci numbers, and with the occurrence of the Fibonacci numbers in geometry and phyllotaxis. The emphasis is on the esthetical, indeed almost magical, properties of the Golden Ratio and the Fibonacci numbers.

In the present dissertation, the notation adopted is essentially that of Hoggatt as presented in his *Fibonacci and Lucas Numbers* and in his numerous publications in *The Fibonacci Quarterly*.

Each of the Fibonacci numbers has been given a name and a symbol:

F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
0	1	1	2	3	5	8	13	21

F_9	F_{10}	F_{11}	F_{12}	F_{13}	F_{14}	F_{15}	F_{16}
34	55	89	144	233	377	610	987

The recursion formula expressing the general relation that each member of the series is the sum of the two preceding members is

$$F_{n+2} = F_{n+1} + F_n \qquad \text{(XI-1)}$$

the two initial terms being specified: $F_0 = 0$ and $F_1 = 1$. Each term of the series can also be calculated by the so-called Binet formula

$$F_n = \frac{\alpha^n - \beta^n}{\alpha - \beta} \qquad \text{(XI-2)}$$

in which α and β are the roots of the so-called Fibonacci quadratic

$$x^2 - x - 1 = 0 \qquad \text{(XI-3)}$$

These roots have the values

$$\alpha = \frac{1 + \sqrt{5}}{2} = 1.618033989\ldots \qquad \text{(XI-4)}$$

$$\beta = \frac{1 + \sqrt{5}}{2} = -0.618033989\ldots \qquad \text{(XI-5)}$$

$$\alpha\beta = -1 \qquad \alpha - \beta = \sqrt{5} \qquad \alpha^2 = \alpha + 1$$

(XI-6) (XI-7) (XI-8)

It is of interest in the present work on the dissemination of mass, that the Fibonacci series extends to negative values of n:

...	F_{-4}	F_{-3}	F_{-2}	F_{-1}	F_0	...
...	-3	2	-1	1	0	...

The Fibonacci numbers with negative subscripts have the same absolute numerical value as those with positive n but the numbers are alternately positive and negative. This is expressed by

$$F_{-n} = (-1)^{n-1} F_n \qquad \text{(XI-9)}$$

Thus, F_{-1} is +1; use of this fact will be made later in this dissertation, in connection with the calibration of a set of weights fabricated on the Fibonacci sequence.

Another set of numbers, known as the *Lucas numbers* and designated by the capital letter L, is intimately related to the Fibonacci sequence. It is also based on the recursion formula $F_{n+2} = F_{n+1} + F_n$, but the initial numbers are 1 and 3 rather than 1 and 1. The early numbers of the two sequences are

n	0	1	2	3	4	5	6	7	8	...
F_n	0	1	1	2	3	5	8	13	21	...
L_n	2	1	3	4	7	11	18	29	47	...

The Lucas series also provides complete representation for the positive integers and could also be used as the basis for a set of weights (Hoggatt, ref. 50, Chapter 12, p. 69).

C. Fibronacci Mathematics. Representation

The term *representation* is used in this dissertation in the same meaning that it is used in mathematics: the combination of various members of a series of numbers to add up to a positive integer. The best introduction to the subject of representation is Chapter 12 of Hoggatt's *Fibonacci and Lucas Numbers* (ref. 50, p. 69). The following definition is taken from Hoggatt:

A sequence of positive integers, a_1, a_2, ..., a_n, ..., is *complete* with respect to positive integers if and only if every positive integer *m* is the sum of a finite number of the members of the sequence, where each member is used at most once in any given representation.

The geometric sequence based on powers of two, defined by

$$a_n = 2^n \qquad (n \geq 0) \qquad \text{(XI-10)}$$

(Hoggatt Theorem I)

is complete; Hoggatt gives a proof for this.

The Fibonacci sequence of numbers is complete, that is

$$a_n = F_n \qquad (n \geq 1) \qquad \text{(XI-11)}$$

(Hoggatt Theorem II)

Hoggatt offers a table illustrating this for values of n up to 8 and then offers a proof based on mathematical induction.

Hoggatt has seven more theorems developing the subject of completeness in the Fibonacci sequence and the related Lucas sequence. These theorems deal with whether one or more members of the sequence can be omitted and with the minimum and maximum number of terms which can made representations for a given integer.

1. Hoggatt Theorem III

The Fibonacci number sequence where $a_n = F_n$ $(n \geq 1)$, with an arbitrary F_n missing is complete.

2. Hoggatt Theorem IV

The Fibonacci sequence, where $a_n = F_n$ $(n \geq 1)$, with any two arbitrary Fibonacci numbers F_p and F_n missing is incomplete.

3. Hoggatt Theorem V

The Lucas number sequence, where $a_n = L_{n-1}$ $(n \geq 1)$, is complete.

4. Hoggatt Theorem VI (the Zeckendorf Theorem)

Each positive integer m can be represented as the sum of distinct numbers in the sequence defined by $a_n = F_{n+1}$ $(n \geq 1)$, using no two consecutive Fibonacci numbers, and such a representation is unique.

5. Hoggatt Theorem VII

Each positive integer m can be represented as the sum of distinct numbers in the sequence defined by $a_n = F_{n+1}$ $(n \geq 1)$ with the condition that whenever F_k $(k \geq 4)$ is used, at least one of each pair F_q, F_{q-1} $(3 \leq q < k)$ must be used, and such a representation is unique.

Hoggatt Theorems VIII and IX are the theorems for Lucas numbers corresponding to Theorems VI and VII.

These theorems are a bare introduction to the subject. Recent advances have carried the subject into some remarkable generalizations dealing with the basic characteristics of sequences which are and are not complete, with the total number of representations for a given integer and how this number can be maximized and minimized, and with unexpected applications to head-or-tail probability problems and to game theory. This advanced literature consists of some twenty-five papers, the principal papers being those of J. L. Brown (15,16,17), Ferns (36), Klarner (63), Carlitz, Scoville and Hoggatt (21,22), Hoggatt and Chow (51), Hoggatt, Cox and Bicknell (52), Hoggatt (49), and Brousseau (11) (Hoggatt (49) carries an extensive bibliography on the subject). These works deal with the representation of all positive integers. Such representation is, of course, important in the use of a set of weights but the problem of subdividing the kilogram with high accuracy involves only a restricted application of the theorems, that is, to only the Fibonacci numbers themselves. In the various papers just mentioned, for simplicity in treatment, only one of the numbers 1 is used, that is, the Fibonacci sequence and the other sequences derived from it which are studied are made to begin with F_2. For the purpose of calibrating a set of weights fabricated on the Fibonacci sequence, it is best to use both F_1 and F_2; indeed, as will be shown, definite advantages accrue in using three 1-g. weights, that is, actually beginning the sequence with the $F_{-1} = 1$ term. Thus, the representation theorems, to the extent that they are used in the present work in addition to a purely empirical approach, take on a slightly different form.

D. Fibonacci Mathematics.

Summation Formulas

One of the astonishing features of the Fibonacci sequence of numbers is the characteristic that the sum of successive numbers follows a definite pattern, a pattern which can be expressed mathematically. Moreover, the sum of alternating Fibonacci numbers, or of every third Fibonacci number, follow still other patterns.

The sum of successive Fibonacci numbers beginning with F_1 is equal to the Fibonacci number two terms farther along minus one. Expressed mathematically

$$\sum_{k=0}^{m} F_k = F_{m+2} - 1 \qquad \text{(XI-S-1)}$$

Thus, for $m = 9$, $F_9 = 34$ and the sum of $1 + 1 + 2 + 3 + 5 + 8 + 13 + 21 + 34 = 88$, that is, $F_{11} - 1 = 89 - 1 = 88$.

The sum of the consecutive odd-numbered Fibonacci numbers, that is, for the terms F_1, F_3, F_5, ..., and so on, is also a Fibonacci number:

$$\sum_{k=1}^{m} F_{2k-1} = F_{2m} \qquad \text{(XI-S-2)}$$

Thus, for k successively 1, 2, 3, 4, 5, 6, that is, for m = 6, $\Sigma(F_1 + F_3 + F_5 + F_7 + F_9 + F_{11})$, the sum is 1 + 2 + 5 + 13 + 34 + 89 = 144, which is equal to F_{12}.

The sum of even-numbered Fibonacci numbers is given by

$$\sum_{k=0}^{m} F_{2k} = F_{2m+1} - 1 \qquad \text{(XI-S-3)}$$

Thus, for m = 6, $F_2 + F_4 + F_6 + F_8 + F_{10} + F_{12} = 1 + 3 + 8 + 21 + 55 + 144 = 232 = F_{13} - 1 = 233 - 1 = 232$.

Taking every third Fibonacci number, three sequences are possible; the sums in each are again related to Fibonacci numbers:

(1) $F_1 + F_4 + F_7 + F_{10} + F_{13} + \ldots$

$$\sum_{k=0}^{m} F_{1+3k} = \tfrac{1}{2}F_{1+3m+2} \qquad \text{(XI-S-4)}$$

(2) $F_2 + F_5 + F_8 + F_{11} + \ldots$

$$\sum_{k=0}^{m} F_{2+3k} = \tfrac{1}{2}(F_{2+3m+2} - 1) \qquad \text{(XI-S-5)}$$

(3) $F_3 + F_6 + F_9 + F_{12} + \ldots$

$$\sum_{k=0}^{m} F_{3+3k} = \tfrac{1}{2}(F_{3+3m+2} - 1) \qquad \text{(XI-S-6)}$$

Taking every fourth Fibonacci number, four sequences are possible; the sums in each sequence are again related to Fibonacci numbers:

(1) $F_1 + F_5 + F_9 + F_{13} + \ldots$

$$\sum_{k=0}^{m} F_{1+4k} = F_{2m+1}F_{2m+2} \qquad \text{(XI-S-7)}$$

(2) $F_2 + F_6 + F_{10} + F_{14} + \ldots$

$$\sum_{k=0}^{m} F_{2+4k} = F_{2m+2}^2 \qquad \text{(XI-S-8)}$$

(3) $F_3 + F_7 + F_{11} + F_{15} + \ldots$

$$\sum_{k=0}^{m} F_{3+4k} = F_{2m+2}F_{2m+3} \qquad \text{(XI-S-9)}$$

(4) $F_4 + F_8 + F_{12} + F_{16} + \ldots$

$$\sum_{k=0}^{m} F_{4+4k} = F_{2m+3}^2 - 1 \qquad \text{(XI-S-10)}$$

For a highly generalized treatment of Fibonacci summation formulas, of which the above equations are special cases, see Freitag (37).

Of the ten summation formulas just given, the first three are of particular interest for the present purpose in that the successive sums are other Fibonacci numbers, or other Fibonacci numbers minus one. They are directly applicable to the calibration problem in that they indicate which combinations of lighter weight will equal a given weight, if, a third 1-g. weight be included in the set. In the set of weights being constructed, such a third 1-g. weight, designated F_{-1}, is being included. The summation formulas (XI-S-1) and (XI-S-3) take on a slightly different form in this context.

The summation formulas taking every third and every fourth Fibonacci number yield for the sums, integers which are not Fibonacci numbers. Conceivably, use could be made of these summation formulas and integers in the calibration of a set of Fibonacci weights, but this has not been attempted in the present work.

In addition to the summation formulas, a vast and astonishing array of identities interrelating the Fibonacci numbers exists and more such identities interconnect the Fibonacci numbers with the Lucas numbers. For the most part these identities involve multiplication of numbers. It is unfortunate that the equal-arm (double-pan) and the single-pan balance will only perform physically the operations of addition and subtraction and thus use cannot be made in a calibration operation of the vast majority of these identities.

E. Use of Representation and Summation in the Calibration of a Set of Fibonacci Weights. A New Symbolism to Facilitate Comprehension and the Handling of the Numerous Terms Involved

Increase in the precision and reliability of a measured quantity can be obtained by repetitions of the measurement and the application of statistics. Better, is to repeat the measurement under different conditions. This is precisely what the uniquc properties of the Fibonacci sequence of numbers offers the high-precision dissemination of a standard mass. Given completeness of representations, which is of course the prime prerequisite of a set of weights, the large number of representations possible with the Fibonacci numbers makes for a large number of independent cross checks. Thus, for calibrating the 8-g. weight in terms of one of the 1-g. weights taken as the standard, including a third 1-g. weight, and of course, working with the lower weights similarly calibrated, six independent measurements are offered:

8 vs. 5 + 3
5 + 2 + 1
5 + 2 + 1'
5 + 2 + 1"

5 + 1 + 1' + 1"

3 + 2 + 1 + 1' + 1"

Of these six representations, one involves two weights, three involve three weights, one four weights and one five weights. Three of the representations involve the two 1-g. weights normal to the Fibonacci sequence (that is, positive subscripts) but this number is doubled by the inclusion of the third 1-g. weight, F_{-1}. The sixth of these representations will be recognized as an application of the summation formula for successive Fibonacci numbers, equation (XI-S-1) above, modified to begin with F_{-1}, that is

$$\left(\sum_{k=0}^{n} F_k\right) + F_{-1} = F_{n+2} \qquad \text{(XI-S-11)}$$

The second of the six representations just given for the 8-g. weight is an application of the summation formula for successive odd-numbered Fibonacci numbers, equation (XI-S-2).

Before proceeding further into the representations as they present opportunities for cross checks for the calibration operation, I advance a new symbolism by which the numerical values and the Fibonacci number can both be grasped instantly at first inspection. This is a singular advantage in this rather involved field which necessarily deals with numerous individual entities under varying conditions. Any particular weight is referred to, for convenience, by the normal Fibonacci name and symbol but, for the handling of the calibration data, is considered to consist of two parts.

Physically, it is just about impossible to fabricate a weight to an exact integral value within one or even ten parts per million. Also, the Fibonacci mathematics applies only to integers. Thus, in the following sections of this dissertation any given weight is treated as being composed of two parts, an *integral* value plus a *departure* from the integral value. I propose that the integral values of the weights be designated by the appropriate Arabic numeral with the Fibonacci designation as subscript but avoiding, however, subscripts to subscripts. For the departure I propose to use the lower case letter a, again with the appropriate subscript. Thus:

Name	Treated mathematically as
F_{-1}	$1_{F(-1)} + a_{1F(-1)}$
F_0	No such weight; corresponds to zeroing the balance
F_1	$1_{F1} + a_{1F1}$
F_2	$1_{F2} + a_{1F2}$
F_3	$2_{F3} + a_{2F3}$
F_4	$3_{F4} + a_{3F4}$
F_5	$5_{F5} + a_{5F5}$
$\vdots$	$\vdots$

Use is made of this symbolism in Figure XI-1, which is a tabular presentation of all of the possible representations of each of the Fibonacci numbers starting with F_1, that is, for the sequence having two numbers 1, and proceeding through F_{16}. Figure XI-1 ("Representations of Fibonacci numbers by an increasing number of smaller Fibonacci numbers") appears as the first of two fold-in charts at the end of this dissertation.

Use is made of the symbolism just proposed also in Figure XI-2, which is a tabular presentation of all of the representations of each of the Fibonacci numbers starting with F_{-1} proceeding through F_8, and then jumping to F_{16}. Figure XI-2 ("Calculation chart (all representations) for a set of Fibonacci weights using the Fibonacci sequence beginning with F_{-1}") appears as the second of two fold-in charts at the end of this dissertation.

Each weight in a set is characterized by a departure and the object of a calibration is to determine the most precise value possible for each departure. Inasmuch as one weight in the set is taken as a known or assumed value and all of the weights referred to it, a very intimate relationship exists between all the members of the set. A set of departures of a set of weights I speak of as the *imputation*. [*Imputation:* (theological meaning) an inherent or original sin; that sin possessed by an individual or species at birth but not resulting from an overt act of an individual]. The goal of a calibration is to make the imputation not only as internally consistent as possible but as correct on an absolute basis as possible. Necessarily, the values finally obtained for the imputation carry the accumulated experimental uncertainties of the measurements. In a good calibration operation, these will have been reduced to a minimum.

It will be observed in the material which follows that a calibration operation in practice begins with one of the very small weights, a 1-gram weight in my case, and proceeds to the heavier weights. The departures become progressively greater and for the larger weights so large as to invite suspicion that the set was poorly prepared. This is an artifact derived from the very nature of the calibration process, however, and not an inherent defect. To reduce the unduly large departures in the larger weight, the data are frequently recalculated transferring the primary standard from the 1-g. weight to, for example, the 100-g. or the 1000-g. weight.

Before proceeding with the application of the symbolism just advanced to the theoretical treatment of the calibration operation, a discussion is presented of the operation of the balance and the nature of the data derived from it.

F. Use of the Single-Pan Balance in the Calibration of a Set of Weights

The measurements of mass reported in this dissertation were made on commercial, modern, single-pan balances, specifically on three manufactured by the Mettler Instrument Corporation: (1) a Model H315 Kilogram Balance, Serial Number 719830, (2) a Model H51AR Semimicrobalance, Serial Number 626447, and (3) a Model M5/SA Microbalance, Serial Number 525505. The modern single-pan balance is highly sensitive to one part in 10^7 on all three ranges of capacity; it is completely damped and rapid in operation; it operates at constant sensitivity and the last four figures in a weighing are obtained by optical readout. This is quite in contrast to the older, equal-arm balances, in which sensitivity varies with load, rest-point is determined by the much slower method of averaging swings, the last four figures are obtained by the cumbersome procedure of positioning a rider on a calibrated beam, and when commercially available with comparable sensitivity, higher in price. The alteration made to the balances used in this work after receipt from the manufacturer are detailed in Chapter V of this dissertation.

The single-pan balance operates on the *substitution principle.* The single-pan balance has only two knife edges. Internal weights are hung on the same, outside knife edge as is the pan on which the object to be weighed is placed and weights are removed equal to the mass of the object weighed. The mass of weights plus object is balanced by a fixed counterweight at the other end of the beam. The balance is highly damped by a piston working loosely in a cylinder so that the beam comes quickly to rest. The total load on the outer knife edge, object plus remaining weights, is constant at all times and the sensitivity (deflection of the rest-point per unit of mass) is constant. The last four significant figures of the mass measured are obtained from the shift of the rest-point from the no-load zero-point, the position of the rest-point being registered by an optical lever system and projected on a scale on the front of the case. For further details of the construction and a picture of the internal mechanism of the single-pan balance, see Diehl, *Quantitative Analysis* (34).

The mode of operation just described is known as *weighing by substitution*. In effect, two weighings were made: (1) the balance is zeroed, that is, the full complement of weights is balanced exactly by a fixed counterweight together with the piston and components of the optical system fixed to the beam and a very small zeroing weight, the position of which can be changed. Mathematically:

$$WL = CR \qquad \text{(XI-W-1)}$$

W being the total of the weights, C the effective mass of the counterweights, and L and R the respective lengths of the arms, front and rear, of the balance; (2) the object M is placed on the pan and weights, W', removed to restore balance:

$$(W - W' + M)L = CR \qquad \text{(XI-W-2)}$$

Equations (XI-W-1) and (XI-W-2) yield

$$WL = (W - W' + M)L$$

$$M = W' \qquad \text{(XI-W-3)}$$

In this weighing by substitution, it is not necessary to know the actual values of the lengths of the arms of the balance inasmuch as both L and R cancel. In the Mettler balances the ratio R/L is actually close to 3/2.

In the calibration of the set of Fibonacci weights, the substitution principle was still further used, the internal weights of the balance serving only as tares. With no load on the pan, the position of the rest-point (zero-point), r_z, was obtained in optical scale divisions. Weight F_{-1} was placed on the pan and one gram dialed into the balance (actually removing the internal 1-g. weight from the assembly of internal weights). The position of the new rest-point, $r_{F(-1)}$, was read and the deflection $d_{F(-1)}$ calculated

$$d_{F(-1)} = r_{F(-1)} - r_z \qquad \text{(XI-W-4)}$$

Because the sensitivity of the balance had been increased over that set by the manufacturer, the optical scale was not direct-reading but required calibration; this calibration was effected by next adding to the pan a small, accurately known weight, the *sensitivity weight*, the mass of which is designated by W_s, and obtaining a new rest-point, r_s. The sensitivity, $\$$, was then obtained by

$$\$ = W_s/(r_s - r_{F(-1)}) \qquad \text{(XI-W-5)}$$

usually in the units of mass per scale division. The mass corresponding to the first deflection was then calculated

$$M = d_{F(-1)}\$ \qquad \text{(XI-W-6)}$$

This quantity was designated by a lower case Greek letter α with appropriate subscript. The measurement thus made of weight F_{-1} is expressed by the equation (T is the tare)

$$1_{F(-1)} + a_{1F(-1)} = T_1 + \alpha_{1F(-1)} \qquad \text{(XI-W-7)}$$

The same sequence of measurements was then repeated with weights F_1 and F_2, leading to the further equations

$$1_{F1} + a_{1F1} = T_1 + \alpha_{1F1} \qquad \text{(XI-W-8)}$$

$$1_{F2} + a_{1F2} = T_1 + \alpha_{1F2} \qquad \text{(XI-W-9)}$$

Subtraction of equation (XI-W-7) from equation (XI-W-8) and cancellation of the integral values, $F_{(-1)} = F_1 = 1$, give

$$a_{1F1} = a_{1F(-1)} - \alpha_{1F(-1)} + \alpha_{1F1} \qquad \text{(XI-W-10)}$$

Similarly, equations (XI-W-7) and (XI-W-9) yield

$$a_{1F2} = a_{1F(-1)} - \alpha_{1F(-1)} + \alpha_{1F2} \qquad \text{(XI-W-11)}$$

And so on through the entire set of weights.

By *operation in the F_{-1} mode* is meant zeroing the balance with the F_{-1} weight on the pan and removing F_{-1} during a weighing when such removal is called for. This will be recognized as conformity to the Fibonacci mathematics in keeping with the normal significance of the minus sign and the possibilities of using subtraction in weighing when using the Fibonacci summation formulas in which the -1 term occurs (equations (XI-S-1) and (XI-S-3)).

Mechanically, zeroing the balance with F_{-1} on the pan is possible. In the Mettler single-pan balances the zero adjustment mechanism consists of a fine adjustment which involves a movement of the otherwise fixed optical scale and a coarse adjustment which consists of a nut mounted on a horizontal screw on the beam. Together, however, in the Model H315 kilogram balance, the range of adjustment is much less than one gram. In the manufacture, however, the maker, to bring the mass of the pan to the correct value, has bolted washers to the pan totaling some ten grams; these washers are of different sizes and by a judicious removal of them, the mass removed can be brought close enough to one gram so that the final adjustment can be made with the coarse zeroing nut on the beam.

Weighing the F_{-1} mode is still weighing by substitution but the equations developed above take a different form to reflect the subtraction. The balance is zeroed with a different tare, designated T*. With F_{-1} on the pan, the balance is zeroed, or more correctly, a reading, r_z, taken, this reading being more or less in the middle of the optical scale. In the calibration on F_1, F_{-1} is removed and F_1 put on the pan. A new rest-point, r_2, is obtained. The sensitivity weight, $\cancel{S}$, is then added and a third rest-point, r_3, obtained. Mathematically, these measurements are expressed by

$$l_{F(-1)} + a_{lF(-1)} = T^* + r_z \qquad \text{(XI-W-12)}$$

$$l_{F1} + a_{lF1} = T^* + r_2 \qquad \text{(XI-W-13)}$$

$$l_{F1} + a_{lF1} + W_s = T^* + r_3 \qquad \text{(XI-W-14)}$$

The sensitivity, $\cancel{S}$, is obtained by subtracting equation (XI-W-13) from equation (XI-W-14) giving

$$\cancel{S} = W_s/(r_3 - r_2) \qquad \text{(XI-W-15)}$$

Subtracting equation (XI-W-12) from equation (XI-W-13) gives

$$l_{F1} + a_{lF1} - l_{F(-1)} - a_{lF(-1)} = r_2 - r_z \qquad \text{(XI-W-16)}$$

The integral values cancel and introducing the sensitivity gives

$$a_{lF1} = a_{lF(-1)} + \alpha_{F1-F(-1)} \qquad \text{(XI-W-17)}$$

in which the more complex subscript of the experimental term indicates that the weighing was made in the F_{-1} mode.

G. Further Development of the New Nomenclature and Symbolism

The preceding sections are essentially explanatory in nature. In them, the names and symbolism more or less standard in the Fibonacci literature are introduced and there is advanced certain additional symbolism necessary to avoid confusion and to promote the efficient handling of the large amount of data expected in the new, highly accurate subdivision of the kilogram being attempted. A review of this symbolism is now made, gathering together and defining more explicitly the nomenclature and symbolism to be used in the remainder of this dissertation.

Name of weight	F_{-1}	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9
Integral (or "nominal") value	$1_{F(-1)}$	0_{F0}	1_{F1}	1_{F2}	2_{F3}	3_{F4}	5_{F5}	8_{F6}	13_{F7}	21_{F8}	34_{F9}
Departure	$a_{1F(-1)}$	a_{0F0}	a_{1F1}	a_{1F2}	a_{2F3}	a_{3F4}	a_{5F5}	a_{8F6}	a_{13F7}	a_{21F8}	a_{34F9}

F_{10}	F_{11}	F_{12}	F_{13}	F_{14}	F_{15}
55_{F10}	89_{F11}	144_{F12}	233_{F13}	377_{F14}	610_{F15}
a_{55F10}	a_{89F11}	a_{144F12}	a_{233F13}	a_{377F14}	a_{610F15}

F_{16}	ISU-1000	ISU-1000-2	ISU-1000-3	ISU-1000-4
987_{F16}	1000	1000-2	1000-3	1000-4
a_{987F16}	a_{1000}	a_{1000-2}	a_{1000-3}	a_{1000-4}

The upper row in the above table gives the name of each weight; that is, the usual designation or name of the Fibonacci number, F_{-1}, F_1, F_2, F_3, ..., is taken to mean weights, each respectively of a mass closely equal to the Fibonacci number. The designations in the second row are here called the *integral* or *nominal* value and are the respective actual values of the mass indicated. The lower case letters a, in the third row, each with an appropriate subscript, represent the *departure* of the designated weight from the integral value, this departure being expressed in µg. (µg. = microgram, 0.000,001 g.).

$$F_1 = 1_{F1} + a_{1F1} = [1.000,000 + (a_{1F1})/(1,000,000)]g.$$

$$F_2 = 1_{F2} + a_{1F2} = [1.000,000 + (a_{1F2})/(1,000,000)]g.$$

$$F_3 = 2_{F3} + a_{2F3} = [2.000,000 + (a_{2F3})/(1,000,000)]g.$$

$$F_4 = 3_{F4} + a_{3F4} = [3.000,000 + (a_{3F4})/(1,000,000)]g.$$

The term F_0 means no weight at all and physically this corresponds to the operation of zeroing the balance, that is, determining the rest-point with no load (zero-point).

The lower case Greek symbols, α, β, γ, δ, and so on, are used to denote experimentally measured quantities expressed in units of mass (micrograms) added to the tare, T. The symbol α is used when the weighing involves one weight on the pan, β when two weights are on the pan, γ three weights on the pan, and so on.

In the numbering of mathematical equations in the following sections, the additional designation -e means that the equation expresses a direct, experimental measurement made on a balance.

H. Schedule for Calibrating a Set of Fibonacci Weights

The simplest representation of any Fibonacci number is the combination of the next two smaller Fibonacci numbers. A representation involving three Fibonacci numbers is obtained by replacing the smaller of the numbers in the two-number representation by the two Fibonacci numbers smaller than it. A representation involving four numbers is obtained by replacing the smallest number in the three-number representation by the two next smaller Fibonacci numbers. The pattern is shown in Figure XI-1.

As will be seen from the pattern, the successive representations for a particular Fibonacci number involve the next lower Fibonacci number, plus alternating lower Fibonacci numbers, plus a final Fibonacci number breaking the alternating sequence:

$$\begin{aligned} F_n &= F_{n-1} + F_{n-2} \\ &= F_{n-1} + F_{n-3} + F_{n-4} \\ &= F_{n-1} + F_{n-3} + F_{n-5} + F_{n-6} \\ &\vdots \\ &= F_{n-1} + F_{n-3} + \cdots + F_{n-(2k+1)} + F_{n-(2k+2)} \\ &\qquad\qquad (2k+2) \leq n \end{aligned}$$

For the odd Fibonacci numbers, the representations involve the successively smaller even-numbered Fibonacci numbers and the longest representation (that being composed of the largest number of Fibonacci numbers) ends with F_1. For the even Fibonacci numbers, the representation involves the successively smaller odd-numbered Fibonacci numbers and the longest representation ends with F_2. For both any even Fibonacci number and the next higher odd Fibonacci number, the number of representations obtained this way and counting the single number as one representation are equal to the number of Fibonacci numbers in the longest representation; thus, there are five representations for F_{10} of which the longest involves the five Fibonacci numbers: $F_9 + F_7 + F_5 + F_3 + F_2$.

The longest of each of the sets of representations appearing in Figure XI-1 does not appear to conform to the Zeckendorf law: Every positive integer can be uniquely represented as the sum of distinct Fibonacci numbers if no consecutive Fibonacci numbers are used in any given sum. The explanation is that, as commonly developed in the Fibonacci literature, an abbreviated sequence, a sequence lacking F_1, is used for convenience (see, for example, Hoggatt, ref. 50, p. 69, Theorem 6; also ref. 52). In the present work, F_1 is included in the interest of obtaining as many representations as possible.

In the representation of any Fibonacci number, the next smaller Fibonacci number may not be omitted for the remaining Fibonacci numbers fall short of a complete representation by one; this is evident from the summation formula

$$\sum_{k=0}^{m} F_k = F_{m+2} - 1 \qquad \text{(XI-S-1)}$$

This defect can be remedied by making F_{-1} a member of the set of Fibonacci numbers being considered:

$$\left\{\sum_{k=0}^{n} F_k\right\} + F_{-1} = F_{n+2} \qquad \text{(XI-S-11)}$$

In the set of weights under construction, a 1-g. weight, designated F_{-1}, is being included; this is reflected in the calibration schedule shown in Figure XI-2. Inclusion of F_{-1}

adds three representations to each Fibonacci number, the additional representation of immediate interest being that composed of all of the weights up to two short of the Fibonacci number being represented, that is, application of equation (XI-S-11). In Figure XI-2, these representations are tracked by a dashed line originating at the summation formula, equation (XI-S-11), reproduced in the upper, left corner.

The goal of the calibration is to derive with the highest accuracy possible the mass of each weight in terms of one of the weights. For the practical purposes of the experimental work, the smallest weight is chosen as the standard and the work proceeds upward. Later, to reduce the size of the departures from the integral values, the calibration is recalculated in terms of the largest weight (1000 g., in this instance). Primarily then, the calibration proceeds vertically, based on the summation theorems. Four of these summation theorems are of direct use and the successive application of each is traced by a dotted line in Figure XI-2.

The mathematical theory by which the data obtained are handled is developed for the principal, 2-weight summation sequence. This development is given in detail below.

In practice, however, the work proceeds horizontally, all of the work of intercomparing all of the representations for a given weight, as displayed on the horizontal rows, being completed before proceeding to the next larger weight.

I. Calculation of Departure from Experimental Data Using Only the Next Two Lighter Weights (Simplest Case)

The simplest representation of a Fibonacci number (weight in this work) is the combination of the preceding two smaller numbers (weights), that is, the representation making use of the basic recursion formula

$$F_n = F_{n-1} + F_{n-2} \qquad \text{(A1)}$$

Starting with F_1, the calibration progresses as follows:

$n = 1 \quad F_1 = 1_{F1} + a_{1F1}$ (A2, definition)

For the purpose of calibration, F_1 is taken as the primary standard. The departure, a_{1F1}, may be arbitrarily taken as zero, although it will certainly take a positive value later when the calibration is recalculated on the basis of a larger weight, and it is best to carry it along in the formal development here.

$n = 2 \quad F_2 = 1_{F2} + a_{1F2}$ (A3, definition)

$F_2 = F_1 + F_0$ (A4, recursion formula)

Experimentally,

$$1_{F2} + a_{1F2} = T_1 + \alpha_{1F2} \qquad \text{(A5-e)}$$

$$1_{F1} + a_{1F1} + 0_{F0} + a_{0F0} = T_1 + \beta_{1,F1+F0} \qquad \text{(A6-e)}$$

The terms F_0 and 0_{F0} mean no weight at all and a_{0F0} is eliminated in practice in the operation of zeroing the balance. Actually, for the zeroing operation a positive reading of the optical scale of the balance is taken, r_z, more or less in the middle of the optical scale (see above). The quantity r_z is eliminated in the immediate handling of the data and for the development here, F_0, 0_{F0}, and a_{0F0} are all zero. Clarity of presentation of the development, however, requires that the symbols be carried along formally.

Elimination of T_1 and cancellation of the integral values 1_{F1} and 1_{F2}, yields

$$a_{1F2} = a_{1F1} + \alpha_{1F2} - \beta_{1,F1+F0} \qquad \text{(A7)}$$

n = 3 $\quad F_3 = 2_{F3} + a_{2F3}$ (A8, definition)

$F_3 = F_2 + F_1$ (A9, recursion formula)

Experimentally,

$$2_{F3} + a_{2F3} = T_2 + \alpha_{2F3} \qquad \text{(A10-e)}$$

$$1_{F2} + a_{1F2} + 1_{F1} + a_{1F1} = T_2 + \beta_{2,F2+F1} \qquad \text{(A11-e)}$$

Giving

$$a_{2F3} = a_{1F2} + a_{1F1} + \alpha_{2F3} - \beta_{2,F2+F1} \qquad \text{(A12)}$$

Introduction of equation (A7) gives

$$a_{2F3} = 2a_{1F1} + \alpha_{1F2} - \beta_{1,F1+F0} + \alpha_{2F3} - \beta_{2,F2+F1} \qquad \text{(A13)}$$

$$n = 4 \quad F_4 = 3_{F4} + a_{3F4} \qquad \text{(A14, definition)}$$

$$F_4 = F_3 + F_2 \qquad \text{(A15, recursion formula)}$$

Experimentally,

$$3_{F4} + a_{3F4} = T_3 + \alpha_{3F4} \qquad \text{(A16-e)}$$

$$2_{F3} + a_{2F3} + 1_{F2} + a_{1F2} = T_3 + \beta_{3,F3+F2} \qquad \text{(A17-e)}$$

Giving

$$a_{3F4} = a_{2F3} + a_{1F2} + \alpha_{3F4} - \beta_{3,F3+F2} \qquad \text{(A18)}$$

Introduction of equations (A13) and (A7) gives

$$a_{3F4} = 3a_{1F1} + 2a_{1F2} - 2\beta_{1,F1+F0} + \alpha_{2F3} - \beta_{2,F2+F1} + \alpha_{3F4} - \beta_{3,F3+F2} \qquad \text{(A19)}$$

$$n = 5 \quad F_5 = 5_{F5} + a_{5F5} \qquad \text{(A20, definition)}$$

$$F_5 = F_4 + F_3 \qquad \text{(A21, recursion formula)}$$

Experimentally,

$$5_{F5} + a_{5F5} = T_5 + \alpha_{5F5} \qquad \text{(A22-e)}$$

$$3_{F4} + a_{3F4} + 2_{F3} + a_{2F3} = T_5 + \beta_{5,F4+F3} \qquad \text{(A23-e)}$$

Giving

$$a_{5F5} = a_{3F4} + a_{2F3} + \alpha_{5F5} - \beta_{5,F4+F3} \qquad \text{(A24)}$$

Introduction of equations (A19) and (A13) gives

$$a_{5F5} = 5a_{1F1} + 3\alpha_{1F2} - 3\beta_{1,F1+F0} + 2\alpha_{2F3} - 2\beta_{2,F2+F1} + \alpha_{3F4} - \beta_{3,F3+F2} + \alpha_{5F5} - \beta_{5,F4+F3} \qquad \text{(A25)}$$

The general formula for the successive departures is itself a Fibonacci sequence, taking the general form

$n = n \quad F_n = |F_n|_{Fn} + a_{|F_n|Fn}$ (A26, definition)

the symbol $|F_n|$ denoting the integral value, in Arabic numerals, of the Fibonacci number F_n.

$F_n = F_{n-1} + F_{n-2}$ (A1, recursion formula)

Experimentally,

$$|F_n|_{Fn} + a_{|F_n|Fn} = T_{|F_n|} + \alpha_{|F_n|Fn} \qquad \text{(A27-e)}$$

$$|F_{n-1}|_{F(n-1)} + a_{|F_{n-1}|F(n-1)} + |F_{n-2}|_{F(n-2)} + a_{|F_{n-2}|F(n-2)} = T_{|F_n|} + \beta_{|F_n|,F(n-1)+F(n-2)} \qquad \text{(A28-e)}$$

Giving

$$\begin{aligned} a_{|F_n|Fn} = {} & |F_n|a_{1F1} + |F_{n-1}|\alpha_{1F2} - |F_{n-1}|\beta_{1,F1+F0} \\ & + |F_{n-2}|\alpha_{2F3} - |F_{n-2}|\beta_{2,F2+F1} \\ & + |F_{n-3}|\alpha_{3F4} - |F_{n-3}|\beta_{3,F3+F2} \\ & \vdots \\ & + |F_1|\alpha_{|F_n|Fn} \\ & \quad - |F_1|\beta_{|Fn|,F(n-1)+F(n-2)} \end{aligned} \qquad \text{(A29)}$$

Thus, for $n = 6$, $F_6 = 8_{F6} + a_{8F6}$, and

$$\begin{aligned} a_{8F6} = 8a_{1F1} &+ 5\alpha_{1F2} - 5\beta_{1,F1+F0} \\ &+ 3\alpha_{2F3} - 3\beta_{2,F2+F1} \\ &+ 2\alpha_{3F4} - 2\beta_{3,F3+F2} \\ &+ \alpha_{5F5} - \beta_{5,F4+F3} \\ &+ \alpha_{8F8} - \beta_{8,F5+F4} \end{aligned} \tag{A30}$$

And for $n = 16$, the weight just below 1000,

$$F_{16} = 987_{F16} + a_{987F16}$$

and

$$\begin{aligned} a_{987F16} = 987a_{1F1} &+ 610\alpha_{1F2} - 610\beta_{1,F1+F0} \\ &+ 377\alpha_{2F3} - 377\beta_{2,F2+F1} \\ &+ 233\alpha_{3F4} - 233\beta_{3,F3+F2} \\ &\vdots \\ &+ \alpha_{610F15} - \beta_{610,F14+F13} \\ &+ \alpha_{987F16} - \beta_{987,F15+F16} \end{aligned} \tag{A31}$$

The magnification that the departure in F_1 has undergone by the time the calibration reaches F_{16} is 987 times. Each of the thirty-two experimental measurements is similarly magnified but by a decreasing, Fibonacci number. Of course, the departures can be negative as well as positive and the final departure in F_{987} may turn out reasonably close to the integral number 987. The importance of independent cross checks on the work is obvious. And that such cross checks are provided is exactly the merit of fabricating the set of weights on the Fibonacci sequence.

J. Calculation of Departure from Experimental Data Using Only the Next Two Lighter Weights But Including F_{-1} in the Set

Some of the most useful of the Fibonacci summation formulas, discussed in a preceding section, involve in the expression for the sum, in addition to a Fibonacci number, the term minus one. By including a third 1-g. weight, such sums can be brought to a Fibonacci number and made use of such summation relations in the calibration of a set of weights. In addition, a third 1-g. weight about doubles the number of calibration operations involving 1-g. weights and contributes considerably to reducing the final uncertainties in the calibration.

Fibonacci number minus one, F_{-1}, has the numerical value positive one and is a legitimate and regular member of the series as expressed by the recursion formula

$$F_n = F_{n-1} + F_{n-2} \tag{AA1}$$

It is logical, therefore, to use F_{-1} as a 1-g. member of the set of weights.

The variation on the development proceeds in the same fashion as before and the final formulas for the successive departures take the same form as before but with three additional terms.

$n = -1 \quad F_{-1} = 1_{F(-1)} + a_{1F(-1)}$ (AA2, definition)

F_{-1} is taken as the primary weight. The departure, $a_{1F(-1)}$, may or may not be zero depending on the circumstances under which the calibration is undertaken.

$n = 0 \quad F_0 = 0_{F0} + a_{0F0}$ (AA3, definition)

The quantities F_0, 0_{F0}, and a_{0F0} are all zero as a result of the steps in the zeroing operation. Clarity in the presentation of the development requires that certain of these symbols be carried along formally.

$n = 1 \quad F_1 = 1_{F1} + a_{1F1}$ (AA4, definition)

$F_1 = 0_{F0} + 1_{F(-1)}$ (AA5, recursion formula)

Experimentally,

$1_{F1} + a_{1F1} = T_1 + \alpha_{1F1}$ (AA6-e)

$$0_{F0} + a_{0F0} + 1_{F(-1)} + a_{1F(-1)} = T_1 + \beta_{1,F0+F(-1)} \quad \text{(AA7-e)}$$

Giving

$$a_{1F1} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} \quad \text{(AA8)}$$

n = 2 $\quad F_2 = 1_{F2} + a_{1F2}$ (AA9, definition)

$F_2 = F_1 + F_0$ (AA10, recursion formula)

Experimentally,

$$1_{F2} + a_{1F2} = T_1 + \alpha_{1F2} \quad \text{(AA11-e)}$$

$$1_{F1} + a_{1F1} + 0_{F0} + a_{0F0} = T_1 + \beta_{1,F1+F0} \quad \text{(AA12-e)}$$

Giving

$$a_{1F2} = a_{1F1} + \alpha_{1F2} - \beta_{1,F1+F0} \quad \text{(AA13)}$$

Introducing equation (AA8) gives

$$a_{1F2} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} + \alpha_{1F2} - \beta_{1,F1+F0} \quad \text{(AA14)}$$

The terms α_{1F1} and $\beta_{1,F1+F0}$ are identical if the zeroing operation is carried out correctly and these terms cancel, giving

$$a_{1F2} = a_{1F(-1)} + \alpha_{1F2} - \beta_{1,F0+F(-1)} \quad \text{(AA14A)}$$

Equation (AA14A) is identical in form to equation (AA8), as expected and a consequence of F_1 and F_2 both having the numerical value of one. Equation (AA14) is used in subsequent work to maintain completeness in the interesting, inverse Fibonacci sequence developing.

n = 3

$$F_3 = 2_{F3} + a_{2F3} \tag{AA15, definition}$$

$$F_3 = F_2 + F_1 \tag{AA16, recursion formula}$$

Experimentally,

$$2_{F3} + a_{2F3} = T_2 + \alpha_{2F3} \tag{AA17-e}$$

$$1_{F2} + a_{1F2} + 1_{F1} + a_{1F1} = T_2 + \beta_{2,F2+F1} \tag{AA18-e}$$

Giving

$$a_{2F3} = a_{1F2} + a_{1F1} + \alpha_{2F3} - \beta_{2,F2+F1} \tag{AA19}$$

Introducing equations (AA14) and (AA8) gives

$$\begin{aligned} a_{2F3} = 2a_{1F(-1)} &+ 2\alpha_{1F1} - 2\beta_{1,F0+F(-1)} \\ &+ \alpha_{1F2} - \beta_{1,F1+F0} \\ &+ \alpha_{2F3} - \beta_{2,F2+F1} \end{aligned} \tag{AA20}$$

n = 4

$$F_4 = 3_{F4} + a_{3F4} \tag{AA21, definition}$$

$$F_4 = F_3 + F_2 \tag{AA22, recursion formula}$$

Experimentally,

$$3_{F4} + a_{3F4} = T_3 + \alpha_{3F4} \tag{AA23-e}$$

$$2_{F3} + a_{2F3} + 1_{F2} + a_{1F2} = T_3 + \beta_{3,F3+F2} \tag{AA24-e}$$

Giving

$$a_{3F4} = a_{2F3} + a_{1F2} + \alpha_{3F4} - \beta_{3,F3+F2} \qquad \text{(AA25)}$$

Introducing equations (AA20) and (AA14) gives

$$\begin{aligned} a_{3F4} = 3a_{1F(-1)} &+ 3\alpha_{1F1} - 3\beta_{1,F0+F(-1)} \\ &+ 2\alpha_{1F2} - 2\beta_{1,F1+F0} \\ &+ \alpha_{2F3} - \beta_{2,F2+F1} \\ &+ \alpha_{3F4} - \beta_{3,F3+F2} \end{aligned} \qquad \text{(AA26)}$$

n = 5 $\quad F_5 = 5_{F5} + a_{5F5}$ (AA27, definition)

$$F_5 = F_4 + F_3 \qquad \text{(AA28, recursion formula)}$$

Experimentally,

$$5_{F5} + a_{5F5} = T_5 + \alpha_{5F5} \qquad \text{(AA29-e)}$$

$$3_{F4} + a_{3F4} + 2_{F3} + a_{2F3} = T_5 + \beta_{5,F4+F3} \qquad \text{(AA30-e)}$$

Giving

$$a_{5F5} = a_{3F4} + a_{2F3} + \alpha_{5F5} - \beta_{5,F4+F3} \qquad \text{(AA31)}$$

Introducing equations (AA26) and (AA20) gives

$$\begin{aligned} a_{5F5} = 5a_{1F(-1)} &+ 5\alpha_{1F1} - 5\beta_{1,F0+F(-1)} \\ &+ 3\alpha_{1F2} - 3\beta_{1,F1+F0} \\ &+ 2\alpha_{2F3} - 2\beta_{2,F2+F1} \\ &+ \alpha_{3F4} - \beta_{3,F3+F2} \\ &+ \alpha_{5F5} - \beta_{5,F4+F3} \end{aligned} \qquad \text{(AA32)}$$

The equation which is developing for the departures is itself a Fibonacci sequence, taking the general form

$$n = n \qquad F_n = |F_n|_{Fn} + a_{|F_n|Fn} \qquad \text{(AA33, definition)}$$

the symbol $|F_n|$ denoting the integral value, in Arabic numerals, of the Fibonacci number F_n.

$$F_n = F_{n-1} + F_{n-2} \qquad \text{(A1, recursion formula)}$$

Experimentally,

$$|F_n|_{Fn} + a_{|F_n|Fn} = T_{|F_n|} + \alpha_{|F_n|Fn} \qquad \text{(AA34-e)}$$

$$\begin{aligned} &|F_{n-1}|_{F(n-1)} + a_{|F_{n-1}|F(n-1)} + |F_{n-2}|_{F(n-2)} \\ &\quad + a_{|F_{n-2}|F(n-2)} = T_{|F_n|} \\ &\quad + \beta_{|F_n|,F(n-1)+F(n-2)} \end{aligned} \qquad \text{(AA35-e)}$$

Giving

$$\begin{aligned} a_{|F_n|Fn} = {} & |F_n|a_{1F(-1)} + |F_n|\alpha_{1F1} - |F_n|\beta_{1,F0+F(-1)} \\ & + |F_{n-1}|\alpha_{1F2} - |F_{n-1}|\beta_{1,F1+F0} \\ & + |F_{n-2}|\alpha_{2F3} - |F_{n-2}|\beta_{2,F2+F1} \\ & + \ldots\ldots \\ & + \ldots\ldots \\ & + |F_1|\alpha_{|F_n|Fn} - |F_1|\beta_{|F_n|,F(n-1)+F(n-2)} \end{aligned} \qquad \text{(AA36)}$$

Thus, for n = 6

$$\begin{aligned} a_{8F6} = 8a_{1F(-1)} &+ 8\alpha_{1F1} - 8\beta_{1,F0+F(-1)} \\ &+ 5\alpha_{1F2} - 5\beta_{1,F1+F0} \\ &+ 3\alpha_{2F3} - 3\beta_{2,F2+F1} \\ &+ 2\alpha_{3F4} - 2\beta_{3,F3+F2} \\ &+ \alpha_{5F5} - \beta_{5,F4+F3} \\ &+ \alpha_{8F6} - \beta_{8,F5+F4} \end{aligned} \qquad \text{(AA37)}$$

And for F_{16}, the weight just below 1000,

n = 16 $\quad F_{16} = 987_{F16} + a_{987F16}$ (AA38, definition)

$F_{16} = F_{15} + F_{14}$ (AA39, recursion formula)

$$\begin{aligned} a_{987F16} = 987a_{1F(-1)} &+ 987\alpha_{1F1} - 987\beta_{1,F0+F(-1)} \\ &+ 610\alpha_{1F2} - 610\beta_{1,F1+F0} \\ &+ 377\alpha_{2F3} - 377\beta_{2,F3+F2} \\ &\vdots \\ &+ 2\alpha_{377F14} - 2\beta_{377,F13+F12} \\ &+ \alpha_{610F15} - \beta_{610,F14+F13} \\ &+ \alpha_{987F16} - \beta_{987,F15+F14} \end{aligned}$$

(AA40)

K. Calculation of Departure from Experimental Data. Horizontal Approach. Combined Treatment of All Representations of Each Weight in Succession

In the two preceding sections, a method was developed for handling the data obtained in a calibration operation on a vertical basis, that is, for a calibration operation proceeding from the 1-g. weight, F_1, to the 987-g. weight, F_{16}. In this particular procedure, only two weights were used at each step, a procedure based on the fundamental recursion formula $F_n = F_{n-1} + F_{n-2}$. The development was made first for a set of Fibonacci weights having as the smallest weight F_1, and was made again for a set having as the smallest weight F_{-1}, that is, for a set having three 1-g. weights.

In this process of passing from the smallest to the largest weight, the departures in the small weights plus the uncertainty inherent in each experimental measurement become increasingly greatly magnified. Short of some considerable amount of contrivance or sheer accident, the departure in any given weight will have some real value, positive or negative. The very objective of a calibration is to determine the best value for each of these departures and for the imputation (the set of departures), making the latter not only as internally consistent as possible, but correct on an absolute basis (in terms of the weight taken as standard).

The great magnification in the departures of the 1-g. weights is shown, for example, in equation (AA40) for F_{16}, and the very limited number of representations for the 1-g. weights would appear to make the intercomparison of the three 1-g. weights, $F_{(-1)}$, F_1 and F_2, crucial indeed. However, it is one of the most astonishing features of the Fibonacci sequence of weights beginning with F_{-1} that by the time the calibration work has been completed through F_{16}, sixteen independent intercomparisons of these three 1-g. weights will have been made. This surprising feature emerges from the following development together with the observation that at any particular stage in the calibration, the actual values of the departures of the lighter weights need not be known. Only the experimentally measured terms are carried forward. The departures of the lighter weights can be calculated at any stage but this is not necessary for the development and is reserved for one grand treatment when the experimental work is finished.

In the following material, equations which are repetitions of equations in the preceding section are numbered the same, that is, with the prefix AA.

n = -1 $a_{1F(-1)}$ = zero, or some assigned value depending on the value given the primary standard weight, F_{-1}.

n = 0 a_{0F0} = zero; made zero by the act of zeroing the balance.

n = 1 There are two representations, F_1 and F_{-1}, as shown in Figure XI-2. These lead to two experimental equations, (AA6-e) and (AA7-e), which lead to the final equation

$$a_{1F1} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} \tag{AA8}$$

n = 2 $F_2 = 1_{F2} + a_{1F2}$ (AA9, definition)

Experimentally, using the three representations

$$1_{F2} + a_{1F2} = T_1 + \alpha_{1F2} \tag{AA11-e}$$

$$1_{F1} + a_{1F1} = T_1 + \beta_{1,F1+F0} \tag{AA12-e}$$

$$0_{F0} + a_{0F0} + 1_{F(-1)} + a_{1F(-1)} = T_1 + \beta_{1,F0+F(-1)} \tag{B1-e}$$

Combination of equations (AA11-e) and (AA12-e) and introduction of equation (AA8) give

$$a_{1F2} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} + \alpha_{1F2} - \beta_{1,F1+F0} \tag{AA14}$$

Combination of equations (AA11-e) and (B1-e) gives

$$a_{1F2} = a_{1F(-1)} + \alpha_{1F2} - \beta_{1,F0+F(-1)} \tag{B2}$$

The experimental equations (AA11-e), (AA12-e) and (B1-e) thus lead to two equations for a_{1F2}. Combination of equations (AA12-e) and (B1-e) gives another equation for a_{1F1}:

$$a_{1F1} = a_{1F(-1)} + \beta_{1,F1+F0} + \beta_{1,F0+F(-1)} \tag{B3}$$

This *carry back* equation is the first of such equations which characterize the subsequent development; because of the nature of F_0, this equation is identical with equation (AA8).

$n = 3$ $\quad F_3 = {}^2_{F3} + a_{2F3}$ (AA15, definition)

Experimentally, using the four representations

$$^2{}_{F3} + a_{2F3} = T_2 + \alpha_{2F3} \tag{AA17-e}$$

$$^1{}_{F2} + a_{1F2} + {}^1{}_{F1} + a_{1F1} = T_2 + \beta_{2,F2+F1} \tag{AA18-e}$$

$$^1{}_{F1} + a_{1F1} + {}^1{}_{F(-1)} + a_{1F(-1)} = T_2 + \beta_{2,F1+F(-1)} \tag{B4-e}$$

$$^1{}_{F2} + a_{1F2} + {}^1{}_{F(-1)} + a_{1F(-1)} = T_2 + \beta_{2,F2+F(-1)} \tag{B5-e}$$

Combination of equations (AA17-e) and (AA18-e) and introduction of equations (AA14) and (AA8) give

$$a_{2F3} = 2a_{1F(-1)} + 2\alpha_{1F1} - 2\beta_{1,F0+F(-1)} + \alpha_{1F2} - \beta_{1,F1+F0} + \alpha_{2F3} - \beta_{2,F2+F1} \tag{AA20}$$

Combination of equations (AA17-e) and (B4-e) gives

$$a_{2F3} = a_{1F1} + a_{1F(-1)} + \alpha_{2F3} - \beta_{2,F1+F(-1)} \tag{B6}$$

and introduction of equation (AA8) gives

$$a_{2F3} = 2a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} + \alpha_{2F3} - \beta_{2,F1+F(-1)} \tag{B7}$$

Combination of equations (AA17-e) and (B5-e) gives

$$a_{2F3} = a_{1F2} + a_{1F(-1)} + \alpha_{2F3} - \beta_{2,F2+F(-1)} \tag{B8}$$

and introduction of equation (AA14) gives

$$a_{2F3} = 2a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)} + \alpha_{1F2} - \beta_{1,F1+F0} + \alpha_{2F3} - \beta_{2,F2+F(-1)} \tag{B9}$$

Equations (AA17-e), (AA18-e), (B4-e), and (B5-e) thus provide three independent checks on a_{2F3} (equations (AA20), (B7), and (B9)). Moreover, by elimination of T_2 and of a_{2F3}, they provide independent checks on a_{1F1} and a_{1F2}. These are, in effect, measurements against a different tare (T_2 - (2_{F3} + a_{2F3})). Thus, combination of equations (B5-e) and (AA18-e) yields

$$a_{1F1} = a_{1F(-1)} + \beta_{2,F2+F1} - \beta_{2,F2+F(-1)} \qquad \text{(B10)}$$

and combination of equations (B4-e) and (AA18-e) yields

$$a_{1F2} = a_{1F(-1)} + \beta_{2,F2+F1} - \beta_{2,F1+F(-1)} \qquad \text{(B11)}$$

$n = 4$ $\quad F_4 = 3_{F4} + a_{3F4}$ (AA21, definition)

Experimentally, five representations

$$3_{F4} + a_{3F4} = T_3 + \alpha_{3F4} \qquad \text{(AA23-e)}$$

$$2_{F3} + a_{2F3} + 1_{F2} + a_{1F2} = T_3 + \beta_{3,F3+F2} \qquad \text{(AA24-e)}$$

$$2_{F3} + a_{2F3} + 1_{F1} + a_{1F1} = T_3 + \beta_{3,F3+F1} \qquad \text{(C1-e)}$$

$$2_{F3} + a_{2F3} + 1_{F(-1)} + a_{1F(-1)} = T_3 + \beta_{3,F3+F(-1)} \qquad \text{(C2-e)}$$

$$1_{F2} + a_{1F2} + 1_{F1} + a_{1F1} + 1_{F(-1)} + a_{1F(-1)} = T_3 + \gamma_{3,F2+F1+F(-1)} \qquad \text{(C3-e)}$$

Combination of equations (AA23-e), (AA24-e), and (AA14) gives [basic recursion formula; two weights]:

$$\begin{aligned} a_{3F4} = 3a_{1F(-1)} &+ 3\alpha_{1F1} - 3\beta_{1,F0+F(-1)} \\ &+ 2\alpha_{1F2} - 2\beta_{1,F1+F0} \\ &+ \alpha_{2F3} - \beta_{2,F2+F1} \\ &+ \alpha_{3F4} - \beta_{3,F3+F2} \end{aligned} \qquad \text{(AA26)}$$

Combination of equations (AA23-e), (C1-e), (AA20), and (AA8) gives [additional; two weights]:

$$\begin{aligned} a_{3F4} = 3a_{1F(-1)} &+ 3\alpha_{1F1} - 3\beta_{1,F0+F(-1)} \\ &+ \alpha_{1F2} - \beta_{1,F1+F0} \\ &+ \alpha_{2F3} - \beta_{2,F2+F1} \\ &+ \alpha_{3F4} - \beta_{3,F3+F1} \end{aligned} \qquad \text{(C4)}$$

Combination of equations (AA23-e), (C2-e), and (AA20) gives [additional; two weights]:

$$\begin{aligned} a_{3F4} = 3a_{1F(-1)} &+ 2\alpha_{1F1} - 2\beta_{1,F0+F1} \\ &+ \alpha_{1F2} - \beta_{1,F1+F0} \\ &+ \alpha_{2F3} - \beta_{2,F2+F1} \\ &+ \alpha_{3F4} - \beta_{3,F3+F(-1)} \end{aligned} \qquad \text{(C5)}$$

Combination of equations (AA23-e), (C3-e), (AA8), and (AA14) gives [all smaller weights; three weights]:

$$\begin{aligned} a_{3F4} = 3a_{1F(-1)} &+ 2\alpha_{1F1} - 2\beta_{1,F0+F(-1)} \\ &+ \alpha_{1F2} - \beta_{1,F1+F0} \\ &+ \alpha_{3F4} - \gamma_{3,F2+F1+F(-1)} \end{aligned} \qquad \text{(C6)}$$

Thus, five data lead to four independent equations for a_{3F4}. The five experimental measurements expressed by equations (AA23-e), (AA24-e), (C1-e), (C2-e), and (C3-e) can also be used to obtain additional values for the smaller weights, F_1, F_2, and F_3; these values are independent of the earlier values inasmuch as the measurements are made against a different tare $(T_3 - (3_{F4} - a_{3F4}))$.

Combination of equations (C1-e) and (C2-e) gives

$$a_{1F1} = a_{1F(-1)} + \beta_{3,F3+F1} - \beta_{3,F3+F(-1)} \qquad (C7)$$

Combination of equations (AA24-e) and (C2-e) gives

$$a_{1F2} = a_{1F(-1)} + \beta_{3,F3+F2} - \beta_{3,F3+F(-1)} \qquad (C8)$$

Combinations of equations (AA24-e), (C3-e), and (C7) gives

$$a_{2F3} = a_{1F(-1)} + \beta_{3,F3+F1} - \beta_{3,F3+F(-1)} + \beta_{3,F3+F2} - \gamma_{3,F2+F1+F(-1)} \qquad (C9)$$

Recapitulating, the various equations, including the carry back equations, are:

n = -1 $a_{1F(-1)}$ = zero, or some assigned value.

n = 0 a_{0F0} = zero; made zero by the act of zeroing the balance.

n = 1 $a_{1F1} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)}$ (AA8)

$= a_{1F(-1)} + \beta_{2,F2+F1} - \beta_{2,F2+F(-1)}$ (B10)

(Carry back from n = 3)

$= a_{1F(-1)} + \beta_{3,F3+F1} - \beta_{3,F3+F(-1)}$ (C7)

(from n = 4)

$= a_{1F(-1)} + \gamma_{5,F4+F2+F1} - \gamma_{5,F4+F1+F(-1)}$ (C22)

(from n = 5)

$$n = 2 \qquad a_{1F2} = a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)}$$

$$+ \alpha_{1F2} - \beta_{1,F1+F0} \qquad \text{(AA14)}$$

$$= a_{1F(-1)} + \alpha_{1F2} - \beta_{1,F0+F(-1)} \qquad \text{(B2)}$$

$$= a_{1F(-1)} + \beta_{2,F2+F1} - \beta_{2,F1+F(-1)} \qquad \text{(B11)}$$

(from $n = 3$)

$$= a_{1F(-1)} + \beta_{3,F3+F2} - \beta_{3,F3+F(-1)} \qquad \text{(C8)}$$

(from $n = 4$)

$$= a_{1F(-1)} + \gamma_{5,F4+F2+F1} - \gamma_{5,F4+F1+F(-1)} \qquad \text{(C24)}$$

(from $n = 5$)

$$n = 3 \qquad a_{2F3} = a_{1F(-1)} + 2\alpha_{1F1} - 2\beta_{1,F0+F(-1)}$$

$$+ \alpha_{1F2} - \beta_{1,F1+F0}$$

$$+ \alpha_{2F3} - \beta_{2,F2+F1} \qquad \text{(AA20)}$$

$$= 2a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)}$$

$$+ \alpha_{2F3} - \beta_{2,F1+F(-1)} \qquad \text{(B7)}$$

$$= a_{1F(-1)} + \alpha_{1F1} - \beta_{1,F0+F(-1)}$$

$$+ \alpha_{1F2} - \beta_{1,F1+F0}$$

$$+ \alpha_{2F3} - \beta_{2,F2+F(-1)} \qquad \text{(B9)}$$

$$= a_{1F(-1)} + \alpha_{3,F3+F1} - \beta_{3,F3+F(-1)}$$

$$+ \alpha_{3,F3+F2} - \gamma_{3,F2+F1+F(-1)} \qquad \text{(C9)}$$

(from $n = 4$)

$n = 4$ a_{3F4} = see preceding section, equations (AA26), (C4), (C5) and (C6) for the four independent equations.

At the time this dissertation was written, work on $n = 5$ was proceeding.

XII. SUMMARY

A. Chapter I

The history of recent work on the faraday, the fundamental constant interconnecting chemistry and electricity, has been reviewed and a tabulation of recent values for the faraday has been made. Emphasis has been placed on the continuing discrepancy between values obtained by direct electrochemical experimentation and by calculation from other physical data. Although the assumption of 100.0000 per cent current efficiency during electrolysis has been called into question by the work of Palit, the greatest source of error causing the discrepancy has been attributed to the measurement of mass, a measurement which must be made in such work on an absolute basis.

The principal problems encountered in measuring mass with an uncertainty less than one part per million have been identified as residing in: (1) the determination of the density of a solid (object weighed and weights), a measurement fraught with surprising difficulties even at the one part per thousand level; (2) the correction for the buoyancy of air on object weighed and weights; in turn dependent on (3) the density of air, again a surprisingly difficult measurement; (4) the calibration of weights, in turn dependent on the transfer of mass from the standard, platinum-iridium kilogram to stainless steel working kilograms and the subdivision of the kilogram into the smaller laboratory weights as affected by the correction for buoyancy and for surface effects.

B. Chapter II

The procedures for the determination of the density of a solid have been examined in detail. A review has been made of the various methods used and of the widely varying results obtained for the density of 4-aminopyridine, a primary chemical used in the evaluation of the faraday. The source of these variations has been traced to the presence in the crystals of long, tubular, cavities, some running the length of the crystals. A method of circumventing the troublesome effects of these cavities, the fusion of the 4-aminopyridine under mild pressure in an inert gas, has been proposed. Variations of three parts per thousand have been found in the densities of various lots of a stainless steel, Carpenter 20CB3, a corrosion-resistant alloy proposed for the construction of high-precision weights. Reasons for the variations have been advanced and the conclusion emphasized that the density of each weight in a set must be determined individually.

C. Chapter III

The correction for the buoyancy of air on object being weighed and weights during a weighing has been examined exhaustively, first theoretically and then experimentally, by two approaches: the invention of an *absolute density cylinder* for the direct measurement of the density of air and by calculation from high-precision measurements of the barometric pressure and temperature and gravimetric determination of the water and carbon dioxide content of the air.

A survey has been made of the use of sealed, hollow vessels, known as *Baxter's Globes*, for the determination of the density of air (a continuation essentially of material presented in my thesis for the degree Master of Science). While the devices used to date have yielded values agreeing to about one part per thousand with values calculated from the prevailing conditions, none have offered a check on the conformity of moist air to the gas laws inasmuch as the calibration involves an air of known density, that is, a density calculated from the prevailing conditions and thus based on the assumptions that the moist air conforms to the gas laws and that the composition of the atmosphere is constant. The characteristics of an ideal Baxter's globe have been listed and such a vessel, in the form of a hollow, perfect right cylinder of stainless steel and called an *absolute density cylinder*, has been devised and fabricated.

The way to obtain the density of this hollow vessel without reference to an air of known density has been shown.

The mathematical equations for calculating the correction for buoyancy and for calculating the density of air from the prevailing conditions have been differentiated and the various coefficients relating the change in density to changes in the individual variables evaluated. For an uncertainty in the density of air of one part per thousand, the corresponding, permissible variation has been calculated for the measurements of barometric pressure, temperature, vapor pressure of water, and relative humidity. The conditions in the laboratory and the devices to measure the prevailing conditions have been appraised in light of these permissible uncertainties and these findings have been used in arriving at decisions regarding improvements in the laboratory and in the measuring devices.

Preliminary experience with an absolute density cylinder, measurements being made at different elevations (Ames, 950 ft.; Boulder, 6600 ft.; Laramie 6700 ft.) has shown that: (1) the normal, in-house and high-grade, traveling, aneroid barometers are very temperature dependent; (2) that 0.1°-thermometers, even when calibrated, at best are not adequate; (3) that fluctuations in the temperature within a balance case, even though the balance be carefully mounted and protected, renders precision weighings about impossible; and (4) that adequate knowledge of the water content and, of course, of the carbon dioxide content of an atmosphere can only be obtained by chemical analysis. An extensive program has been mounted, aimed at obtaining an absolute value for the density of air with an uncertainty less than four parts per 10,000, the principal steps being to surmount the defects in each of the individual measurements involved.

D. Chapter IV

A walk-in constant temperature box, 10 ft. by 5 ft. in floor area and 8 ft. tall, has been constructed to house balances, barometer, cathetometer, gas pipet, absorption tubes, and other gear. The temperature within this box was held within ±0.075°, the box itself being located within a constant temperature room (Room 137A Chemistry Hall) held within ±1°. The temperature within the constant temperature box was held uniform by a continual circulation of air through duct work and by the presence in the box of heat sinks in the form of some 100 gallons of water and some 2600 pounds of concrete (the supporting piers for the instruments). The incoming air was warmed by electric heaters in the duct work as measured by thermistors and controlled electronically. The temperature at suitable places within the box was measured by platinum resistance thermometers. A source of heat, 123 watts, closely equal to the body heat of the operator, was operated continually except when the operator was present.

Piers for the instruments have been built of alternating layers of concrete block (treated to eliminate dusting) and sheets of plastic foam, thus providing firm and loose coupling needed to eliminate vibrations. The piers rested on concrete slabs poured on the original, poured-and-reinforced concrete flooring of the building and located close to an outside wall of the building. The piers, and instruments, were isolated physically from the asphalt floor of the building and from all elements of the constant temperature box. No vibration was observed on these piers from local or distant (railroad train) traffic.

Temperature within the constant temperature box and within the balance case, both in the compartment enclosing the pan and that enclosing the beam, have been measured with platinum resistance thermometers. These instruments have been calibrated by Mr. Anderson and Professor Swenson of the Department of Physics against standards calibrated at the National Bureau of Standards. The instrumentation, circuit, constant current sources, and White double potentiometer, necessary to make the measurements have been described.

A Fortin-type barometer with two large-bore, glass, vertical tubes and a large cistern, 12 in. in diameter, has been constructed. With this barometer, the pressure of the atmosphere in the constant temperature box has been measured accurately. The height of the mercury column in this barometer was measured with a Wild Heerbrugg cathetometer working in conjunction with a micrometer used to measure changes in the height of the mercury in the cistern. The space above the mercury in the closed tube of this barometer was evacuated with an oil pump (the barometer being protected from oil from the pump by a liquid air trap) and the gas pressure in this space was measured with a thermocouple pressure gauge.

Readings of barometric pressure made with this instrument have been corrected for (a) the expansion of the glass scale of the cathetometer from the temperature, 20°, at which it was calibrated, (b) reduction of the height of the mercury column at 0°, and (c) conversion of the height of the mercury column from the local acceleration of gravity, 980,292.96 mgal., to standard gravity (45° longitude and sea level), 980,665 mgal.

A dry, gas pipet has been designed, built, and used for measuring the volume of a large sample of gas, about 3000 cm.^{3}, with an accuracy of 4 parts per 10,000. This was a piston-cylinder device with a precision-bored cylinder and provision for measuring the displacement of the piston of 0.001 in. Leakage under moderate pressure has been eliminated by the use of O-rings on the piston and the design was such that the face of the piston was maintained perfectly perpendicular to the axis of the cylinder. The piston was screw-driven by a variable-speed, reversible electric motor so that the sample of gas could be drawn in or expelled at any convenient rate. The gas pipet has been used in conjunction with dry absorbents, anhydrous magnesium perchlorate and Ascarite, for the high-precision determination of water and of carbon dioxide in the atmosphere inside the case of a balance.

A bench mark, a stainless steel plate anchored in the floor, has been established in Room 137A Chemistry Hall, Iowa State University. The elevation of this bench mark has been determined by first-order leveling to be 291.533 m. above mean sea level, the standard error in this value being estimated to be 2 mm. The presence through central Iowa of the Midcontinent Gravity Anomaly and the location of Ames on the adjacent low-gravity band make the usual calculation of the local acceleration of gravity from latitude and altitude inaccurate. The knowledge of the altitude of Room 137A and of the pans of balances on the pier in this room may, however, prove of interest in some future work.

The acceleration of gravity at the bench mark in the floor of Room 137A and at the level of the pans of balances mounted on the pier in the constant temperature box has been determined with a Worden Gravity Meter and related to the Iowa Gravity Base Station Network and thus to the U. S. National Base Net at Station Minneapolis. The following values have been obtained: Bench Mark 137A, 980,293.38 mgal.; top of balance pier, 980,292.96 mgal.

E. Chapter V

Three Mettler, single-pan balances, covering different ranges, have been acquired, modified, and mounted on specially built piers in a constant temperature room. These balances were respectively: a Mettler Model H315 Kilogram Balance, capacity 1 kg., optical readout 1 g. in 10,000 divisions of 0.1 mg.; a Mettler Model H51AR Semimicro-balance, capacity 160 g., optical readout 0.1 g. in 10,000 scale divisions of 10 μg.; a Mettler Model M5/SA, capacity 20 g., optical readout 10 mg. in 10,000 divisions of 1 μg.

The capacity of the kilogram balance has been increased by the installation of additional stainless steel counterweights, bringing the capacity of 1164 g. so as to accommodate a kilogram weight plus a stainless steel vacuum weighing bottle.

The sensitivity of the kilogram balance has been greatly increased by the installation of a new, much heavier, sensitivity nut. At a sensitivity of 3 μg. per optical scale division, the zero-point has been found subject to unexplainable, erratic fluctuations and the final sensitivity chosen for routine work was 6.5 μg. per division. A technique for calibrating the optical scale at the increased sensitivity has been developed. Similar modifications have been made to the semimicrobalance, final sensitivity being 3.0 μg. per optical scale division.

The taring mechanism of the kilogram balance, and of the semimicrobalance, supplied by the manufacturer has been removed and a further improvement in the reproducibility of the zero-point obtained.

Experience has shown that the Mettler single-pan balance at increased sensitivity tends to behave erratically and this behavior has been traced to electrostatic effects. The construction of the balances makes them in effect sensitive electrometers, responding, for example, to charges induced by the mere presence of a human body four feet away. These effects have been eliminated by enclosing the balances in an electrically-grounded metal shell, by electrically grounding the operator and nearby persons, by installing a grounded wire screen to cover all glass walls, by penetrating the enamel finish and grounding all metal walls, by placing inside the lower and upper chambers uranium compounds in open plastic tubes, by placing fine points (sewing needles) on the electrically insulated parts (pan, stirrup, yoke and beam) of the balance, and by installing grounded brush wires by which the insulated, moving parts, which cannot be permanently grounded, could be touched lightly and momentarily for the removal of electrostatic charge.

The kilogram balance has been further modified by the installation on the beam release handle of a stop so that the beam could be partially arrested without removing the knife edges from the plates; in this position the beam was held firmly enough to permit change in the load on the pan but the exact positioning of the knife edges on the plates not altered during a sequence of weighings.

The Mettler balances have been further modified by removing the electric transformers used to power the lamps which illuminate the optical readout scale from the balance case. The lamp housing also was rebuilt to place it farther from the balance case and to provide several layers of heat insulation and infrared-absorbing glass between lamp and balance case. In these ways, operation of the lamp has been made to have no effect on the temperature within the balance and on the zero-point.

F. Chapter VI

A hollow cylinder of stainless steel has been made in the shape of a perfect right cylinder. The external volume of this cylinder has been calculated from precise measurements of the dimensions. The mass of this cylinder has been determined in an actual vacuum. Thus, the density of the cylinder has been obtained directly from the physical measurements. The density of air has been obtained by weighing this cylinder in air and combining this mass with the density of the cylinder. The method has been further improved by preparing a solid counterweight, a tube of stainless steel, having the same mass and the same surface area and handling it in the same manner and simultaneously with the cylinder; surface moisture effects have thus been eliminated. Because a prior knowledge of the density of air is not involved in determining either the mass or the volume of the cylinder or the counterweight, this cylinder is referred to as an *absolute density cylinder*.

The cylinder was constructed of thin-walled (0.001 in.) stainless steel tubing, the ends closed with caps of stainless steel sealed into place by electron beam welding. When finished, the cylinder was highly polished, was 1 in. in diameter and 2.5 in. in length, and was only 17 g. in mass so that it could be weighed accurately on the microbalance. Three such absolute density cylinders were made.

The diameter and length of each of the three cylinders have been measured precisely on an optical comparator calibrated against gage blocks. The uncertainty in the volume calculated for each of the cylinders, close to one part per thousand, although just sufficiently good to enable a measurement of the density of air with sufficient accuracy to permit a correction for buoyancy to be made to one part per million, was still considered unacceptably large. The major source of the uncertainty was traced to minor dents and scratches in the thin-walled tubing used.

An adjustable lapping block has been devised by which two of the cylinders have been lapped to remove surface imperfections. This device consisted of a block of brass bored lengthwise and slotted lengthwise from the outside into the bore. By suitably placed bolts, the width of the slot, and thus the diameter of the bore, could be changed. The block was placed around the cylinder to be lapped, the cylinder turned slowly in a lathe, and a suspension of grinding compound fed into the block. As the cylinder turned, the block was moved back and forth and the diameter of the bore of the lapping block occasionally reduced. Absolute density cylinders Number 2 and Number 3 have been so polished. Repetition of the measurements of diameter and length has shown that improvement in the physical characteristics resulted, the uncertainty (standard deviation) in the volume being reduced by half. Unfortunately, the strains relieved or produced during the lapping caused cracks in the weld and both cylinders were rendered useless.

Measurement of the dimensions of absolute density cylinder Number 1 (no lapping) has been repeated in another shop with another set of gage blocks. The agreement between the volumes calculated was good (31.769,8 cm.^{3} and 31.784,4 cm.^{3}; difference, 43.2 parts per 100,000) and the uncertainties (standard deviations) at the same level, 98 parts in 100,000. The volume of the cylinder has also been determined by hydrostatic weighing, in water (three determinations) and in the completely fluorinated hydrocarbon FC-75 (four determinations). The values for the volumes (water, 31.778,6 cm.^{3}; FC-75, 31.777,8 cm.^{3}) agree closely and the average of the two departed from the average obtained from the dimensions by 3.46 parts in 100,000. The precision of the hydrostatic measurements, however, was considerably better, the uncertainties (standard deviations) being 4.4 parts per 100,000 for the measurements in water and 1.6 parts in 100,000 for those in FC-75. It has been concluded that the best value for the volume of absolute density cylinder Number 1 is 31.778,2 cm.^{3} at 22.5°.

A counterweight has been fabricated to match absolute density cylinder Number 1 in both mass and surface area, the latter characteristic being built in so that effects of changes in adsorbed water with changing humidity would affect both objects alike. The counterweight has been made of stainless steel in the form of a tube. The counterweight has been subjected to the same sets of measurements as was the cylinder: two independent sets of measurements of the length and internal and external diameters, hydrostatic weighing in water, and hydrostatic weighing in FC-75. The volumes obtained and the uncertainty (standard deviation in parts per 100,000) were: from the dimensions (ISU), 2.080,91 cm.^{3} (227); from the dimensions (Hach), 2.092,47 cm.^{3} (63); by hydrostatic weighing in water, 2.102,4 cm.^{3} (36); by hydrostatic weighing in FC-75, 2.101,9 cm.^{3} (2.8). It has been concluded that the best value for the volume of the tubular counterweight was 2.102,2 cm.^{3}.

G. Chapter VII

A *vacuum weighing bottle* has been invented by which the mass ("true mass", "mass in vacuum") of an object can be measured in an actual vacuum. The vacuum weighing bottle consists of a hollow, thin-walled cylinder of stainless steel closed permanently at one end. The other end is closed by a cap which bears on an O-ring carried in a groove on a flange on the end of the cylinder. The cap carries a vacuum valve and a fitting for attachment to a vacuum line. The weighing bottle is evacuated and weighed, then opened and an object inserted, then again evacuated and again weighed. The buoyant force of air on the bottle being the same during each weighing, the difference in the observed masses gives the mass of the object. Adsorbed moisture and other volatile materials are removed from the surface of the object during the evacuation.

By means of the vacuum weighing bottle, the masses of hollow, absolute density cylinder Number 1 and its solid, tubular counterweight have been determined in an actual vacuum. The uncertainty in the difference between the two objects, 0.033,19 g., is estimated to be three parts in 10,000.

A second vacuum weighing bottle, larger in size to accommodate a kilogram mass of stainless steel, has also been fabricated.

H. Chapter VIII

A series of measurements of the density of air have been made by weighing hollow, stainless steel cylinder Number 1 and its counterweight of equal area and mass; simultaneously, measurements of the prevailing conditions of barometric pressure, temperature, and relative humidity have been made and the density of air obtained by calculation. Nine sets of such measurements have been made during a seventeen day period, August 6 to 22, 1979, during which time the barometric pressure and the density fell, rose, remained steady, and again fell. The value for the density obtained from the cylinder and counterweight was always higher than that by calculation and during the period, the difference between the values became steadily greater, rising from 0.002,8 g./liter to 0.005,0 g./liter. This change was not correlated with changing barometric pressure; it might have resulted from a change in the response of the hygrometer or from the failure to measure the carbon dioxide content of the air. On two days, at the end of the period, water and the carbon dioxide content were also measured gravimetrically; the difference was the same on these two days, 0.003,8 g./liter, and on each day lower than the differences obtained when the gravimetric analyses were not taken into consideration (0.004,5 and 0.005,0 g./liter).

The uncertainty in the density as determined by the cylinder and counterweight has been placed at 0.3 parts per thousand and the discrepancy just reported, 3.4 parts per thousand, is thus ten times greater. A search has been made for sources of errors in the measurements leading to these differing values for the density of air and it has been concluded, because of the great care exercised in obtaining each measurement, that the difference is real.

Several explanations for the difference in densities found have been considered: nonconformity of moist air to the gas laws; an error in the gas constant; variations in the composition of air; and an error in the composition (fixed oxygen content) assumed for the atmosphere in calculating a molecular weight for air. The first two of these considerations have been ruled out by the very careful and painstaking character of the work which has gone into evaluating the physical properties of oxygen and through them to the gas constant. It has been concluded that variation in the composition of the atmosphere offers the most reasonable explanation and in particular a variation in the oxygen content. However, the variation in oxygen content necessary to change the density of air by 3.4 parts per thousand is so large, some 1.5 per cent oxygen, that it appears highly unlikely that variation in oxygen content is solely responsible.

Because the observed discrepancy between the density of air obtained by the two methods is considered real, it has been recommended that in the precise measurement of mass the buoyancy correction be calculated using a density for air obtained by weighing a hollow cylinder and counterpoise such as those described in this dissertation.

I. Chapter IX

A survey of the literature dealing with the oxygen content of the atmosphere has been made, with special scrutiny directed at the methods for the determination of oxygen. It has been concluded that the best method of analysis, and probably the best values for the oxygen content of the atmosphere over the northern hemisphere, is that of Regnault, done in the period of 1847 to 1852. Regnault perfected and employed, for the analysis of the numerous samples brought to Paris by international travelers, the hydrogen eudiometer, a method inherently free from the errors which affect the liquid absorbent and other methods employed by workers of the twentieth century. The best value for the oxygen content of the atmosphere is probably the Regnault average of 20.96 per cent with an uncertainty (one standard deviation) of 0.02 per cent oxygen, a figure with which the values of the twentieth century are in agreement but for which the uncertainties are undoubtedly greater. It has been concluded further that the results reported for the oxygen content of the atmosphere to 0.000,1 per cent oxygen are ridiculous, that the widely adopted value of 20.946 per cent oxygen stretches too far, and that the use of this value, and reliance on it to 0.001 per cent oxygen, has been unrealistic and imprudent. It has been concluded further that the variations with geographical origin, values as low as 20.3 per cent oxygen (Regnault on samples from the Mediterranean, Lockhart and Court from the Antarctic) are indeed fact and that, by implication, skepticism should be shown toward the current practice in atmospheric physics of assuming the oxygen content of the atmosphere is a fixed value and one of the physical constants of nature.

A new, gravimetric method has been proposed for the determination of the oxygen content of the atmosphere, making use of the high-precision, dry, gas pipet developed in the present work and of the 3000 cm.^{3} sample of dry and carbon dioxide-free air left over from the determination of water and carbon dioxide in the atmosphere in the balance case. The idea is to absorb the oxygen on hot copper, to then reduce the copper oxide in a stream of hydrogen, and to collect and weigh the water produced. The method uses a very large sample, is free of the troubles common to liquid absorbents, and should prove good to a few parts in 60,000.

J. Chapter X

The present arrangements for the maintenance of standards of mass have been reviewed and possible sources of uncertainty at the parts per million level in the existing system, in the dissemination (subdivision of the standard kilogram), and in the actual measurement of mass have been identified. It has been concluded that at present, measurement of mass cannot be made with an uncertainty less than five parts per million. It is believed that the hollow, stainless steel cylinder devised for the determination of the density of air, described earlier in this dissertation, offers a solution to the principal problem, the correction for buoyancy, but that other serious problems remain. These problems revolve around such questions as: the density of the platinum standards, the stability of the surfaces of these and other secondary standard weights toward cleaning, the extent of the adsorption of water and other gases on the surfaces, and the variability of these adsorption with changing atmospheric conditions. The conclusion has been reached that a completely new approach to the mass problem should be taken.

It has been proposed to make a set of weights of a corrosion-resistant stainless steel; to give the weights a surface treatment which renders the surface essentially non-polar in character and reproducible on cleaning by vapor degreasing; to calibrate this set, making the weighings in the vacuum weighing bottle described earlier in this dissertation; and then to relate the new set of weights through a new stainless steel kilogram weight to the International Kilogram. It has been decided to fabricate the new set of weights on the basis of the Fibonacci series. A start has been made in the fabrication of such a set of weights.

A highly corrosion-resistant stainless steel, stabilized by niobium, Carpenter 20CB3, has been selected for the fabrication of this set of weights.

Various lots of Carpenter 20CB3, in the form of rods of varying diameter, have been obtained. The density of each lot has been determined, and discs of the rods cut, rolled to plates and sheets, and drawn into wire have been used for the fabrication of the weights.

Blanks for the various weights have been cut and machined, weights 1 g. through 34 g. being made flat, and weights 55 g. through 987 g., and four 1000-g. weights, being in the form of cylinders.

The flat surfaces of these weights have been polished on a Syntron Lapping-Polishing Machine using aluminum oxide polishing powders. Holders have been designed so that the edges of the flat weights can also be polished.

The cylindrical surfaces of the larger weights have been polished on a *cylindrical-surface polishing machine*, designed and built especially for this work. The cylinder being polished is rotated on a horizontal axis while partially submerged in a suspension of aluminum oxide polishing powder in water and the polishing effected by a rotating buffing wheel which sweeps back and forth across the cylinder.

Highly polished pieces for the weights have now been prepared, a few approaching the desired (nominal) values in mass. Surface treatment and the calibration have not yet been started.

K. Chapter XI

Of the various sequences of numbers which can be used as the basis for a set of weights, the Fibonacci sequence has been selected because it offers an opportunity to build up an extensive network of cross checks in a calibration operation, that is, in relating the masses of the smaller weights to the larger and to some arbitrary standard.

A plan has been developed for the calibration of a set of Fibonacci weights using for the experimental measurements the Mettler single-pan balances and taking advantage of the method of weighing, weighing by substitution, on which these balances operate. The overall calibration plan has been presented in the form of flow sheets.

A mathematical treatment has been made of the data obtained in the calibration of a set of Fibonacci weights taking advantage of the existing, extensive literature of the Fibonacci mathematics, particularly of the sub-fields of identity, summation, and representation. Because the Fibonacci mathematics deals with integral numbers but, in the calibration of the set of weights, concern is principally with the deviations from integral values, it has been necessary to superimpose on the commonly used Fibonacci nomenclature and symbolism a new symbolism whereby each Fibonacci number (weight) is handled as the sum of two terms, an *integral value* and a *departure*. This lends itself admirably to the data of weighings by substitution, for the integral values cancel and the body of the final picture develops as a neat package in terms of the departures and values obtained experimentally, the experimental values (weighings) appearing in reverse Fibonacci order.

Because of certain characteristics in the summation laws of Fibonacci numbers, it has been found advantageous for the experimental work to incorporate a third one-gram weight (designated "Fibonacci minus one") into the set, so that the set is composed of the weights (name and (integral value in grams)): F_{-1} (1), F_0 (0, the zeroing operation), F_1 (1), F_2 (1), F_3 (2), F_4 (3), F_5 (5), F_6 (8), F_7 (13), F_8 (21), F_9 (34), F_{10} (55), F_{11} (89), F_{12} (144), F_{13} (233), F_{14} (377), F_{15} (610), F_{16} (987), ISU-1000 (1000). Together with the 1000-g. weight, the set consists of eighteen weights in all.

The mathematical treatment has been made thorough in that it treats all of the representations (cross checks) theoretically possible. A remarkable feature has emerged from the development in that in the overall body of the final equations, there are as many independent evaluations of the departures for the smaller weights as are obtained for the larger weights.

XIII. BIBLIOGRAPHY

1. Batuecas, T. The Most Probable Up-to-Date Value of the Normal Molecular Volume V_0 of an Ideal Gas. In "Proceedings of the Second International Conference on Nuclidic Masses", W. H. Johnson, Ed., Springer-Verlag, Vienna, 1964.

2. Batuecas, T., and G. Garcia Malde. Experimental Investigations of Gases Based on Density Limits and the Rigorous Determination of Molecular and Atomic Masses. I. Results Obtained for Oxygen and Sulfur Dioxide. *Anales Real Soc. Espan. Fis. Quim. Madrid*, *46B*, 517 (1950).

3. Baxter, G. P. A Rapid Method for Determining the Density of Air. *J. Am. Chem. Soc.*, *43*, 1317 (1921).

4. Baxter, G. P., and H. W. Starkweather. The Density of Oxygen. *Proc. Natl. Acad. Sci.*, *10*, 479 (1924).

5. Baxter, G. P., and H. W. Starkweather. The Density of Oxygen and Its Compressibility Below One Atmosphere. II. *Proc. Natl. Acad. Sci.*, *12*, 699 (1926).

6. Benedict, F. G. "The Composition of the Atmosphere with Special Reference to Its Oxygen Content". Carnegie Institution of Washington, Washington, D. C., 1912.

7. Bicknell, M., and V. E. Hoggatt, Jr. "A Primer for the Fibonacci Numbers". The Fibonacci Association, San Jose State University, San Jose, California, 1973.

8. Bowman, H. A., R. M. Schoonover, and C. L. Carroll. A Density Scale Based on Solid Objects. *J. Res. Natl. Bur. Stds.*, *78A*, 13 (1974).

9. Bowman, H. A., R. M. Schoonover, and M. W. Jones. Procedure for High Precision Density Determinations by Hydrostatic Weighing. *J. Res. Natl. Bur. Stds.*, *71C*, 179 (1967).

10. Brombacher, W. G., D. P. Johnson, and J. L. Cross. Mercury Barometers and Manometers. In "Precision Measurement and Calibration", Vol. 8, National Bureau of Standards Special Publication 300, U. S. Government Printing Office, Washington, D. C., 1972.

11. Brousseau, A. (Brother Alfred Brousseau). A Primer for the Fibonacci Numbers. Part X: On the Representation of Integers. *The Fibonacci Quarterly*, *10*, 635 (1972). Reproduced in Reference 7, p. 118.

12. Brousseau, A. (Brother U. Alfred). "An Introduction to Fibonacci Discovery". The Fibonacci Association, San Jose State University, San Jose, California, 1965.

13. Brousseau. A. (Brother Alfred Brousseau; Brother U. Alfred). "Linear Recursion and Fibonacci Sequences". The Fibonacci Association, San Jose State University, San Jose, California, 1971.

14. Brown, G. M., and H. J. Zabsky. Unit Cell and Space Group of 4-Aminopyridine. *Acta Cryst*., *16*, 852 (1963).

15. Brown, J. L., Jr. A New Characterization of the Fibonacci Numbers. *The Fibonacci Quarterly*, *3*, 1 (1965).

16. Brown, J. L., Jr. Some Sequence-to-Sequence Transformations Which Preserve Completeness. *The Fibonacci Quarterly*, *16*, 19 (1978).

17. Brown, J. L., Jr. Zeckendorf's Theorem and Some Applications. *The Fibonacci Quarterly*, *2*, 163 (1964).

18. Brulmans, J., and H. L. Eschbach. Procedure for Simple, High Precision Density Determinations of Air for Buoyancy Corrections. *Rev. Sci. Instr*., *41*, 1680 (1970).

19. Burg, W. G., and D. A. Veith. The Correction for Buoyancy Using a Single-Pan Balance. *J. Chem. Ed*., *47*, 192 (1970).

20. Cantwell, F. F., B. Kratochvil, and W. E. Harris. Air Buoyancy Errors and the Optical Scale of a Constant Load Balance. *Anal. Chem*., *50*, 1010 (1978).

21. Carlitz, L., R. Scoville, and V. E. Hoggatt, Jr. Addendum to the Paper "Fibonacci Representations". *The Fibonacci Quarterly*, *10*, 527 (1972).

22. Carlitz, L., R. Scoville, and V. E. Hoggatt, Jr. Fibonacci Representations. *The Fibonacci Quarterly*, *10*, 1 (1972).

23. Carmichael, R. S. The Earth's Gravity Field. *Iowa Sci. Teachers J.*, *16*, No. 3, 3 (1979).

24. Carpenter, T. M. The Constancy of the Atmosphere with Respect to Carbon Dioxide and Oxygen Content. *J. Am. Chem. Soc.*, *59*, 358 (1937).

25. Casado, F. L., and T. Batuecas. Experimental Investigations of Related Gases by the Method of Limiting Densities and Rigorous Determination of the Molecular and Atomic Weights. II. Compressibility and Mass of a Liter of Oxygen at 0° Between 1 and 1/4 Atmosphere; "Normal Molecular Volume". *Anales Real Soc. Espan. Fis. Quim. Madrid.*, *48B*, 5 (1952).

26. Chadwick, C. R. "The Elimination of Static by Means of a Radioactive Material". B.S. Thesis in Chemical Engineering, Iowa State University, 1940.

27. Clardy, J. C., Department of Chemistry, Iowa State University, Private Communication, 1976.

28. Cohen, E. R., and B. N. Taylor. The 1973 Least-Squares Adjustment of the Fundamental Constants. *J. Phys. Chem. Ref. Data*, *2*, 663 (1973).

29. Conant, J. B. "The Overthrow of the Phlogiston Theory". The Chemical Revolution of 1775-1789. Harvard University Press, Cambridge, 1955.

30. Coulomb, C. A. First Account on Electricity and Magnetism. *Mem. de l'Acad. de Paris*, 569 (1785).

31. Craig, D. N., J. I. Hoffman, C. A. Law, and W. J. Hamer. Determination of the Value of the Faraday with a Silver-Perchloric Acid Coulometer. *J. Res. Natl. Bur. Stds.*, *64A*, 381 (1960).

32. Deslattes, R. D., A. Henins, H. A. Bowman, R. M. Schoonover, C. L. Carroll, I. L. Barnes, L. A. Machlan, L. J. Moore, and W. R. Shields. Determination of the Avogadro Constant. *Phys. Rev. Letters*, *33*, 463 (1974).

33. Diehl, H. High-Precision Coulometry and the Value of the Faraday. *Anal. Chem.*, *51*, 318A (1979).

34. Diehl, H. "Quantitative Analysis", Second Edition, Oakland Street Science Press, Ames, Iowa, 1974.

35. Dijksterhuis, E. J. "Archimedes". The Humanities Press, New York, 1957.

36. Ferns, H. H. On the Representation of Integers as Sums of Distinct Fibonacci Numbers. The Fibonacci Quarterly, 3, 21 (1965).

37. Freitag, H. T. On Summations and Expansions of Fibonacci Numbers. The Fibonacci Quarterly, 11, 63 (1973).

38. Gibson, J. S. "Devices for the Rapid Determination of the Density of Air". Master of Science Thesis, Iowa State University, 1977.

39. Glueckauf, E. Composition of the Atmosphere. In "Compendium of Meteorology", T. F. Malone, Ed., American Meteorological Society, Boston, 1951.

40. Gopfert, W. "Expansion of the Iowa Gravity Base Station Network to Ames, Story County, Iowa". Report of Project in Geology 590L, Iowa State University, 1973. Available from Professor R. L. Hardy, Department of Civil Engineering, Iowa State University.

41. Hamer, W. J. Resume of Values of the Faraday. J. Res. Natl. Bur. Stds., 72A, 435 (1968).

42. Hardy, R. L., Department of Civil Engineering, Iowa State University, Private Communication, 1977.

43. Harris, W. S. On the Elementary Laws of Electricity. Phil. Trans. Roy. Soc. London, 124, 213 (1834).

44. Harrison, L. P. Fundamental Concepts and Definitions Related to Humidity. In "Humidity and Moisture", Vol. III, A. Wexler and W. A. Wildhack, Eds., Reinhold Publishing Corp., New York, 1965, Chapter 1.

45. Hase, D. H., R. B. Campbell, and O. J. Van Eck. "Iowa Gravity Base Station Network. Report of Investigations 8." Iowa Geological Survey, Iowa City, Iowa, 1969.

46. Heath, T. L. "The Works of Archimedes". Cambridge University Press, Cambridge, 1897.

47. Heicklen, J. The Structure of the Atmosphere. In "Atmospheric Chemistry", Academic Press, New York, 1976, Chapter 1.

48. Hockey, S. W. "Fundamental Electrostatics". Methuen Educational Ltd., London, 1972.

49. Hoggatt, V. E., Jr. Generalized Zeckendorf Theorem. The Fibonacci Quarterly, 10, 89 (1972).

50. Hoggatt, V. E., Jr. "The Fibonacci and Lucas Numbers." Houghton Mifflin Company, Boston, 1969.

51. Hoggatt, V. E., Jr., and B. Chow. Some Theorems on Completeness. The Fibonacci Quarterly, 10, 551 (1972).

52. Hoggatt, V. E., Jr., N. Cox, and M. Bicknell. A Primer for the Fibonacci Numbers: Part XII. On Representation of Integers Using Fibonacci Numbers. The Fibonacci Quarterly, 11, 317 (1973). Reproduced in Reference 7, p. 127.

53. Holland, H. D. The Chemistry of the Atmosphere. In "The Chemistry of the Atmosphere and Oceans", John Wiley & Sons, New York, 1978, Chapter VI.

54. Hoyle, W. C. "The High-Precision Thermometric and Coulometric Assay of Primary Standard 4-Aminopyridine". Ph.D. Dissertation, Iowa State University, 1973.

55. Hoyle, W. C., W. F. Koch, and H. Diehl. An Electrode for the Coulometric Generation of Hydrogen Ion. Talanta, 22, 649 (1975).

56. Hughes, E. E. A Simple Technique for the Absolute Determination of Atmospheric Oxygen. Environ. Sci. Technol., 2, 201 (1968).

57. Huntley, H. E. "The Divine Proportion". Dover Publications, Inc., New York, 1970.

58. Johnson, D. P. Geometrical Considerations in the Measurement of the Volume of an Approximate Sphere. J. Res. Natl. Bur. Stds., 78A, 41 (1974).

59. Jones, F. E. The Air Density Equation and the Transfer of the Mass Unit. J. Res. Natl. Bur. Stds., 83, 419 (1978).

60. Le Gallic, Y. Problems in Microweighing. Nucl. Instr. Methods, 112, 333 (1973).

61. Lewis, J. E., and L. A. Woolf. Air Buoyancy Corrections for Single-Pan Balances. J. Chem. Ed., 48, 639 (1971).

62. Lockhart, E. E., and A. Court. Oxygen Deficiency in Antarctic Air. Monthly Weather Rev., 70, 93 (1942).

63. Klarner, D. A. Representation of N as a Sum of Distinct Elements from Special Sequences. The Fibonacci Quarterly, 4, 289 (1966).

64. Knoeck, J., and H. Diehl. A Cell for High-Precision Constant-Current Coulometry with External Generation of Titrant. Talanta, 16, 567 (1969).

65. Knoeck, J., and H. Diehl. Coulometric Assay of the Primary Standard Potassium Dichromate and Ammonium Hexanitratocerate. Talanta, 16, 181 (1969).

66. Koch, W. F., and H. Diehl. Additional Results on the Value of the Faraday. Talanta, 23, 509 (1976).

67. Koch, W. F., D. L. Biggs, and H. Diehl. Tris(hydroxymethyl)aminomethane, A Primary Standard? Talanta, 22, 637 (1975).

68. Koch, W. F., W. C. Hoyle, and H. Diehl. A High-Precision Titration of 4-Aminopyridine. A Value for the Faraday. Talanta, 22, 717 (1975).

69. Kroeger, F. R., and W. A. Rhinehart. Low Cost, Versatile Highly Stable Constant Current Supply. Rev. Sci. Instr., 42, 1532 (1971).

70. Machta, L., and E. Hughes. Atmospheric Oxygen in 1967 to 1970. Science, 168, 1582 (1970).

71. Modell, J. H., C. I. Hood, E. J. Kuck, and B. C. Ruiz. Oxygenation by Ventilation with Fluorocarbon Liquid (FX-80). Anesthesiology, 34, 312 (1971).

72. Moles, E. The Method of Limiting Densities for Determination of Molecular and Atomic Weights. Variation in Limiting Molecular Weights. Bull. Soc. Chem. France, 1006 (1950).

73. Moles, E., T. Toral, and A. Escribano. Limiting Densities and Molecular Weights of Oxygen, Carbon Dioxide, and Hydrogen Sulfide. Atomic Weights of Carbon and Sulfur. Trans. Faraday Soc., 35, 1439 (1939).

74. Nicolet, M. The Properties and Constitution of the Upper Atmosphere. In "Physics of the Upper Atmosphere", J. A. Ratcliffe, Ed., Academic Press, New York, 1960, Chapter 2.

75. Page, C. H., and P. Vigoureux. "The International Bureau of Weights and Measures 1875-1975". Translation of the BIPM Centennial Volume. National Bureau of Standards Special Publication 420. U. S. Government Printing Office, Washington, D. C., 1975.

76. Palit, S. R. A Novel Observation on Electrolysis of Dye Solutions: Formation of One or More Sharp Boundaries. J. Indian Chem. Soc., 49, 963 (1972).

77. Palit, S. R. Liberation of Gas in the Intermediate Zone during Electrolysis. Indian J. Phys., 46, 338 (1972).

78. Palit, S. R. Liberation of Hydrogen and Oxygen Together on the Electrodes during Electrolysis Accompanied by Electrode Glow. Indian J. Phys., 42, 414 (1968).

79. Palit, S. R. Non-Faradaic Electrolysis: Concurrent Migration of Nitrogen and Other Electroneutral Molecules during Electrolysis. J. Indian Chem. Soc., 50, 466 (1973).

80. Palit, S. R. Occurrence of Chemical Reaction in the Intermediate Zone during Electrolysis. J. Indian Chem. Soc., 50, 625 (1973).

81. Palit, S. R. Possibility of a Real Deviation from Faraday's Law of Electrolysis. Indian J. Phys., 41, 309 (1967).

82. Palit, S. R., and M. Guha. Formation of Single Boundary and Double Boundary on Electrolysis of Cr(VI) Solutions. J. Indian Chem. Soc., 51, 518 (1974).

83. Paneth, F. A. The Chemical Composition of the Atmosphere. Quart. J. Meteorol. Soc., 63, 433 (1937).

84. Partington, J. R. "A Short History of Chemistry". Macmillan and Co., London, 1951.

85. Pontius, P. E. "Mass and Mass Values". National Bureau of Standards Monograph 133. U. S. Government Printing Office, Washington, D. C., 1974.

86. Pontius, P. E. Mass Measurement: A Study of Anomalies. Science, 190, 379 (1975).

87. Quinn, T. J. A Proposal for a New Determination of the Gas Constant. In "Atomic Masses and Fundamental Constants 4", J. H. Sanders and A. H. Wapstra, Eds., Plenum Press, New York, 1972.

88. Quinn, T. J., A. R. Colclough, and T. R. D. Chandler. A New Determination of the Gas Constant by an Accoustical Method. Phil. Trans. Roy. Soc. London, A238, 367 (1976).

89. Quinn, T. J., A. R. Colclough, and T. R. D. Chandler. A New Determination of the Gas Constant by an Acoustic Technique. In "Atomic Masses and Fundamental Constants 5", J. H. Sanders and A. H. Wapstra, Eds., Plenum Press, New York, 1976.

90. Regnault, V. Investigations on the Composition of the Atmosphere. Ann. Chim. Phys., [3] 36, 385 (1852).

91. Regnault, V., and J. Reiset. Chemical Research on the Respiration of Various Classes of Animals. Ann. Chim. Phys., [3] 26, 299 (1849).

92. Rowlinson, J. S., and D. J. Tildesley. The Determination of the Gas Constant from the Speed of Sound. Proc. Roy. Soc. London, A358, 281 (1977).

93. Sargent, J. W., and R. J. Seffl. Properties of Perfluorinated Liquids. Fed. Proc., 29, 1669 (1970).

94. Schoonover, R. M. National Bureau of Standards, Gaithersburg, Maryland, Private Communication, 1976.

95. Stock, A., H. Ramser, and G. Eyber. Measurements with the Suspension Balance Described Earlier. Variations in the Density and Oxygen Content of Atmospheric Air. Z. Phys. Chem., A163, 82 (1933).

96. Swindells, B. Centenary of the Convention of the Metre. International Standards Manufactured in Iridium-Platinum. Platinum Metals Rev., 19, 110 (1975).

97. Taylor, B. N. Is the Present Realization of the Absolute Ampere in Error? Metrologia, 12, 81 (1976).

98. Thomson, W. Report on Electrometers and Electrostatic Measurements. Report to the British Association for the Advancement of Science, Thirty-seventh Meeting, 489-512 (1867).

99. Toropin, S. I., and V. C. Snegov. Evaluation of Air Density for Calculating Aerostatic-Force Correction in Precise Measurements of Mass. Izmer. Tekn., 18, No. 12, 75 (1975). English translation: Measurement Techniques, 18, 1874 (1975-76).

100. Ulbricht, H. Determination of Air Density with the Aid of a Balance and Two Masses of Unequal Volume. Chem.-Ztg., 81, 708 (1957).

101. Wild Herrbrugg, Inc., Farmingdale, New York, Correspondence and Telephone Communications, 1976-79.

102. Winward, M. R., E. M. Wooley, and E. A. Butler. Air Buoyance Equations for Single-Pan Balances. Anal. Chem., 49, 2126 (1977).

103. Yoshimori, T., S. Ishiwari, Y. Watanabe, T. Harada, and S. Yamada. Coulometric Microdetermination of Surface Water on Various Metals and Glasses and of Hydrogen in Beryllium Metal. Trans. Japan Inst. Metals, 14, 396 (1973).

XIV. ACKNOWLEDGEMENTS

I am indebted foremost to Professor Harvey Diehl for his guidance during the course of this research and the assistance, interest, and energy he contributed to the research and the preparation of this dissertation. I also wish to thank Professor Diehl for the confidence he showed in my managerial ability during the six quarters that I supervised the Chemistry 211 laboratory and was permitted to gain invaluable managerial experience.

I wish to thank the following organizations and persons for stipends and scholarships covering twenty-one of the twenty-two quarters of residence at Iowa State University during which the investigations leading to the M. S. thesis and the present dissertation were performed: College of Sciences and Humanities, Iowa State University, budget as a half-time teaching assistant (18 quarters); Sciences and Humanities Research Institute (1.5 quarters); Mr. and Mrs. Clifford C. Hach (1.5 quarters); Graduate College, special emergency assistance fund (one month).

I wish to acknowledge a grant to Professor Diehl from the Iowa State University Research Foundation totalling $11,900 which was used in part to purchase shop time and the following equipment: the Mettler, Model M5/SA Microbalance; a set of Ainsworth Class M Weights; a dehumidifier; the Mettler, Model H51AR Semimicrobalance; a Hewlett-Packard

Strip Chart Recorder; a WeatherMeasure Recording Barometer; two WeatherMeasure Hygrothermographs; the Keithley Null Detector Microvoltmeter. I also wish to thank Mr. and Mrs. Clifford C. Hach for various grants to Professor Diehl which were used to support this research through the purchase of equipment, supplies, and shop time.

I wish to acknowledge the expert craftsmanship of Mr. Eldon Ness, machinist *extraordinaire*, of the machine shop of the Department of Chemistry; Mr. Ness constructed the various devices described in this dissertation with the able assistance of Mr. George Steininger, Mr. John Sauke, Mr. Kenneth Dayton, and Mr. Raymond Seymour, all of the machine shop.

I am indebted to Mr. and Mrs. Clifford C. Hach of the Hach Chemical Company, Loveland, Colorado, for the loan of the Mettler, Model H315 Kilogram Balance and the Syntron Lapping-Polishing Machine. I wish to thank Mr. Hach also for having personally made the series of highly precise measurements of the dimensions of the absolute density cylinder and counterweight described in Chapter VI. I also thank the electrical engineers of the Hach Chemical Company who designed and built the sensitive, thermistor-electronic devices, described in Chapter IV, which were used to control the temperature of air entering the constant temperature box.

I wish to acknowledge the following individuals for the loan of instruments which were crucial to the investigations leading to the present dissertation: Professor David Peterson of the Department of Materials Science and Engineering for the loan of the vacuum pump and thermocouple gauge described in Chapter IV; Professor Harry Svec of the Department of Chemistry for the loan of the cathetometer described in Chapter IV and the aneroid barometer described in Chapter III; Professor Bernard Gerstein of the Department of Chemistry for the loan of the White Double Potentiometer described in Chapter IV; Dr. Robert McBeth of the National Center for Atmospheric Research, Boulder, Colorado, for the loan of the digital, aneroid barometer described in Chapter III; Professor Victor Ryan of the Department of Chemistry, University of Wyoming, Laramie, for the loan of the altimeter described in Chapter III; Mr. Jack Gilmore of the Iowa Geological Survey, Iowa City, Iowa, for the loan of the Worden Gravity Meter used for the measurement of the local acceleration of gravity as described in Chapter IV. Each of these men made these loans at inconvenience to themselves but always willingly and cheerfully, with advice about their use derived from their own experience.

I am particularly indebted to Professor C. A. Swenson of the Department of Physics for the suggestion of installing fine points on the insulated, moving components of the

balance to obviate electrostatic effects. I also wish to thank Mr. M. S. Anderson who, under the supervision of Professor Swenson, calibrated the platinum resistance thermometers and the standard resistor described in Chapter IV.

I am also deeply indebted to Professor David Peterson for making available his extensive knowledge of metallurgy and the machining and polishing of metals, knowledge which led to the choice of niobium-stabilized stainless steel for the set of high-precision weights and to an insight into the chemical changes accompanying the degreasing of metals. I also wish to thank Mr. Harlan Baker for his advice about polishing stainless steel and the operation of the Syntron Lapping-Polishing Machine.

I wish to acknowledge Professor R. L. Hardy of the Department of Civil Engineering for his advise and assistance during the measurement of the local acceleration of gravity. The elevation of the bench marks and balance pier described in Chapter IV was also determined under the supervision of Professor Hardy.

I wish to thank Professor Donald L. Biggs of the Department of Earth Sciences for taking the photomicrographs of 4-aminopyridine which appear in Chapter II.

I am indebted to Mrs. Sue Musselman who typed this dissertation and provided invaluable advice during its

preparation. I also wish to thank Mrs. LaDena Bishop, Thesis Editor, for her patience and advice, particularly concerning the preparation of Figures XI-1 and XI-2.

Finally, thanks to my wife Cheryl who was always there with love and patience; let's go somewhere a bit warmer.

Figure XI-1. Representations of Fibonacci numbers by an increasing number of smaller Fibonacci numbers. Normal Fibonacci sequence

Note 1. The symbolism on this line (general formulations) has been changed from the new symbolism to the simple Fibonacci name in the interest of saving space.

(The text dealing with this table appears in the dissertation at page 246.)

Fibonacci Name	Symbol Giving Numerical Value and Name			
		Two Numbers	Three Numbers	Four Numb
F_0	${}^{0}{}_{F0}$			
F_1	${}^{1}{}_{F1}$			
F_2	${}^{1}{}_{F2}$	${}^{1}{}_{F1}+{}^{0}{}_{F0}$		
F_3	${}^{2}{}_{F3}$	${}^{1}{}_{F2}+{}^{1}{}_{F1}$		
F_4	${}^{3}{}_{F4}$	${}^{2}{}_{F3}+{}^{1}{}_{F2}$		
		${}^{2}{}_{F3}+{}^{1}{}_{F1}$		
F_5	${}^{5}{}_{F5}$	${}^{3}{}_{F4}+{}^{2}{}_{F3}$	${}^{3}{}_{F4}+{}^{1}{}_{F2}+{}^{1}{}_{F1}$	
F_6	${}^{8}{}_{F6}$	${}^{5}{}_{F5}+{}^{3}{}_{F4}$	${}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F2}$	
			${}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F1}$	
F_7	${}^{13}{}_{F7}$	${}^{8}{}_{F6}+{}^{5}{}_{F5}$	${}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{2}{}_{F3}$	${}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{1}{}_{F2}+{}^{1}{}_{F1}$
F_8	${}^{21}{}_{F8}$	${}^{13}{}_{F7}+{}^{8}{}_{F6}$	${}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{3}{}_{F4}$	${}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F}$
				${}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F}$
F_9	${}^{34}{}_{F9}$	${}^{21}{}_{F8}+{}^{13}{}_{F7}$	${}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{5}{}_{F5}$	${}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{2}{}_{F}$
F_{10}	${}^{55}{}_{F10}$	${}^{34}{}_{F9}+{}^{21}{}_{F8}$	${}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{8}{}_{F6}$	${}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+$

Representation		
Four Numbers	Five Numbers	Six Numbers
$8_{F6}+3_{F4}+1_{F2}+1_{F1}$		
$13_{F7}+5_{F5}+2_{F3}+1_{F2}$		
$13_{F7}+5_{F5}+2_{F3}+1_{F1}$		
$21_{F8}+8_{F6}+3_{F4}+2_{F3}$	$21_{F8}+8_{F6}+3_{F4}+1_{F2}+1_{F1}$	
$34_{F9}+13_{F7}+5_{F5}+3_{F4}$	$34_{F9}+13_{F7}+5_{F5}+2_{F3}+1_{F2}$	
	$34_{F9}+13_{F7}+5_{F5}+2_{F3}+1_{F1}$	
$55_{F10}+21_{F8}+8_{F6}+5_{F5}$	$55_{F10}+21_{F8}+8_{F6}+3_{F4}+2_{F3}$	$55_{F10}+21_{F8}+8_{F6}+3_{F4}+1_{F2}+1_{F1}$

presentation		
Six Numbers	Seven Numbers	Eight N

Seven Numbers	Eight Numbers

F_{11}	${}^{89}F_{11}$	${}^{55}F_{10}+{}^{34}F_{9}$	${}^{55}F_{10}+{}^{21}F_{8}+{}^{13}F_{7}$	${}^{55}F_{10}+{}^{21}F_{8}+{}^{8}F_{6}+$
F_{12}	${}^{144}F_{12}$	${}^{89}F_{11}+{}^{55}F_{10}$	${}^{89}F_{11}+{}^{34}F_{9}+{}^{21}F_{8}$	${}^{89}F_{11}+{}^{34}F_{9}+{}^{13}F_{7}$
F_{13}	${}^{233}F_{13}$	${}^{144}F_{12}+{}^{89}F_{11}$	${}^{144}F_{12}+{}^{55}F_{10}+{}^{34}F_{9}$	${}^{144}F_{12}+{}^{55}F_{10}+{}^{21}$
F_{14}	${}^{377}F_{14}$	${}^{233}F_{13}+{}^{144}F_{12}$	${}^{233}F_{13}+{}^{89}F_{11}+{}^{55}F_{10}$	${}^{233}F_{13}+{}^{89}F_{11}+{}^{34}$
F_{15}	${}^{610}F_{15}$	${}^{377}F_{14}+{}^{233}F_{13}$	${}^{377}F_{14}+{}^{144}F_{12}+{}^{89}F_{11}$	${}^{377}F_{14}+{}^{144}F_{12}+{}^{5}$
F_{16}	${}^{987}F_{16}$	${}^{610}F_{15}+{}^{377}F_{14}$	${}^{610}F_{15}+{}^{233}F_{13}+{}^{144}F_{12}$	${}^{610}F_{15}+{}^{233}F_{13}+{}^{8}$
F_n	$\lvert F_n \rvert F_n$	$F_{n-1}+F_{n-2}$ ↑↑Note 1	$F_{n-1}+F_{n-3}+F_{n-4}$	$F_{n-1}+F_{n-3}+F_{n-5}+$

	${}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F1}$	
${}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{5}{}_{F5}$	${}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{2}{}_{F3}$	${}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{1}{}_{F2}+{}^{1}{}_{F1}$
${}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{8}{}_{F6}$	${}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{3}{}_{F4}$	${}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F2}$
		${}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{2}{}_{F3}+{}^{1}{}_{F1}$
${}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{13}{}_{F7}$	${}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{5}{}_{F5}$	${}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{3}{}_{F4}+{}^{2}{}_{F3}$
${}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{21}{}_{F8}$	${}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{8}{}_{F6}$	${}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+{}^{5}{}_{F5}+{}^{3}{}_{F4}$
${}^{377}{}_{F14}+{}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{34}{}_{F9}$	${}^{377}{}_{F14}+{}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{13}{}_{F7}$	${}^{377}{}_{F14}+{}^{144}{}_{F12}+{}^{55}{}_{F10}+{}^{21}{}_{F8}+{}^{8}{}_{F6}+{}^{5}$
${}^{610}{}_{F15}+{}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{55}{}_{F10}$	${}^{610}{}_{F15}+{}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{21}{}_{F8}$	${}^{610}{}_{F15}+{}^{233}{}_{F13}+{}^{89}{}_{F11}+{}^{34}{}_{F9}+{}^{13}{}_{F7}+$
${}^{F}{}_{n-1}+{}^{F}{}_{n-3}+{}^{F}{}_{n-5}+{}^{F}{}_{n-6}$	${}^{F}{}_{n-1}+{}^{F}{}_{n-3}+{}^{F}{}_{n-5}+{}^{F}{}_{n-7}+{}^{F}{}_{n-8}$	${}^{F}{}_{n-1}+{}^{F}{}_{n-3}+{}^{F}{}_{n-5}+{}^{F}{}_{n-7}+{}^{F}{}_{n-9}+{}^{F}{}_{n-10}$

$1F_{8}+8F_{6}+3F_{4}+1F_{2}+1F_{1}$

$4F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{2}$

$4F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{1}$

$55F_{10}+21F_{8}+8F_{6}+3F_{4}+2F_{3}$

$89F_{11}+34F_{9}+13F_{7}+5F_{5}+3F_{4}$

$144F_{12}+55F_{10}+21F_{8}+8F_{6}+5F_{5}$

$233F_{13}+89F_{11}+34F_{9}+13F_{7}+8F_{6}$

$_{n-3}+F_{n-5}+F_{n-7}+F_{n-9}+F_{n-10}.$

$144F_{12}+55F_{10}+21F_{8}+8F_{6}+3F_{4}+1F_{2}+1F_{1}$

$233F_{13}+89F_{11}+34F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{2}$

$233F_{13}+89F_{11}+34F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{1}$

$377F_{14}+144F_{12}+55F_{10}+21F_{8}+8F_{6}+3F_{4}+2F_{3}$

$610F_{15}+233F_{13}+89F_{11}+34F_{9}+13F_{7}+5F_{5}+3F_{4}$

$F_{n-1}+F_{n-3}+F_{n-5}+F_{n-7}+F_{n-9}+F_{n-11}+F_{n-12}$

$377F_{14}+144F_{12}+55F_{10}+21F_{8}+$

$610F_{15}+233F_{13}+89F_{11}+34F_{9}+$

$F_{n-1}+F_{n-3}+F_{n-5}+F_{n-7}+F_{n-9}+$

$2+55F_{10}+21F_{8}+8F_{6}+3F_{4}+1F_{2}+1F_{1}$	
$13+89F_{11}+34F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{2}$	
$3+89F_{11}+34F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{1}$	
$4+144F_{12}+55F_{10}+21F_{8}+8F_{6}+3F_{4}+2F_{3}$	$377F_{14}+144F_{12}+55F_{10}+21F_{8}+8F_{6}+3F_{4}+1F_{2}+1F_{1}$
$15+233F_{13}+89F_{11}+34F_{9}+13F_{7}+5F_{5}+3F_{4}$	$610F_{15}+233F_{13}+89F_{11}+34F_{9}+13F_{7}+5F_{5}+2F_{3}+1F_{2}$
$+F_{n-3}+F_{n-5}+F_{n-7}+F_{n-9}+F_{n-11}+F_{n-12}$	$F_{n-1}+F_{n-3}+F_{n-5}+F_{n-7}+F_{n-9}+F_{n-11}+F_{n-13}+F_{n-14}$

Name	Symbol for Integral Value	Summation Formula		
			One Weight	Two Weigh Basic Addit
		Basic formula: $F_n = F_{n-1} + F_{n-2}$ Sums, all F_n: $\sum_{k=-1}^{m} F_k = F_{m+2}$ Sums, even F_n: $\left(\sum_{k=0}^{m} F_{2k}\right) + F_{-1} = F_{2m+1}$ Sums, odd F_n: $\sum_{k=1}^{m} F_{2k-1} = F_{2m}$		
$F_{(-1)}$	${}^{1}{}_{F(-1)}$			
F_0	${}^{0}{}_{F0}$			
F_1	${}^{1}{}_{F1}$	Note 1 →	${}^{1}{}_{F(-1)}$	$({}^{0}{}_{F0}+{}^{1}{}_{F(}$
F_2	${}^{1}{}_{F2}$	Note 1 →	${}^{1}{}_{F1}$	$({}^{1}{}_{F1}+{}^{0}{}_{F(}$
		Note 2 →	${}^{1}{}_{F(-1)}$	
F_3	${}^{2}{}_{F3}$			${}^{1}{}_{F2}+{}^{1}{}_{F1}$ ${}^{1}{}_{F1}+$ ${}^{1}{}_{F2}+$
F_4	${}^{3}{}_{F4}$			${}^{2}{}_{F3}+{}^{1}{}_{F2}$ ${}^{2}{}_{F3}+$

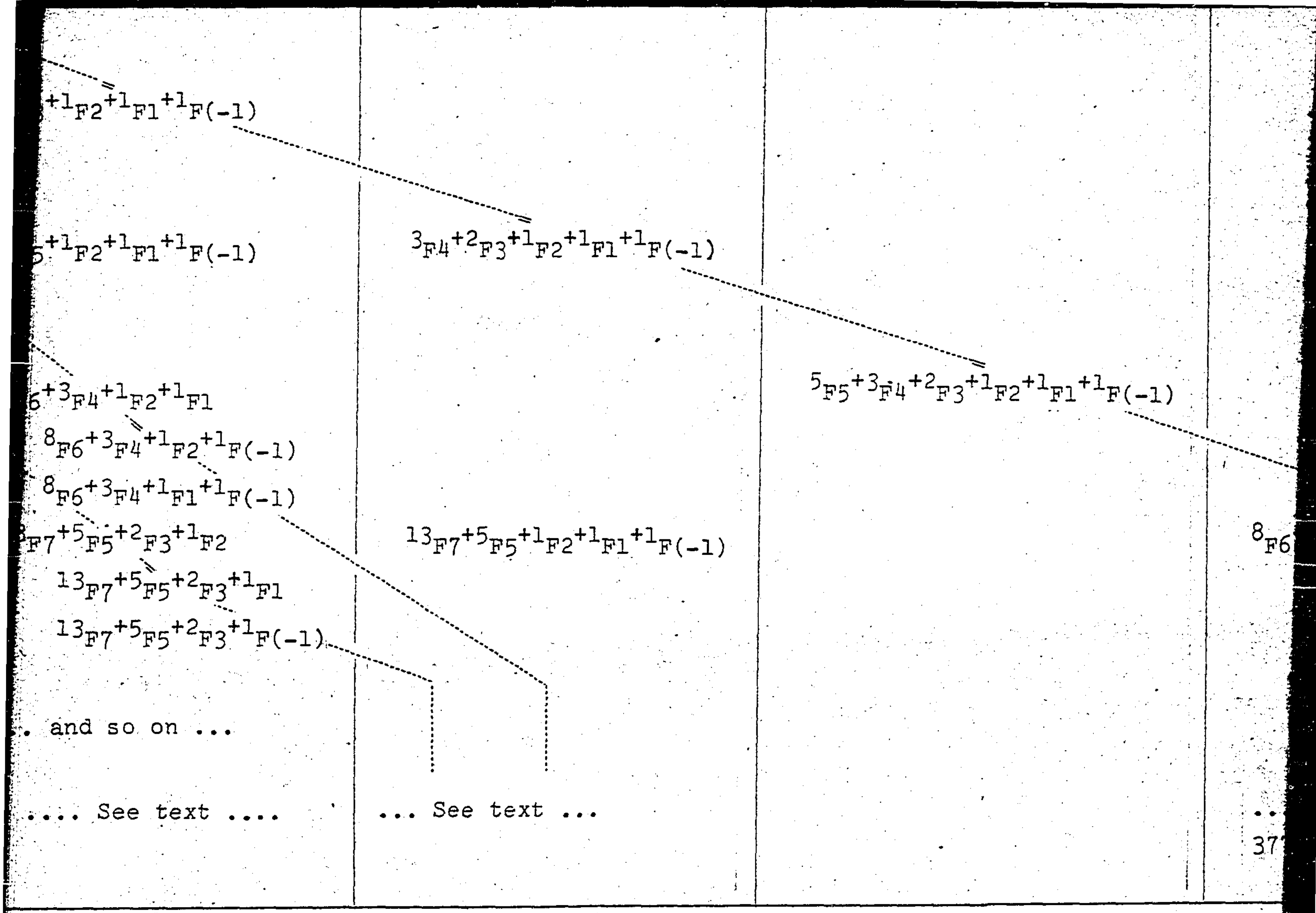
							Representat	
One Weight	Two Weights		Three Weights		Four Weights		Five We	
	Basic	Additional	Basic	Additional	Basic	Additional	Basic	Addi
${}^{1}F_{(-1)}$	$({}^{0}F_{0}+{}^{1}F_{(-1)})$							
${}^{1}F_{1}$	$({}^{1}F_{1}+{}^{0}F_{0})$							
${}^{1}F_{(-1)}$								
	${}^{1}F_{2}+{}^{1}F_{1}$							
		${}^{1}F_{1}+{}^{1}F_{(-1)}$						
		${}^{1}F_{2}+{}^{1}F_{(-1)}$						
	${}^{2}F_{3}+{}^{1}F_{2}$		${}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$					
		${}^{2}F_{3}+{}^{1}F_{1}$						
		${}^{2}F_{3}+{}^{1}F_{(-1)}$						

Representations			
	Five Weights Basic Additional	Six Weights Basic Additional	Seven Weights Basic Additional

	Six Weights Basic Additional	Seven Weights Basic Additional

					$_{F3}$ $2_{F3}+1$
F_5	5_{F5}				$3_{F4}+2_{F3}$
F_6	8_{F6}				$5_{F5}+3_{F4}$
F_7	13_{F7}				$8_{F6}+5_{F5}$
F_8	21_{F8}				$13_{F7}+8_{F6}$
$\vdots$ F_n $\vdots$	$\|F_n\|_{Fn}$	←Note 3→			$\vdots$ $F_{n-1}+F_{n-}$ $\vdots$
F_{16}	987_{F16}				$610_{F15}+$

	F_3 F_1 $^{2}F_{3}+^{1}F(-1)$			
	$^{3}F_{4}+^{2}F_{3}$	$^{3}F_{4}+^{1}F_{2}+^{1}F_{1}$ $^{3}F_{4}+^{1}F_{2}+^{1}F(-1)$ $^{3}F_{4}+^{1}F_{1}+^{1}F(-1)$	$^{2}F_{3}+^{1}F_{2}+^{1}F_{1}+^{1}F(-1)$	
	$^{5}F_{5}+^{3}F_{4}$	$^{5}F_{5}+^{2}F_{3}+^{1}F_{2}$ $^{5}F_{5}+^{2}F_{3}+^{1}F_{1}$ $^{5}F_{5}+^{2}F_{3}+^{1}F(-1)$	$^{5}F_{5}+^{1}F_{2}+^{1}F_{1}+^{1}F(-1)$	^{3}F
	$^{8}F_{6}+^{5}F_{5}$	$^{8}F_{6}+^{3}F_{4}+^{2}F_{3}$	$^{8}F_{6}+^{3}F_{4}+^{1}F_{2}+^{1}F_{1}$ $^{8}F_{6}+^{3}F_{4}+^{1}F_{2}+^{1}F(-1)$ $^{8}F_{6}+^{3}F_{4}+^{1}F_{1}+^{1}F(-1)$	
	$^{13}F_{7}+^{8}F_{6}$	$^{13}F_{7}+^{5}F_{5}+^{3}F_{4}$	$^{13}F_{7}+^{5}F_{5}+^{2}F_{3}+^{1}F_{2}$ $^{13}F_{7}+^{5}F_{5}+^{2}F_{3}+^{1}F_{1}$ $^{13}F_{7}+^{5}F_{5}+^{2}F_{3}+^{1}F(-1)$	13
	$F_{n-1}+F_{n-2}$	$F_{n-1}+F_{n-3}+F_{n-4}$	... and so on ...	
	$^{610}F_{15}+^{377}F_{14}$	$^{610}F_{15}+^{233}F_{13}+^{144}F_{12}$	.... See text	...


$+{}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
$5+{}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
${}^{3}F_{4}+{}^{2}F_{3}+{}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
$6+{}^{3}F_{4}+{}^{1}F_{2}+{}^{1}F_{1}$
${}^{8}F_{6}+{}^{3}F_{4}+{}^{1}F_{2}+{}^{1}F_{(-1)}$
${}^{8}F_{6}+{}^{3}F_{4}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
$F_{7}+{}^{5}F_{5}+{}^{2}F_{3}+{}^{1}F_{2}$
${}^{13}F_{7}+{}^{5}F_{5}+{}^{2}F_{3}+{}^{1}F_{1}$
${}^{13}F_{7}+{}^{5}F_{5}+{}^{2}F_{3}+{}^{1}F_{(-1)}$
${}^{13}F_{7}+{}^{5}F_{5}+{}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
${}^{5}F_{5}+{}^{3}F_{4}+{}^{2}F_{3}+{}^{1}F_{2}+{}^{1}F_{1}+{}^{1}F_{(-1)}$
${}^{8}F_{6}$
. and so on ...
.... See text ....
... See text ...
..
37

$5_{F5}+3_{F4}+2_{F3}+1_{F2}+1_{F1}+1_{F(-1)}$

)

$8_{F6}+5_{F5}+3_{F4}+2_{F3}+1_{F2}+1_{F1}+1_{F(-1)}$

... Fifteen weights:

$377_{F14}+\ldots+1_{F(-1)}$