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INTRODUCTION AND MICROBALANCE REVIEW

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CHAPTER I OF "MICROWEIGHING IN VACUUM AND CONTROLLED ENVIRONMENTS," TO BE PUBLISHED BY ELSEVIER, AMSTERDAM, IN LATE 1979

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NOTICE

PREFACE

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This report is the first chapter in a ten-chapter book entitled "Microweighing in Vacuum and Controlled Environments," to be published by Elsevier, Amsterdam, in late 1979. It was prepared by Alvin W. Czanderna of SERI and S. P. Wolsky of P. R. Mallory and Son, Inc., Burlington, Mass. An earlier version of the chapter was published in 1969 as given in reference 1, but the book is now out-of-print. This updated chapter was begun in the fall of 1977, while Dr. Czanderna was on the faculty of Clarkson College of Technology, and was completed as part of his task at SERI. The references listed since 1969 provide examples of the new work that continues to be published using the vacuum microbalance as the primary measuring technique. A more complete listing of recent references is given in reference 18.

The authors are pleased to acknowledge the sources of support for this effort; namely, Ultramicrobalance Instruments; Elsevier; Clarkson College; P. R. Mallory and Son, Inc.; and the Department of Energy through a prime contract to SERI. The assistance of Dr. R. Vasofsky and various staff members at SERI is gratefully acknowledged; the camera-ready plates prepared for Elsevier by Lucile Czanderna, were used by SERI for reproduction of this report with the consent of the relevant parties.

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OUTLINE

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Chapter 1

INTRODUCTION AND MICROBALANCE REVIEW

A.W. Czanderna and S.P. Wolsky

1. INTRODUCTION

The subject matter of this book and this chapter will be discussed briefly to provide an overview. The progress of many important physical processes can be followed through observation of associated mass changes. Adsorption, desorption, oxidation, reduction, and evaporation are only a few of the more common phenomena that fall into this category. Although the phenomena can be studied by measuring other physical and/or chemical changes, the simple, direct, and absolute nature of gravimetric measurements is very attractive.

The increased interest in the microbalance has resulted, in part, from the recent rapid progress in scientific instrumentation. From a current view, it is difficult to realize that as recently as 1960 the ranks of microbalance experts were limited to those few with the resources and ability to fabricate their own instruments. Today, highly sophisticated automatic recording devices adequate to satisfy most requirements are available commercially. Parallel progress in vacuum science and technology has provided a means for careful environmental control required for many microgravimetric experiments.

Access to the literature on applications of the microbalance was relatively simple until the last few years. In the last two decades, studies with microgravimetric techniques graduated from using custom-made apparatus, designed and constructed by pioneers in the field to solve specific problems, to wide use of commercially available microbalances. As summarized in the only treatise in the field [1], usage of commercially available units dominated applications of the microbalance by 1969 [2]. Until 1971, the bulk of the development of microbalance technology has been tidily covered in ref. 1, the reviews cited in ref. 2, and in the proceedings of the first eight conferences under the title *Vacuum Microbalance Techniques* [3-10]. In recent years, the microbalance has been increasingly employed as a routine analytical instrument. As a result, abstracts

only infrequently mention using a microbalance, and even in the experimental section it may be referenced as a gravimetric method. Considerable access to the recent literature on microbalance technology and applications can still be gained from the proceedings of the ninth, tenth, and twelfth conferences on microbalance techniques under the title *Progress in Vacuum Microbalance Techniques* [11-13], of the fourteenth and sixteenth conferences in *Thermochimica Acta* [14], and of the eleventh, thirteenth, and fifteenth conferences in *The Journal of Vacuum Science and Technology* [15-17]. However, coverage in these three sources now needs to be supplemented by direct contact with appropriate journals because of the difficulty in finding pertinent articles from citation indices which are based on abstracts in the various journals. It is the prime purpose of this book to provide a single reference source for detailed and critical discussions of the important features, limitations, and applications of the beam microbalance. The contributors to this volume are recognized internationally for specific contributions, and many have pioneered some aspect of the development and application of the microbalance.

This book has been designed to be practical. Detailed discussions are deliberately included on classifications, auxiliary equipment, design, fabrication, artifacts, theory, operation, and applications of beam microbalances. This information is sufficient to allow the reader to evaluate the microbalance before initiating his own effort. The first three chapters deal with an overview, theory, design, and artifacts. The last seven chapters consider various applications. Each chapter is a separate entity and can be read by a knowledgeable worker. Cross referencing has also been used to integrate the entire treatise.

In this chapter, a review of the microbalance literature provides a current assessment of the field. Details of microbalance theory, design, and fabrication in the second chapter will assist those willing to build their own or to modify commercially available apparatus. The third chapter provides insight into instrumental and environmental factors affecting the sensitivity of beam balances.

The applications considered in the last seven chapters were chosen from the mainstream of problems being addressed with the vacuum microbalance. The physical and chemical adsorption and desorption of gases, the study of oxidation and catalytic reactions, the simultaneous measurement of mass and infrared or residual gases present covers the vast bulk of current applications of microgravimetry in controlled environments. Using beam microbalances for studying reduction reactions, decomposition, dehydration, evaporation, condensation, surface pressure, surface tension, and magnetic susceptibility was addressed in a recent noncritical

review [18]. The reader's imagination should be stimulated by the various applications cited, especially those presented in the final chapter.

Thermogravimetry has not been considered in this book, as a deliberate omission. Using balances for thermogravimetric studies has been well covered in other texts starting with the treatise by Wendlandt [19], successor books, and related journals such as *J. Thermal Analysis* and *Thermochimica Acta.*

The subject matter in this chapter provides a broad introductory review for this volume. The intent of this chapter is to summarize the historical development of the various types of balances, to cite references to the significant complexities that may be introduced in the measurements, and to reference the most important groups of microbalance applications. It is hoped that this discussion will aid the new host of microbalance experimentalists in avoiding needless repetitious studies of the undesirable mass and force changes that accompany the application categories.

The detection of changes in mass (or weight) is one of the fundamental measurements in the physical sciences. As a result, considerable effort has been expended in the design, construction, and use of ultrasensitive weighing apparatus. The advent of the simple precision microbalance is generally attributed to Warburg and Ihmori in 1886 [20]. The steady progress in this field has been discussed in review articles [21-34] and the published proceedings of a series of conferences on vacuum microbalance techniques [3-17]. Since extensive references are available in these articles and volumes, no attempt will be made to produce a complete bibliography of the microbalance literature in this chapter. Rather, references will be used for illustrative purposes and to provide a more detailed account of some important topics that were left somewhat incomplete in the most recent reviews [29,31-34]. These topics will include classification of microbalances based on the response to an applied force, on the method used for monitoring the response, and on the method of automatic operation. Then, an account of various types of auxiliary equipment required to operate a microbalance will be presented. This will be followed by a discussion of the undesirable disturbances encountered in vacuum microgravimetry. Here, the radiometric forces that result from the thermomolecular flow of gases will be reviewed in some detail because they represent the greatest constraint to precise measurement of mass changes uncovered in the last two decades. Finally, the use of different types of microbalances for various applications will be cited.

Only brief mention will be made of the materials used for the construction of microbalances and of the techniques of calibration since these will be covered in detail by Schwoebel in Chapter 2.

Most microweighing to date has been carried out using cantilever, spring, and beam microbalances rather than the quartz crystal oscillator, which will be treated in another volume (Part II).

The versatility of using microbalance techniques for the measurement of small force or mass changes of samples *in situ* has been recognized [35]. However, all microweighing techniques are constrained to monitoring *only* the change in mass of the specimen. The challenge when an ultrasensitive weighing device has been developed, then, is to be unequivocally certain that the mass change observed *is actually occurring on the specimen under investigation* because of controlled or specified changes in the temperature, pressure, gas composition, etc. This very considerable challenge will be apparent in the remaining sections of this book.

Some confusion may arise in reading the literature concerning microgravimetric results reported as weight or mass changes. The weight, **W**, of a body is the gravitational force exerted on it by the earth. From Newton's second law, the mass m of the body is given by $m = \mathbf{W}/\mathbf{g}$ where g is the acceleration due to gravity. In a uniform gravitational field, an equal arm balance can be used to determine an unknown mass from a known mass by establishing the point of equivalence of weight. Most calibrations are referred to a mass standard, directly or indirectly. Hence, it is proper to report microgravimetric results as mass changes. It is also obvious that results reported as weight changes should indeed be labeled in units of force (dynes, newtons, or pounds) rather than in units of mass (g, slugs). Arbitrary conversion of weight to mass without the knowledge of the gravitational constant could result in an error of up to 0.4%.

II. HISTORY

Microbalances have been used for a long time to study such diverse topics as adsorption, desorption, oxidation, reduction, solubilities, stoichiometry, phase change, surface tension, gas densities, magnetic susceptibilities, and long-range forces of molecular attraction. In most of the work before 1945 the emphasis of each researcher was simply to develop a suitable method for measuring microgram and submicrogram amounts of material. The result was a proliferation of custom-built balances which were delicate, invariably unmanageable in high vacuum, and required unusual craftsmanship to build and operate.

Progress in precision microgravimetry, which follows somewhat the progress in instrumentation, can be divided into three periods of development. During the first period, from 1886 to about 1945, the

number of workers was few and the difficulties were great. As pointed out by Rhodin [26], Emich and Donau made outstanding contributions during this era of custom-made balances. In the next period, from 1945 to 1960, the number of workers in the field increased considerably. Techniques were developed for building microbalances in quantity with a minimum amount of craftsmanship. Toward the end of this era, the pioneering work on various types of automation for microbalances was carried out. In the third period, from 1960 to date, the number of scientists and technicians using microbalances has increased nearly a hundredfold primarily because of the advent of commercially available automatic recording apparatus. There has been a concomitant shift from an emphasis of designing microbalances to obtain specific results to one of mass production of microgravimetric data. The latter has not necessarily carried with it a corresponding increase in the understanding of the physical systems under investigation because of a lack of detailed understanding of the uncertainties and spurious effects that accompany the techniques used.

III. DEFINITIONS

The definitions encountered in microgravimetry are easier to understand if they are separated into two broad categories. The following discussion is concerned, therefore, first with the definitions that are characteristic properties of the instrument itself and then with those unique to using the instrument in a microweighing system. Further discussion of the definitions is given in Chapter 2.

A *microbalance* is a highly responsive instrument capable of detecting very small changes in the mass of a specimen or an equivalent force. The lower limit of detectability of the microbalance is not well defined and may range from 10^{-10} to 10^{-5} g or an equivalent force range from 10^{-12} to 10^{-7} newtons. The possible range of mass or force has been narrowed by the use of the term *ultramicrobalance* to indicate a detectability of at least 10^{-7} g or 10^{-9} newtons [36]. The *sensitivity* is the magnitude of the reversible or elastic displacement per unit variation in mass or weight. The sensitivity is an inherent property of the instrument; its particular value is specified by the design and construction of the balance although obviously some measurement is necessary to determine its magnitude. The *response* is the reciprocal of the sensitivity and is expressed in micrograms per unit of arc (or per unit of displacement of the pointer at a given distance from the fulcrum). Values of response are often given in the literature in mass units; that is, micrograms. While these are not reciprocal

sensitivities as defined here, enough information is usually available in any given article to identify the true value of the response. The *period* is the time required to complete one oscillatory or vibrational cycle of motion of the balance. The *capacity* is the maximum load that can be suspended and placed on the balance without injury to the balance or its operation. In the case of beam balances, the capacity must also include the mass of the beam.

The *precision* of a balance is the minimum variation in mass that can be observed experimentally in a reproducible manner in the absence of any effects from the microbalance system. The *sensibility* indicates the minimum variation in mass that can be observed experimentally in a reproducible manner *in a microweighing system.* Sensibility is a more practical term than either sensitivity or precision since it is a characteristic of the complete weighing system; that is, its value depends on the response of the instruments and/or operators used to detect the balance deflection and on effects of thermal, pressure, electrical, and mechanical instabilities. The ultimate sensibility obtained when the errors associated with the system are negligible will, by definition, be equivalent to the precision of the balance. *Resolution or mass resolution* refer to the minimum mass change that is detectable using the microbalance. These two terms should be used with care since they may represent a statement of either precision or sensibility. The *range*, generally stated for *in situ* measurement, is the maximum variation in mass change that can be measured with the balance at a given load. The *zero-point stability or long-term stability* of the balance refers to any time-dependent variation of the precision of the balance or the sensibility of the system. The stability is an especially important balance characteristic when a particular application requires monitoring submicrogram quantities of mass change for days, weeks, or months. A systematic drift in the zero point for any reason will result in a decrease of the precision of measurement.

Before discussion of the various classifications of microbalances, it is important to provide a useful term that relates the ratio of the sample load to the minimum detectable mass change in any planned microbalance application. The load to precision ratio (LPR), favored by the authors, and the ratio of load to sample mass resolution, used in Chapter 2, are equivalent for properly describing the necessary balance characteristic. The load to sensitivity ratio (LSR) which is often encountered in the literature is of no value for either (1) planning applications of the balance or (2) describing one of the fundamental characteristics of the balance. The criticism of LSR for (1) is evident from the definition of terms in which both precision and mass resolution are derived from an experimental

capability while sensitivity is a particular property of the balance design and/or material. For (1), Schwoebel has shown the uselessness of LSR for evaluating the true characteristics of widely differing balances [37]. High values of LSR could indicate either large loads or low sensitivities which invalidates its use as an index. However, he has found that the load sensitivity product (LSP) provides a proper quantitative basis for comparing the true performance characteristics of various types of microbalances (Chapter 2, Tables 1-3). The adoption of LSP, which was developed during the preparation of Chapter 2, is strongly endorsed as a future standard.

The LPR is of special importance in applications where small mass changes of large samples occur. For example, if we hypothetically consider single crystal wafers of silver, 0.01 cm thick with an area of 1 cm^2, then 100 wafers would weigh 10.49 g and have an area of 200 cm^2 but would adsorb only 5 μg of oxygen at monolayer coverage. A balance with a LPR of 10^8 would detect changes of 0.105 μg, or only 2% of an adsorbed monolayer. Wafers 0.01 cm thick can be prepared from a single crystal [38], but there are numerous other problems that arise in the measurement of the adsorption of submonolayer quantities of gas using microbalance techniques. The reader may find it enlightening to perform similar calculations for measurements of desorption, solubilities, thin film stoichiometry, iron impurity concentration in magnetic susceptibility measurements, etc. It will be shown that design and operation of a balance with a LPR of 10^8 is a creditable accomplishment, and there will be considerable focus on this problem in this book.

IV. CLASSIFICATION OF VARIOUS TYPES OF MICROBALANCES

A. Introduction: The Ideal Microbalance

The ideal microbalance, which is most closely approached by the beam microbalance, should optimize a number of characteristics. It should have a large capacity and range, zero point stability, and a precision that is invariant with load; it should exhibit minimal pressure and temperature coefficients, be free from electrostatic and vibrational disturbances, be simple to calibrate, and be stable. It should be possible to subject the chemically inert balance material, frame, and housing to a bakeout at ca. 225°C for producing ultrahigh vacuum without altering the operation or characteristics of the balance. Finally, the balance should be automated. Fused silica coated with gold [39] probably comes closest to representing the ideal choice of balance material although satisfactory results have been obtained by employing fused silica [1-17,20-

34,40], gold-coated aluminum [41], and even alloys of aluminum [42,43] (see Section IV.E for further discussion of beam materials).

B. Types of Instruments

It is of interest to compare the various types of microbalances by their mode of operation from a pseudohistorical approach to demonstrate the evolution of the microbalance to the currently held view of the ideal instrument. The various designs can be classified as cantilever, spring, beam, or quartz crystal. In general, this classification is based on the response of the instrument to a change in sample mass.

1. Cantilever Microbalances

The cantilever microbalance, which is the simplest type of balance, depends on the measurement of the deflection of a thin fiber to determine the change in weight. In its simplest form, as shown in Fig. 1, one end of the fiber is fixed and the other end is loaded. An increase in the mass will result in the downward displacement of the free end. It is customary to measure the displacement by an optical technique because of the severe limitation of the capacity of the balance. Characteristics of typical cantilever balances have been discussed [26]. Historically, the cantilever balance can be traced to Salvioni [44] in 1901; papers continue to be published [45-47] in which this type of design is used. Details of construction of cantilever balances have been presented in a recent paper [45]. The virtues of these balances include

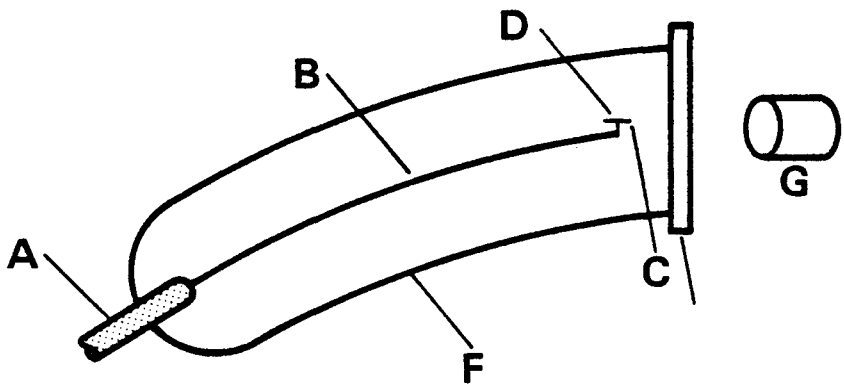

Fig. 1. Cantilever balance. A. glass rod: B. quartz fiber; C. glass pan: D. fiducial fiber: E. optical flat: F. glass housing; G. microscope. (After J. Skelly. Rev. Sci. Instr.. 38 (1967) 985. American Institute of Physics.)

simplicity, relative freedom from vibration, and adaptability. They are particularly susceptible to air currents, temperature inhomogeneities, and electrostatic charge. However, the design by Kessler and Moore [46], which is automated by a capacitance technique, indicates that balances of this type can be made very convenient by employing sophisticated electronics. Automation of a quartz fiber microbalance with sensibilities to 10^{-5} to 10^{-11} g has been described [47]. Some of the important properties of the cantilever and other types of microbalances are summarized in Table 1.

2. Spring Microbalances

The spring microbalance consists of a helical spring, usually made of fused silica (Editors' Note: The terms "quartz," "fused quartz," and "fused silica" are often used interchangeably to indicate a glassy silica material rather than the crystalline state of the material.), suspended vertically in a tube, as shown in Fig. 2 (from ref. 48). The extension of the spring is nearly proportional to the load where Hooke's law holds and the helix remains essentially circular. The

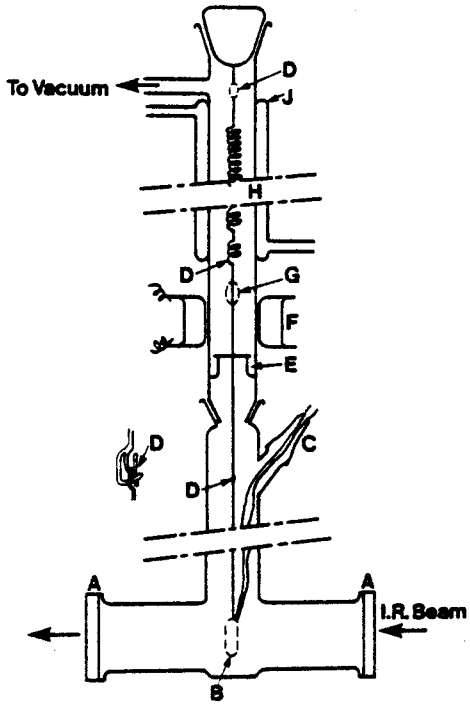

Fig. 2. Spring microbalance. A, infrared transparent windows; B, sample holder with sample; C, thermocouple; D, nontracking hooks (shown enlarged on the left); E, cross bar and stop; F, coil; G, magnet; H, quartz spring; J, thermal jacket. (After D. Seanor and C. Amberg, Rev. Sci. Instr., 34 (1963) 917, American Institute of Physics.)

TABLE I

Some Important Properties and Characteristics of Cantilever, Spring, and Beam Microbalances

Consideration	Balance type				
	Cantilever	Spring	Beam-knife edge	Beam-torsional	Beam-pivotal
Response to small change in mass	Bending of a beam	Stretching of a spring	Rotation of beam at primary fulcrum	Rotation of beam at primary fulcrum	Rotation of beam at primary fulcrum
Capacity	10 to 0.1 mg	Variable depending on helix size; 0.01 to 10 g, but see LPR	200 g	Less than 1 g in general but see ref. 83	Up to 20 g
Approximate minimum mass resolution	10 to 100 ng	100 ng	500 ng	1 ng	10 ng
Range of Load to Precision Ratio (LPR)	10^3 to 10^5	10^4 to 10^6	10^8 or less	2×10^8 or less	2×10^8 or less
Typical operation: Manual	Optical lever	Optical lever for vertical displacement	Riders in a bell jar	Optical lever; torsion head	Optical lever
Automatic*	Capacitance	P, T, and C	P, T, and C	P, T, and C	P, T, and C
Usual calibration method	Standard weights	Standard weights	Standard weights	Standard weights, buoyancy	Buoyancy, standard weights
Range	Variable; limited to beam deflection; typical 1 to 10 mg	Variable; limited by size of helix; typical 1 to 10 mg	Largest of all balances, 200 g	Deflection: 0.01 to 0.5 mg Automatic: over 10 mg	Deflection: 0.2 to 1 mg Automatic: over 10 mg

Virtues	Simple; adaptable to unusual temperatures and pressures; relatively free from vibrations	Simplest in design, operation and for incorporation into a vacuum system; readily outgassed	Large LPR; rugged; easy to use; large range	Large LPR; simple symmetrical design; versatile; adaptable to vacuum and ultrahigh vacuum operation; excellent sensibility over extended pressures and temperatures; can be operated using manual or automatic null techniques; large range; superior zero point stability	
				Superior deflection sensitivity	Extremely rugged, doesn't yaw during use; insensitive to vibrations; good deflection sensitivity
Disadvantages	Susceptible to air currents and electrostatic charge; sensibility limited by incremental resolution at total load; critically limited in capacity and range; fragile	Total load must be weighed to the full accuracy of the helix; limited LPR and range; susceptible to vibrations, especially in vacuum; magnetic-damping reduces useful load, must be carefully thermostatted to achieve precision below 1 μg; fragile	Absolute accuracy limited by rider technique; difficult to construct and adapt to ultrahigh vacuum operation; lowest sensitivity about 1 μg; high initial cost	Thermostatting may be needed, costly to buy attendant apparatus for manual and/or automatic operation; limited range on use as a deflection instrument; requires some manual skills to build; costly jigs are almost essential; zero shifts may result from beam banging arrest or from lateral impacts on balance support stand	
				Fragile; requires manual skills to maintain**; sensitive to vibrations; yaws during use	

* P: photoelectric; T: transducer; C: capacitance.

** These disadvantages are negated when suitable instruments are available commercially.

load to precision ratio (LPR) of this type of microbalance is its most serious limitation (Table 1). The spring balance, which was originated by Emich [49], is sometimes called a McBain-Bakr [50] balance because of their extensive use of it for sorption studies. Kirk and Schaffer [51] have written an excellent review of the construction and application of quartz helix balances. Rand [52] has described a method to prevent the reference arm from tangling with the helix. Spring balances are sensitive to vibration, especially in high vacuum; notoriously fragile; and should be thermostatted to prevent serious reading errors. However, Madorsky [53] has shown that tungsten springs give dependable performance for years and do not have the usual disadvantages. Others have used tungsten helices [54-56], but most devices described employ fused silica [48,57-65]. The balances are amenable to magnetic compensation [48,58,61,64,65] and to automatic operation using capacitance [62], transducer [59,65], and photoelectric sensors [58,60,63]. They are simple, commercially available, and adaptable to many types of studies. Dell [57], for example, has made use of silica springs in a flow system and discussed buoyancy effects. Moreau [65] and Harrison and Delgrosso [66] have described complete systems although the latter is not of microbalance sensitivity. The spring microbalance is discussed further in other reviews [26,31-33].

3. Beam Microbalances

All beam microbalances use the principle of center point balancing in which the primary fulcrum serves as an axis of rotation for equal clockwise and counterclockwise moments of force. The moments arise from the action of a force at the secondary fulcrums or yokes where the distance from the primary to the secondary fulcrum is the moment arm as shown schematically in Fig. 3. It is customary to classify beam balances according to the type of primary fulcrum used. The three categories include the knife edge, torsional, and pivotal balances. Most microbalances in use today are variants of one of the last two types.

a. Knife Edge. The knife edge balance is of historical importance because it is the prototype of the modern precision vacuum microbalance. It was used first by Warburg and Ihmori [20] and developed considerably by Steele and Grant [67]. The conventional silica or agate knife edge bearing on a flat plate constitutes the primary fulcrum of this balance and is also used for the secondary fulcrum in many models. The limitations of this type of balance for vacuum microgravimetry have been reviewed [26] and discussed in technical detail [68]. Of these, the problems of detecting and compensating

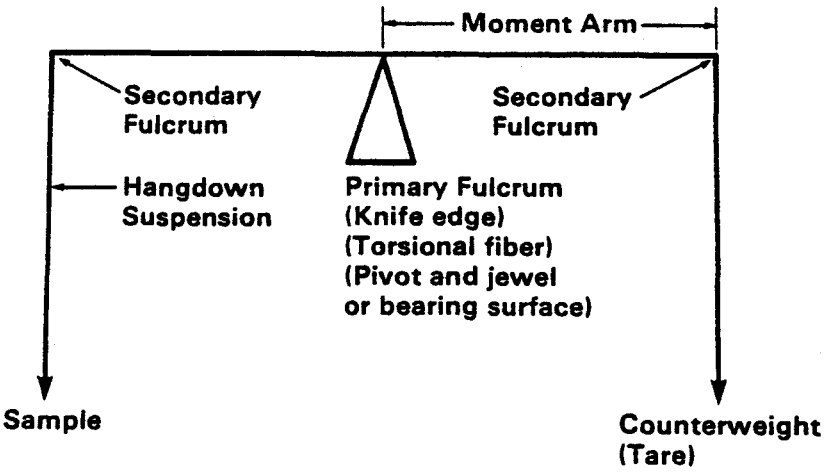

Fig. 3. Beam microbalance. Schematic showing principal of center point balancing.

mass changes into the submicrogram mass region and obtaining very high vacuum on the large volume of the vacuum enclosure stand out. However, in recent years, the use of the knife edge balance has increased considerably because of the commercial availability of automatic recording instruments and the improvements in vacuum technique, such as feed-through collars, base plates, and high-speed pumps applicable to systems with a large volume.

b. Torsional Horizontal Suspension. The most widely used balance is the torsional suspension balance in which the primary fulcrum is a wire, usually of quartz or tungsten, that is attached to the beam. In this type of balance, the torsional moment of the wire is made extremely small compared with the moment exerted by the sample and counterweight suspended from the secondary fulcrums. The early designs of Weber [69], Nernst and Riesenfeld [70], and Pettersson [21] were improved by Emich and Donau [71,72]. The improvement of the Donau version by Gulbransen [73] and Rhodin [74] ushered in the second period of development of vacuum microbalance techniques. It is therefore a proper tribute that many torsional balances are designated Gulbransen-type balances. A lightweight trussed beam was used by Kirk et al. [75] and others [76] to obtain rigidity. The Jennings and Gray microbalance [77] is another widely used trussed beam torsional microbalance; it was one of the first models to be automated using photoelectric techniques.

The operation of a torsional balance is extraordinarily reliable and offers the numerous advantages given in Table 1 that allow it to approach the ideal microbalance. The major disadvantages include their delicacy, tendency for sidewise yawing, susceptivity to vibration, and in some cases variation of sensitivity with load. However, these may not be serious problems (Chapter 2). The variation of sensitivity with load has been used advantageously for some experiments by Wolsky and Zdanuk [78].

Descriptions of torsional balances that continue to appear in the literature can usually be classified as Gulbransen type [35,42,79-83] or Jennings and Gray type [84-87]. Rodder's patented ultrasensitive instrument [88], which has long torsional fibers and a small beam mass, has unusually desirable characteristics as demonstrated by Fink and Merrill [89]. Balances made from Invar [83] and Dural aluminum [43] are not only rugged but can be designed to accept high loads [83]. Bakeable variants of the time-honored designs that permit operation in ultrahigh vacuum have been described by Wolsky [79], Schwoebel [85,86], and others [87-94]. Gouault [95] has discussed the theory of the problems of operation, sensitivity, and stability of torsional balances using tungsten at the primary fulcrum. A general discussion of these problems is included in Chapter 2. Many recent descriptions of torsional balances have been concerned with the mode of automation; i.e. by photoelectric [82,85-87,90,96-104], capacitance [81,91,105], or inductive [106-108] null point sensing techniques. Some form of magnetic compensation [82,84-87,100-104] is usually employed although Moret and Louwerix [92] used a rider adjustment mechanism. Two widely used commercial instruments employ a torsion type primary support and magnetic compensation; Cahn [101-104] prefers a photoelectric sensor while a magnetic inductive sensor is used in the Sartorius [106-108]. A new commercially available unit with a sensibility of 0.05 (ultimate) to 0.1 μg, a capacity of 5 g, and a load to precision ratio (LPR) of 5×10^6 has been described [108]. The authors report that the automatic balance has a rugged design and excellent stability. The principle of automatic operation is similar to that of the Cahn RG.

c. Torsional Vertical Suspension. In this technique, a torque is produced on a device suspended by a vertical torsion fiber. The technique, which was introduced by Volmer [109], is frequently referred to as the torsion effusion method. As shown in Fig. 4, the device is designed so that the rate of change of momentum of some particulate matter produces a torque or a force couple acting about the vertical axis of rotation. The extent of rotation of the fiber is measured frequently by optical techniques. However, it is amenable to compensation at a null position using torsion head [110,111],

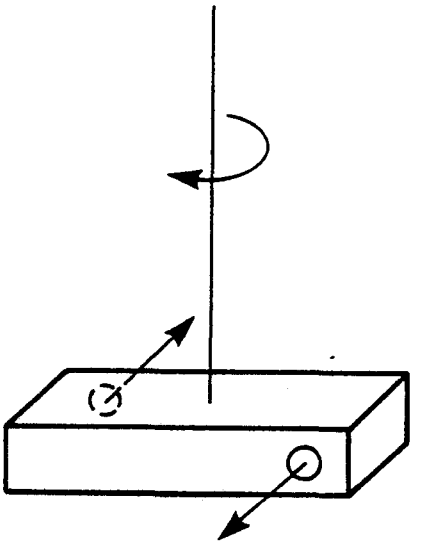

Fig. 4. Torsional beam microbalance: vertical suspension.

magnetic [112], capacitance [113], and photoelectric [114] techniques. The steady progress in the use of this technique has increased in the last few years as indicated by the sophisticated descriptions [115-123], which include a bakeable design [120] and discussion of associated problems [123]. Extensive references on applications of the device to problems of chemical interest including vapor pressure measurements, sputtering yields, and thin film studies have been cited in the review by Thomas and Williams [29] and the paper by Peleg and Alcock [122]. Freeman and Gwinup [123] have cited references extensively in discussing disturbing effects that result from thermomolecular flow (see Section VII.F) on vertically suspended torsion fibers. This technique has been combined with the use of beam balances, usually of the pivotal [123] or torsional [114] design, by a number of investigators [114,116,123-125] to gain information on both the rate and total mass loss. Edwards has provided a recent contribution on using this technique [125].

d. Pivotal. In the pivot balance, two sharp points bearing on a surface serve as the primary fulcrum. The choice of the point (pivot) and bearing (jewel) materials has led to an apparent large number of modifications. However, the gas density balance of Stock and Ritter [126,127] is the basic design which has been modified by others [124,128-145]. The development of the pivotal balance that has resulted in an increased use was led by Honig and co-workers [131-134,138]. Czanderna [140-142] continued the development of the tungsten-quartz pivot-bearing balance [140,141]. He improved the transducer method of automation developed by Cochran [135,136]

and designed an all-quartz bakeable beam [141]. The latter was the prototype of a patented trussed beam design [142,146] that can operate satisfactorily after UHV bakeout at loads of at least 20 g while maintaining an optimum LPR of 2×10^8. J.A. van Lier [147] automated the unit described in ref. 142 using a photoelectric technique and showed that the beam withstands extensive cyclic baking at 375°C. With Kollen and Biegen contributing significantly [148], the high gain electronic photoelectric system developed by Rodder [88,89] was adapted to provide a true UHV high-load ultramicrobalance. Others have used the balance satisfactorily [149], even when it was fabricated from Pyrex [150]. The plastic flow experienced by tungsten [142] appears to be an important asset to the remarkable operation achieved [131-133,142]. The most recent UHV adaptation [148] includes an all stainless steel frame for the beam supports, gold flags on silica fused to the beam, and a stainless steel housing. Simons et al. [130] used a capacitance technique to automate their balance.

Poulis and co-workers [151,152] have engaged in greatly needed theoretical and experimental work concerning the pivot, which included studies of choice of materials used for the pivot and jewel surface. They have shown that LPRs of 10^8 are possible and have tested balances operable at 25 g loads. Additional exploration on the limitations of the pivot systems described [124,128,135,136, 141-143] will be useful.

Although the LSPs are comparable (Chapter 2, Tables 2 and 3), the chief disadvantage of the current designs of pivotal balances is that a deflection sensitivity that is comparable with the most sensitive torsional models has not been achieved. This has been circumvented to a considerable extent by the use of the techniques developed recently to detect very small changes in the deflection [135,136,140,141].

e. Other. In 1944, Vieweg and Gast [153] designed a recording microbalance with a mass resclution of 10 μg that operates on the principle of magnetic coupling between an energized coil mounted on the beam and a permanent magnet at the top of a freely suspended sample. Deflection of the beam induces a current in stationary coils on either side of the beam. The induced current is amplified and used in a feedback loop to restore balance. Gast continued this pioneering development until his magnetic suspension balance [154] is now dependable to 0.3-1.0 μg [155]. A balance based on the same principle of operation has been described by Beams et al. [156,157]. The outstanding advantage of the magnetic suspension method, which is applicable to any type of high-load balance, is that it permits the balance and the sample suspension to be in separate chambers.

The Worden balance [158], which could be classified as a vertically suspended pivot balance, is an intriguing design that has been used extensively by Wade and co-workers [159]. The balance is all quartz, compact, inexpensive, and exhibits a very high deflection sensitivity but is no longer commercially available.

Behrndt [160] and Vasserberg [161] successfully combined the advantages of beam and spring microbalances to achieve bakeable operation and/or greater sensitivity although their designs are intricate.

Some of the important properties and characteristics of cantilever, spring, and beam microbalances are compared in Table 1. The disadvantages cited may depend markedly on the particular experimental system.

C. Methods of Monitoring Mass Changes

It would be proper to classify microbalances by the method used for monitoring mass changes. These would include deflection and null operation, which are both amenable to automatic operation.

1. Deflection Operation, Manual or Automatic

The measurement of the elongation or the deflection of the balance by the use of optical levers or cathetometers has been used for all balances. With this measurement the mass changes that can be monitored are limited to the free swing of the beam, which restricts the range of the instrument. This method of monitoring, which is exemplified by the Gulbransen gravity balance, is still in use today.

Satisfactory automation has been achieved using capacitance, transducer (linear variable differential transformer), or photoelectric techniques. However, even in the automated form deflection techniques are restrictive, and in general most balances are monitored with some form of null technique.

2. Null Operation, Manual or Automatic Compensation

The most effective technique for either manual or automatic operation of any balance is the null method; viz. the change in weight of the sample is compensated by the adjustment of some other calibrated force in the system. Compensating forces that have been applied for null techniques include the adjustment of riders, of a buoyancy force, of the torsional moment at the primary fulcrum, and of electrical and magnetic forces.

a. Compensation with Riders. The limitations on the use of adjustment by riders have been discussed [26,134]. These include uncertainties that are introduced because it is difficult to reposition the rider and achieve submicrogram precision, and it is not easy to adapt the balance to vacuum operation.

b. Buoyancy Compensation. In the use of buoyancy effects [67], mass changes are monitored by careful measurement of changes in pressure. This technique does not allow changes in weight to be measured in a vacuum or when the samples under study are affected by the pressure of the ambient gas.

c. Torsion Drum Compensation. The application of a torsional moment [75,162] to the supporting torsion fiber can also be used to restore the balance to the null position. However, care must be exercised to avoid nonlinearities, drift, and breakage of the torsion wheel. This procedure also presents considerable difficulties when used in vacuum.

d. Electrostatic Compensation. Capacitance techniques [46,62, 81,91,105,130] have been devised in which the force betweem two charged parallel plates is varied by the amount of charge on the plates. This technique is amenable to high vacuum operation, but considerable difficulties are encountered because of the different dielectric properties of gases that might be used in any given experiment.

e. Electromagnetic Compensation. One of the first applications of electromagnetic compensation was made by Angstrom [163] in which 10^{-6} g of material was weighed. The technique was refined by Emich to permit changes of less than 10^{-7} g to be detected. Since then, some form of magnetic coupling has become the most widely used scheme for balancing by a null technique. In the basic electromagnetic compensation technique, a permanent magnet is attached or enclosed on a hangdown suspension fiber. One end of the magnet is placed at the center of a solenoid; the position of the other end is either outside the solenoid or at least in the weaker magnetic field to establish the requisite magnetic field gradient. The compensating force then varies linearly with the current in the solenoid, according to the basic equations for the field of a solenoid [164]. Typical modifications of this type have been reported in recent papers [48,64,65,84-87,131-138]. This form of electromagnetic compensation will be discussed in more detail in Chapter 2, Section IV.B. The alternate method is to place a coil on the beam in a uniform magnetic field; the restoring torque, which rotates the

beam about the primary fulcrum, is obtained by changing the current in the coil. This method has been used by Vieweg and Gast [153], Cahn et al. [101-104], and in the Sartorius balance [106,107, 165]. This alternate method is difficult to adapt to ultrahigh vacuum operation whereas the basic method must be modified for use in the presence of variable stray magnetic fields.

In principle, all of the methods of compensation for using a balance as a null instrument can be applied to manual or automatic operation. Again, some form of electromagnetic compensation has been used in nearly every scheme developed for automatic or semiautomatic elimination of an error signal as will be discussed later in this article.

f. Light Pressure Compensation. Zinnow and Dybwad [94] have described a torsional balance placed in a standard UHV bell jar with a sensibility of 0.01 μg and a capacity of 0.2 g. They used the pressure of light as the restoring force.

g. Other. In a continuing series of papers, Gast [166] deals with the general subject of automatic control. In the last two papers he has demonstrated great progress in the development of a magnetic suspension balance. The main advantage to the latter concept is that the balance and sample chambers may be in separate volumes.

D. Methods for Automatic Sensing of Movement from the Null Point

1. Introduction: Automatic Recording Microbalances

Some of the early attempts to automate vacuum microbalances have been summarized by Cochran [135,136]. It is interesting that at the First Informal Conference on Microbalance Techniques [3] agreement was not unanimous concerning the value of automatic operation compared with manual techniques [35,80,versus 134,136]. There is no doubt today that automatic operation using some type of null balancing with a potentiometric readout offers tremendous advantages for both kinetic and equilibrium studies. A significant advance in technique, which is represented by the development of the automatic recording beam microbalance, is often the precursor to significant scientific discovery. This is simply a manifestation of providing the observer with an abundance of dependable experimental data--and of increasing the time he has for critical analytical evaluation. There are, of course, experimental situations where manual or deflection techniques should be used. In the last two decades, most investigators have selected or constructed automated microbalances, probably based on the type of considerations summarized in Table 2.

TABLE 2

Some Considerations of Automatic Operation of Beam Microbalances using Magnetic Compensation and Manual Operation Employing a Deflection Method

Considerations	Automatic operation, null magnetic compensation (AONMC)	Manual operation, deflection or null methods (MO)
Adaptability	Can be used effectively and efficiently for all beam balances	Can be used for all types of microbalances except for quartz crystal oscillators
Capacity	No effect: probes, mirrors, magnets, etc. are used as tare	Same as AONMC
Range	Large range provided by magnetic compensation	Deflection operation is limited to free swing of beam; null operation same as AONMC
Variation in sensitivity with load and effect on calibration	Precision may vary with load but not the calibration factor	Sensitivity and hence calibration factor vary with load
Zero point stability	Balance stability unaltered but null point sensor may have a significant temperature dependence	Zero point has very small temperature dependence
Zero point detectability	Electronic sensors of deflection from null are superior to manual methods	The best methods possible must be used to detect changes in beam position
Data	Continuous data. Other parameters, e.g. T, P, gas composition, etc., simultaneously recorded; zero shifts from any source automatically recorded	Intermittent readings; quality of data may vary from tired or different operators; small zero shifts may be missed

TABLE 2 (continued)

Considerations	Automatic operation, null magnetic compensation (AONMC)	Manual operation deflection or null methods (MO)
Temperature control	Necessary for some types of automation; otherwise, as for MO	Necessary for data of highest precision
Vibrational disturbances	Low level steady vibrations are handled without difficulty	Vibrations may be annoying for observation of beam position
Pressure and temperature	Temperature control necessary for null point sensor eliminates further concern	Temperature coefficient of beam may require thermostatting as carefully as for automatic operation with temperature sensitive sensor
High temperature bakeout	Operation not possible during bakeout; repeated bakeout cycles may alter calibration by demagnetizing compensation magnet	Operation not possible during bakeout; readily adaptable to repeated bakeout without altering calibration; operation with temperature sensitive sensor
Cost, dollars	Initial investment: ten to twenty-five thousand dollars	Initial investment: two to five thousand dollars
Cost, personnel	Continuous attention by technical personnel not necessary	Continuous attention necessary. Continuous twenty-four-hour operation very costly
Adaptation to computer	Digital methods-may be operated directly from voltage output and evaluation of data completed by computer program	Data may be evaluated by computer after manual recording of data

Automatic operation provides continuous monitoring of all mass changes, more reliable data, an extensive range of compensation, and far better use of operator time. Deflection methods and manual methods of compensation using a null technique are in many cases simpler to use for short-term experiments, which seems to be their only important asset.

The two main disadvantages of automation are cost and difficulty for high temperature bakeout. The initial cost is easily justifiable relative to the advantages gained. The difficulty of maintaining automatic operation during bakeout to 300 to 400°C has not been resolved; however, Addiss' and then Schwoebel's successful use of iron single crystals [84-87] has made a very significant contribution to eliminating this troublesome materials problem. According to van Lier [167], Cunife slowly loses its magnetization on repeated bakeout at 400°C, thus altering the balance calibration.

A general scheme for automation of a microbalance is shown in the block diagram in Fig. 5. It is customary to operate the balance at a null position. A sensing device (A) will provide an error signal (B) from the mechanical movement (C) of the beam away from the null. The error signal is presented most advantageously as a voltage to a servo feedback circuit (D). The latter alters a force acting on the balance (E), usually by changing the current in a magnetic compensation circuit, to eliminate the error signal. The changes in the current in the compensation circuit (F) are then used to provide

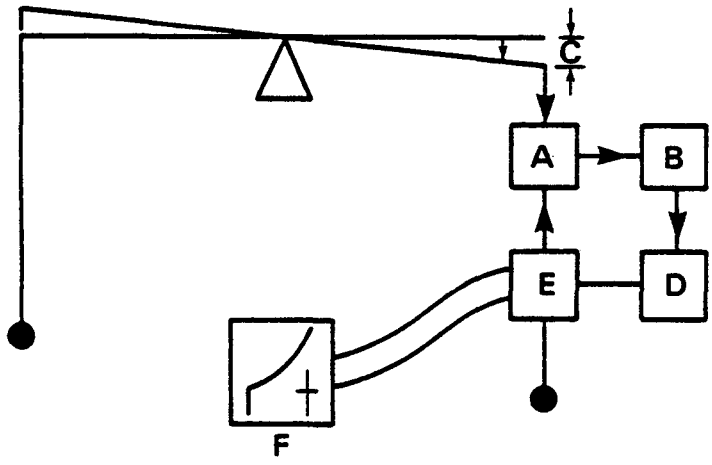

Fig. 5. Block diagram showing general scheme for automation of a beam microbalance. A, sensing device; B, error signal because of movement of beam; C, mechanical movement of beam; D, servo feedback circuit; E, restoring force on hangdown suspension; F, recorder.

a voltage that is related to mass change by some calibration factor. A detailed presentation of a typical automated system is presented in Chapter 2, Section IV.C.

The most widely used sensing devices depend on the change in capacitance, magnetic induction, or intensity of light falling on a photocell because of the mechanical movement of the beam. Typical examples are shown in Fig. 6.

2. Capacitance

In the capacitance technique (Fig. 6a), one plate of the capacitor moves because of the deflection of the balance. For a parallel plate capacitor, $C = Ke_oA/d$ where C is the capacitance, A is the area of the plates, d is the distance of separation, e_o is a constant, K is the dielectric coefficient, and Ke_o is the permittivity of the dielectric between the plates. Since very small changes in C can be detected by beat frequency techniques, it is seen that small values of d can also be sensed with this method even when the requisite leads are attached to the balance. Unfortunately, the value of K (K = 1 in vacuum) depends on the gas and the pressure of the gas in the system. While this sensing technique might not seem to be desirable

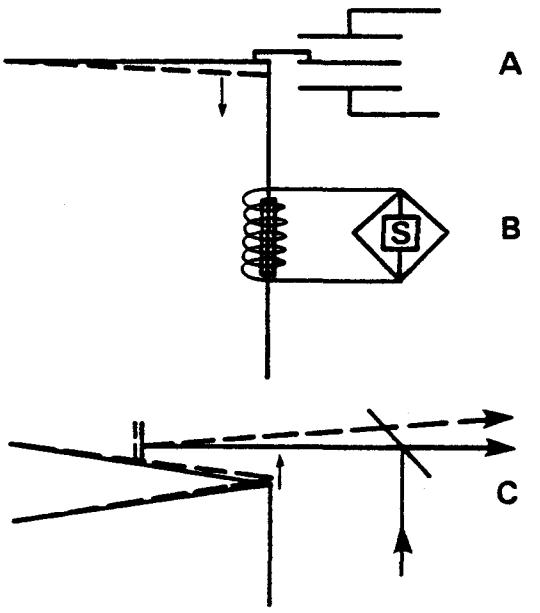

Fig. 6. Schematics of sensing devices. A, capacitance; B, magnetic induction; C, photoelectric.

for microbalance systems where pressure dependent studies are planned, a reference capacitor could be placed in the system to minimize the ambient effects.

3. Magnetic Induction

In the magnetic induction technique (Fig. 6b) the movement of the microbalance hangdown produces inductive effects in a bridged circuit. Again, the imbalance in the bridge can be used to detect very small changes in displacement. The geometry of the devices used for inducing the current imbalance provides difficulties. The method that depends on the movement of a probe in the core of a transducer or differential transformer [140,141] is difficult to adapt to ultrahigh vacuum operation. It is also extremely sensitive to temperature changes and gradients which requires elaborate thermostatting.

The inverted method of using the movement of a conductor in a uniform magnetic field [101-104,106-108,153-155] requires the attachment of a current loop to the beam of the balance. This method is not only difficult to adapt to ultrahigh vacuum operation but also has an adverse influence on the deflection sensitivity of the balance and the inertness of the beam, especially to organic gases. Deterioration of the torque motor in water vapor was shown explicitly in a recent publication [168].

4. Photoelectric

In the photoelectric method (Fig. 6c), the movement of the balance produces either a change in the path of light incident on a mirror attached to the beam [86] or a change in the position of an opaque flag in a light beam [148]. Alternatively, a beam splitter may be used [38]. In all cases the result is a change in intensity of light incident on a photosensitive detector. The change in photovoltage is then a measure of the movement of the balance. This technique not only provides adequate sensitivity to deflection but is readily adaptable to ultrahigh vacuum and is insensitive to changes in pressure and temperature. Of the three methods of sensing deflection described, the photoelectric method had become the most widely used because of the inherent advantages and lack of disadvantages.

E. Materials for Microbalance Fabrication

A critical discussion and comparison of the various materials used in the construction of microbalances is presented in Chapter 2. It is

sufficient, therefore, to note that quartz has been used for fabrication of an overwhelming number of balances because of its advantages. It is chemically inert, has a low density, high tensile strength, and a low coefficient of thermal expansion; it can be easily manipulated, drawn, and fused; it has a high purity and homogeneity and can be readily cleaned and outgassed. The principal disadvantages include a low thermal and electrical conductivity. However, these latter factors are sufficiently important to have led to the investigation of other suitable beam materials [40-43]. Aluminum and its alloys have been shown to be comparable to quartz as a beam material. Characteristics that are superior to either quartz or aluminum and its alloys have been obtained with a gold-plated quartz beam [39] because the metallic coating provides high thermal and electrical conductivity in addition to the advantages of quartz. Since the platinized beam preferred by Rhodin [26] was used in a thermostatted enclosure, it remains to be established whether gold, platinum, or some other metal will provide the ideal coating for a quartz beam. Both studies [26,39] were carried out on Gulbransen-type beams.

F. Conclusion: The Ultimate Microbalance

In Section IV.A, an attempt was made to define an ideal microbalance. A better term might have been the ultimate instrument for microgravimetric studies. It is rather obvious that not every investigator will require the ultimate instrument for a given study. In this case, compromises based on information presented in detail in Chapter 2 will be made until a suitable instrument design is reached. However, from the knowledge currently available, the ultimate instrument should be a torsion or pivot beam microbalance made of fused quartz with a metallic (gold) coating. It should operate automatically as a null instrument using a photoelectric sensor and an electronic servo feedback to a magnetic compensation scheme. For the latter, the suspension of a permanent magnet in the field of a solenoid is preferred. The entire system should be designed to permit the attainment of ultrahigh vacuum operation. The pivotal model [142,148] is preferred by many experimentalists because it is rugged, versatile, and has a load capacity that is usable for a great breadth of studies. The only apparent disadvantage is that it is less sensitive than the torsional model. This loses its prominence, however, because for many studies, a host of undesirable effects, discussed in Section VII, can be considerably greater than the precision of the instrument. Thus, the challenge of being assured that the mass change is actually occurring on the sample under investigation is again noted.

All the other choices made for the ideal balance are practically dictated when a balance is built to operate in ultrahigh vacuum (UHV). When UHV is not needed, other schemes for automation and magnetic compensation have significant merit and should be seriously considered. At the present time, the automatic bakeable torsional balances, described by Schwoebel [86] and Rodder [88,89], and the pivotal balances described by Czanderna et al. [148] and van Lier [147] represent the closest approaches to the ultimate design described in the literature. For those who prefer to modify widely used commercially available instruments, UHV can also be achieved with appropriate attention to good vacuum practice [169].

Finally, the goal of attaining a LPR of $>10^8$ has been reached with both torsional and pivotal balances (see refs. 74,75,86,88,89,142,146, and Chapter 2). According to Poulis and Thomas [170] (see also Chapter 3), attaining greater sensitivities may be fundamentally limited by Brownian motion. The relevance of fluctuation to this problem [170] and to the determination of micromagnetic susceptibilities has been discussed [138,171].

V. CALIBRATION TECHNIQUES

Because this subject is extensive, no attempt will be made here to assess the development of the various direct and indirect techniques used for calibration of a balance. It is obvious that calibration is a prerequisite for accurate measurements and the method of calibration used will depend on the anticipated design and use of the instrument. The calibration usually required is to establish a relationship between mass change and a voltage change of a resistor in a servo feedback loop. The direct calibration technique, in which mass standards are added to one hangdown suspension of the balance, is probably the most widely used method because of its simplicity and accuracy. However, the technique of using two buoyancy bulbs of the same mass but different volumes, which evolved from an interdisciplinary collaboration [132,138] and was described by Czanderna and Honig [131,132,134,137], is especially desirable. With this technique, it is not only possible to establish the relation between mass change and the voltage drop over a standard resistor in the compensation circuit but also the sensibility of the balance. Over 40 data points can be taken with either buoyancy bulb in a normal working day. By judicious choice of the volume of the bulbs, data can be obtained which are insensitive to reading errors in the pressure or the null position of the balance. The data can then be subjected to analysis by the method of least squares [172] to obtain the standard deviation, confidence limits,

etc., including differentials [131,132,134,142] for the precision of the balance *and* the pressure measuring device in the system. Thus, the buoyancy method provides a simple test of the linearity, precision, and accuracy of any gauge that might be used in the operation of the balance at pressures exceeding 1 to 2 kPa. Detailed data and discussions of the buoyancy bulb calibration method are presented in the appendices of a thesis by Biegen [173].

The papers by Macurdy [174] and Fennell and Webb [175] are interesting contributions. Methods for calibration and assessment of a quartz torsion balance are described [175]; a standard deviation of 0.08 μg was obtained for submicrogram ranges. Calibration procedures are also discussed in Chapter 2, Section IV.E.

VI. AUXILIARY EQUIPMENT FOR OPERATION OF A VACUUM MICROBALANCE

A. Introduction

In Section IV, the state of development of microweighing devices was the primary concern rather than their operation. The auxiliary equipment discussed in this section will be restricted to the needs for "classic operation." In classic operation, the balance is operated in a vacuum system; attendant facilities are provided that permit the temperature, pressure, and gas composition to be varied about a sample suspended from the balance. In Section VII.B undesirable disturbances that arise in classic operation will be reviewed. The simultaneous measurement of mass change and additional parameters will be treated in Section VIII.B and in Chapters 6, 7, and 8.

The cost of fabrication of the balances described in Section IV may be as little as $30. However, when special jigs are used for construction of a balance similar to those described by Podgurski [35], Wolsky and Zdanuk [79], Schwoebel [86], Czanderna [142], and Boggs [87], the cost of fabrication can run well into four figures for the first balance. The cost of the auxiliary equipment for the classic operation of a precision microbalance can easily reach $50,000. Typical needs include a vacuum system and attendant instrumentation, a sturdy vibration resistant mount, furnaces and cryostats, equipment for automatic and/or manual operation and recording, and apparatus for thermostatting an enclosure about the balance and/or hangdown tubes. A typical arrangement of the auxiliary equipment for classic operation is shown in Fig. 7.

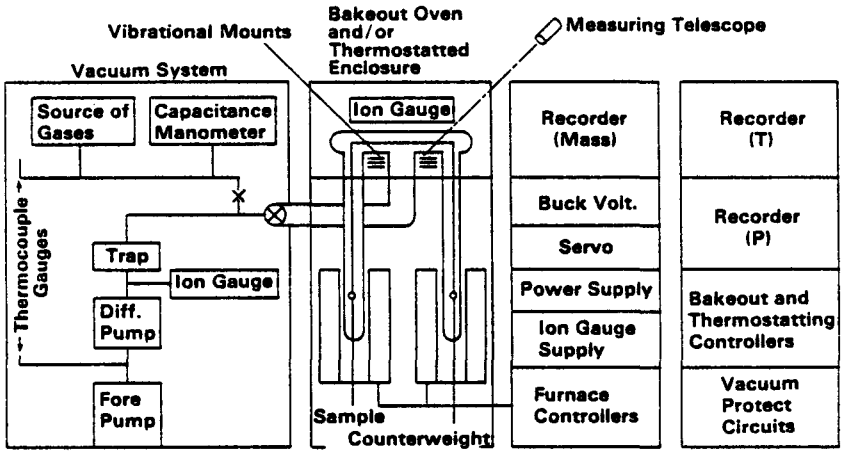

Fig. 7. Typical arrangement of auxiliary apparatus for classic operation of a beam microbalance.

B. Vacuum Operation

The essential components required for vacuum operation include a chamber for the balance (balance housing), hangdown tubes to enclose the sample and counterweight suspensions, a gas handling system used for adjusting the gas composition and pressure about the sample, and a pumping system.

1. Balance Housing

The chamber for housing the vacuum microbalance is usually of Pyrex glass, quartz, brass, or stainless steel with suitable windows, ports, and flanges attached. The detailed geometry of the arrangement of the balance in the housing, access to pumps and gas handling facilities, and hangdown tubes for beam and vertical torsion balances varies widely with the intended use of the balance. The extensive references cited in this book provide a considerable body of source material for any type of needed application.

2. Hangdown Tubes

A system designed for precision studies should employ a symmetrical design of the housing and hangdown tubes (Fig. 8) as introduced by Rhodin [26,74]. The importance of this design will be appreciated more when undesirable forces that result from buoyancy and thermomolecular flow are considered (SectionVII.E,F). The size of the tubes should be chosen to provide the desired pumping speed and

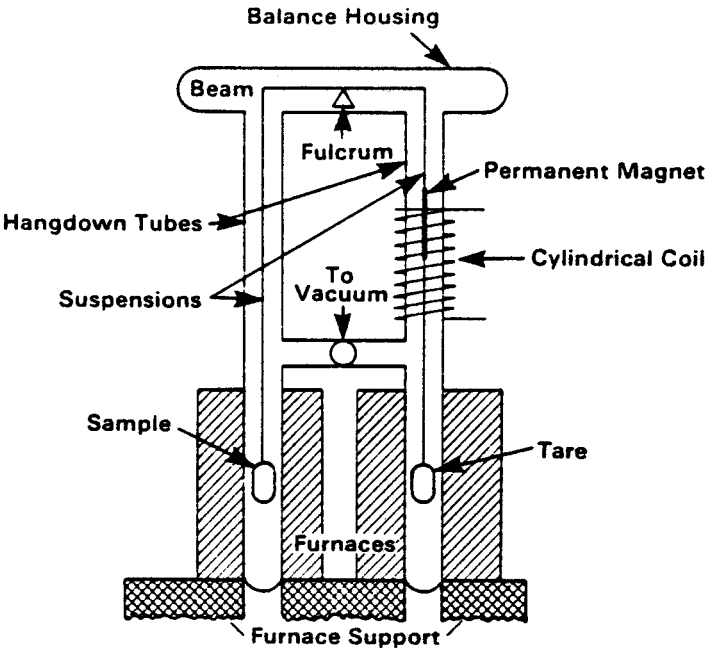

Fig. 8. Beam microbalance of symmetrical design employing electromagnetic compensation.

to minimize thermomolecular effects. Hangdown tubes are frequently coated with a conductive material and grounded to eliminate forces from static charges (Section VII.C). Pressure gauges, traps, getters, thermocouple wells or feed-throughs, and radiation baffles are frequently attached to hangdown tubes. Since the final design is governed by the anticipated use, systems employing interchangeable metal flanges with copper gaskets permit maximum flexibility.

3. *Sample Suspension Fibers*

The nature of the suspension fibers used depends on the method of preparing the sample and inserting it into the vacuum system. Rhodin [26] and Gulbransen [27,35] have reviewed the importance of careful sample preparation for precision studies. It is unfortunate that little detailed information is available on suspension fibers. Silica drawn into thin fibers has been used by many investigators for experimental work up to about 1100°C. The small manual by Faeth [137] contains simple detailed instructions which

serves as a good starting point. For low temperature operation nichrome, Pyrex, and other metal wires have been used. For temperatures approaching 1600°C, Gulbransen employed alumina, platinum, and platinum-rhodium [35]. Walker [80], after encountering difficulties with platinum, iridium, rhodium, and tungsten suspensions while employing an induction heating technique, successfully used a chain of sapphire single crystal rods to 1800°C. Tripp et al. [176] employed alumina rods for oxidation studies up to 1800°C.

A double hook suspension was used by Singer [177] and Soule et al. [178] in anisotropy studies. A copper tube with ultra thin walls cemented to the double hook provided the necessary completely rigid suspension [178]. Teflon monofilaments, less than 1 μ in diameter also have been used effectively [178].

4. *Vacuum Technique*

The advancement in vacuum technology has been phenomenal in the last two decades. Excellent books have been published on vacuum technique [179] and ultrahigh vacuum and its applications [180-181] which include extensive references. A general list of references to ultrahigh vacuum, general vacuum, and pertinent vacuum journals is also available from the Education Committee of the American Vacuum Society [182]. Therefore, no attempt will be made to review vacuum science further, but the importance of utilizing the remarkable techniques for the production and measurement of vacuum cannot be overemphasized. Microbalance systems that employ good design and excellent vacuum technique will be found in the applications chapters of this book. The application of the relevant pumping speed equations to design a system for a particular ultimate pressure has been reported [183]. A composite vacuum system is blocked out in Fig. 9 for illustrative purposes.

It is worth noting that pressure measurements made at room temperature *when the sample is at a different temperature* must be corrected for thermal transpiration as discussed in ref. 179, p. 59. The empirical correction formulas of Liang [184] are especially helpful.

C. Vibrational Mounts

Special mounts to eliminate undesirable vibrational effects have been used by numerous investigators [26,42,79,85,131,132,135,136,141, 142,185] as a general practice. These range from use of concrete pillars for the microbalance base [87] to simply isolating the balance from sources of vibration [79] and can be very unusual [186]. Pivotal microbalances have been used effectively without any

vibrational mounts [135,148]; the balance housing was supported by an angle aluminum table bolted to basement floors of three and four story buildings. Vibrational effects can be serious, especially at the upper levels of multistory buildings. It appears from a concensus of the literature that the safest way to deal with vibrational problems is to erect the microbalance support system on the ground floor of a building and isolate the support from the walls. The housing should be supported by a rigid framework. According to Kissa [187], further attempts to minimize or eliminate vibrational effects should be restricted since the indiscriminate use of resilient materials may magnify vibrations. Potential sources of vibration must be considered, however, in locating a balance [42,185] despite claims to the contrary [101-104] because of the effect on the ultimate sensibility. Further discussion of vibration problems may be found in Chapters 2 and 3.

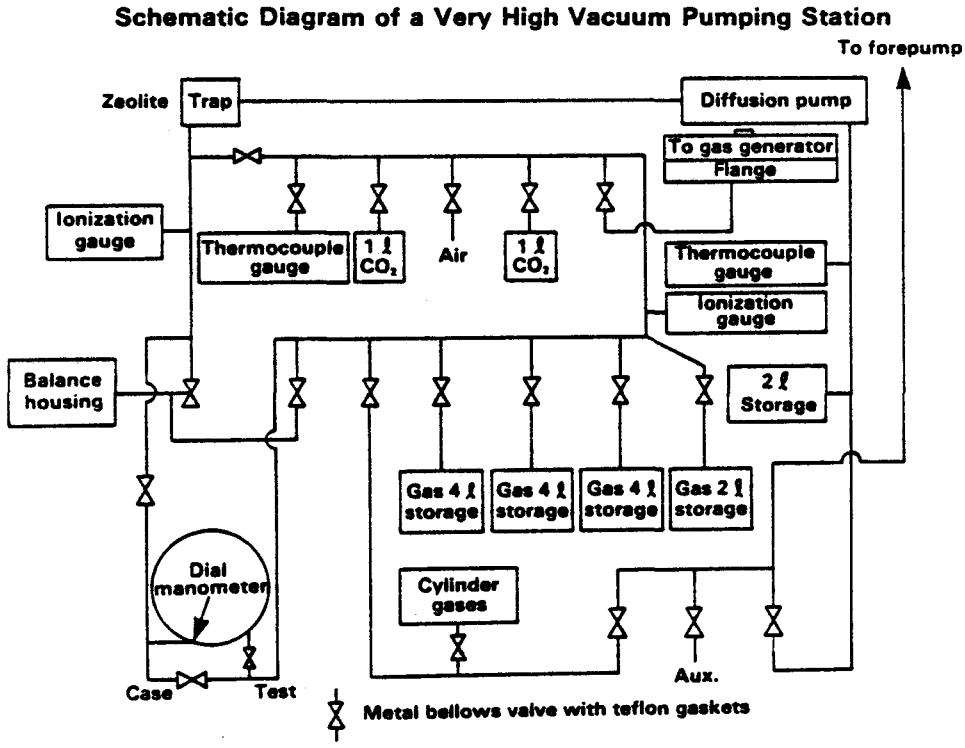

Fig. 9. Schematic diagram of a high vacuum pumping station and gas handling system.

D. Thermostatic Operation

Thermostatted enclosures [26,74,135,141] have been employed to maintain temperatures to within ± 0.03 to ± 0.1°C. In the simplest form air is drawn over a water-cooled heat exchanger from the enclosure with a centrifugal blower and returned to it through two heating elements. The power input of the heaters is regulated by an on-off controller and powerstats. When bakeout ovens are employed, they may also serve as the enclosure for thermostatting. It is convenient to raise and lower ovens and thermostats with a hoist.

E. Automatic Operation

The apparatus required for automatic operation includes the items shown in Fig. 5. Multipen recorders are especially valuable for displaying simultaneously the change in mass of the sample, its temperature, the pressure in the system, and the temperature of thermostatted enclosures. Other physical parameters measured simultaneously with mass change, which will be reviewed later, also can be conveniently recorded.

F. Manual Operation

Even though the era of automation has descended on vacuum microweighing, many investigators find numerous advantages in alternate manual operation [35,79,85,178,188]. Good results can be obtained by using a cathetometer with a resolution of ± 1 μm and some form of magnetic compensation. Satisfactory results can be obtained with a simple potentiometric circuit as described by Czanderna [131], Honig [134], and Faeth [137].

G. High Temperature Operation

The furnace used to heat the sample may present difficult materials problems when very high temperatures are desired. Gulbransen [27,35,83,189] has pioneered studies of the performance of materials for high temperature furnace tubes and high vacuum operation. Measurements of pressure, apparent pressure, and leak rates in vacuum and in various gases were carried out prior to studies of high temperature reactions. In Chapter 9, Gulbransen discusses high temperature reactions in detail. The measurement and control of temperature can be achieved by the usual engineering techniques except at very high temperatures [27,35,80,83,176,189, 190]. Control can be achieved with intermittent controllers or by maintaining a constant voltage input to the furnace. Gradientless

furnaces [191] and radiation shields [192] are helpful where large samples are used.

Temperatures can be determined with thermocouples or pyrometers. The thermocouples can be mounted either in the reaction chamber as close to the sample as possible or cemented to the walls of the tube furnace outside the vacuum system. In the latter case, Faeth [137] has shown that a calibration curve (Fig. 10) relating the thermocouple temperature to the temperature of the sample must be obtained because of radiation loss. When stainless steel hangdown tubes are used instead of glass, as was the case in Faeth's work, Prince et al. [193] have shown that the temperature correction is much larger, as plotted in the inset to Fig. 10. Other recent contributions on the subject of sample temperature measurement are available [194].

Special care must be exercised to correct for the brightness of the surface, which is measured with an optical pyrometer for the emissivity of the surface [189]. For samples enclosed in opaque furnace tubes, the Stephan-Boltzmann radiation law has been found

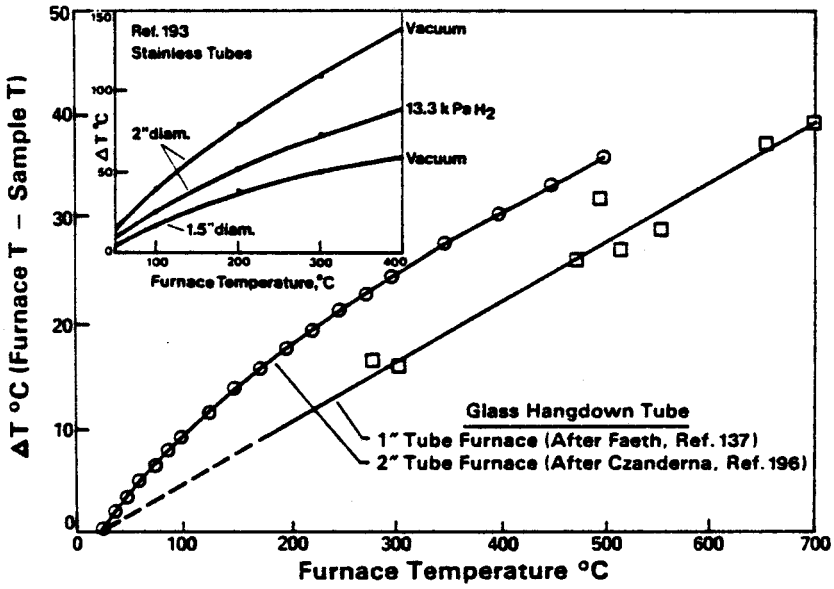

Fig. 10. Sample temperature correction and various furnace temperatures. The sample temperature is always lower for the tube furnaces because of radiation losses. (After Faeth, ref. 137, Prince, Vasofsky, and Czanderna, ref. 193, and Czanderna, ref. 196.)

useful for estimating the surface temperature of a sample [189]. For temperatures above 50°C, there are now pyrometers commercially available which could markedly change the mode of experimental design in the near future.

Some problems in induction heating to achieve temperatures of the order of 2000°C have been described [91,190].

H. Low Temperature Operation

For low temperature operation the hangdown tubes can be immersed in liquid-gas or solid-gas refrigerants contained in dewars to maintain a constant low temperature; it is critical to maintain the level of the refrigerant for precision studies. For intermediate temperatures, standard cryogenic techniques can be employed involving controlled heat leaks to refrigerated chambers (for example, see the journal *Cryogenics*). Again, it is important that both sample and tare suspensions be subjected to the same temperature conditions. For precision studies of the surface area, the temperature of the refrigerant must be determined because of the critical temperature dependence of the monolayer coverage. This eliminates the need to trust the purity of the liquid refrigerants or the fluctuation of their boiling points with change in the atmospheric pressure. Caution is particularly advised concerning the sample temperature at -196°C [11-14].

VII. UNDESIRABLE DISTURBANCES OR FORCES

In carrying out measurements with a microbalance, a number of undesirable forces and mass changes are encountered. These disturbances are sometimes referred to as spurious because they mask the measurement desired but in fact they are painfully real. The undesirable disturbances arise because of buoyancy, convection currents, thermomolecular flow (TMF), static electricity, temperature fluctuations about the sample and the balance case, and adsorption and desorption. These topics will be discussed briefly in the subsequent paragraphs; Massen and Poulis will discuss some of the more important effects in depth in Chapter 3.

A. Adsorption and Desorption Effects

Adsorption and desorption effects from the beam of a balance have been used by some [132,156] to account for unknown measured quantities. However, they can be dismissed for most studies by a simple calculation. The total surface area of a typical Gulbransen-

type torsion balance (cf. ref. 35) is about 0.58 cm^2; the area of oversize hangdown suspensions 40 cm long and 0.25 mm in diameter is only 0.02 cm^2. Even with an unrealistically large roughness factor of five, the total available surface is only 3 cm^2. Using the accepted value of 10.6 $Å^2$ per molecule of water for adsorption on an oxide surface [117], the mass gain at monolayer coverage would be 2.87×10^{-8} g/cm^2 or a total of about 0.09 μg. When the symmetry of the entire system is taken into account and it is realized that the balance will only detect changes because of a *differential* surface area, it can be seen that monolayer adsorption effects can in general be ignored. However, adsorption and desorption are important when materials are used in the system that could condense or react with the beam. Thus the attachment of plastics, glue, etc., to the microbalance is not an acceptable technique because multilayer adsorption may occur. It will be shown in Chapter 2 that part of the choice of materials is based on preventing condensation or reaction with the beam. Thus care should be exercised to prevent mercury vapor from reaching silver globules on the beam of the balance or organic vapors from sorbing on polymethylmethacrylate. It is apparent that a balance will register mass changes from adsorption and desorption when proper precautions and great cleanliness are *not* observed. These effects are distinguished from those of interactions of a vapor with organic polymers used in the torque motor (Section VII.G). The response of the microbalance to the momentum of the desorbing molecules may mask the mass lost by the sample [195]. These authors cleverly used a support pan of wire mesh to permit desorption to take place uniformly in "all" directions.

B. Temperature Fluctuations

Errors that could result from temperature fluctuations about the balance can be minimized by using thermostatted enclosures or by using a metallic coating on a fused silica beam for beam balances without thermostatting [140]. The plot in Fig. 11 shows the need for thermostatting to attain submicrogram operation of observed mass change versus temperature in an all quartz pivot balance of the type described by Czanderna and Honig [131,132]. These data [196] were obtained with the balance, housing, hangdown tubes, and vacuum system situated in an air-conditioned room. A vacuum of 2.6×10^{-5} Pa was maintained while the temperature outside the balance case was monitored with a 40-junction iron constantan thermocouple. The balance was operated manually as a null instrument with magnetic compensation. The quartz sample and tare bulbs were

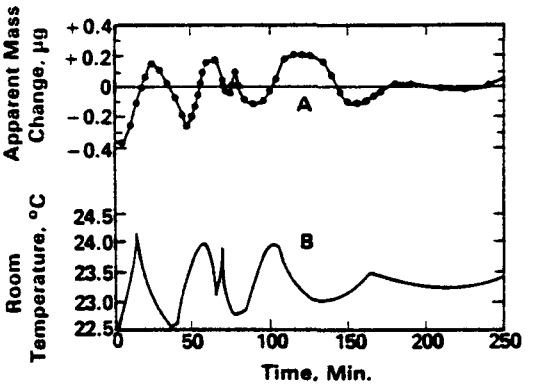

Fig. 11. Effect of temperature fluctuations about an unthermostatted beam microbalance. The need for temperature control to minimize the 0.3 µg/°C mass variation is evident. A, "mass" change relative to "zero" at 23.75°C. B, temperature of the balance housing in an air conditioned room.

empty. As can be seen, the temperature coefficient of the balance was 0.3 µg/°C.

C. Static Charge Forces

Disturbances that arise from static electricity may be avoided by using grounded conductive coatings such as tin oxide on the balance housing and hangdown tubes. Using a grounded metallic coating on the balance beam or using a metal beam is the preferred technique for dissipating static charge from the beam [26,42,74,79,80,101-104]. Others have found that heating [192], radioactive sources [196], and other ion-forming techniques [197] are useful to dissipate static charge. Hawley and Williams reported quantitatively on the effectiveness of an α-emitter for relieving electrostatic charge [198]. The use of a grounded silver hangdown tube with an ungrounded hangdown suspension has also been effective.

D. Convection Currents

At pressures exceeding 13.3 to 45 kPa, convection currents arise in a heated hangdown tube that produce continuous oscillation of an undamped balance. Several workers have studied this problem in varying detail. Robens summarized the available literature through 1970 in an excellent review article on thermal gas motion [199]. Thomas and Williams [42] noted effects of convection at 13.3 kPa and at temperatures below 0°C. After two more papers were published on this effect in the early 1970s [200,201], the number of reported studies diminished.

As shown in Fig. 12, the effect of convection currents is to decrease the precision of the measurements. Automatic operation, some form of eddy current damping, the use of baffles [199], or all three significantly decrease the annoyance of convection currents. The lowest pressure where convection currents become noticeable depends on the temperature, geometry, and the gas in the system [42,131]. If microbalances are used extensively at both high pressures and high temperatures, further study of this topic will be required to obtain a better characterization of limits imposed by convective flow.

E. Buoyancy Forces

Unless a microbalance is being used explicitly to determine the density of gases [126,127,129,130,144], raw data must be corrected for the buoyancy of the gas. A buoyant force, F_z, will exist if an unequal volume, ΔV, is occupied by the beam, suspensions, sample containers, etc., on either side of the fulcrum. The magnitude of F_z equals the weight (mg) of the displaced fluid which in most work is a gas. For a gas obeying the equation of state PV = nRT, the mass m of the displaced fluid is given by

$$F_z/g = m = PM\Delta V/RT \quad (1)$$

where P is the pressure in torr, M is the gram molecular weight of the gas, ΔV is in cm^3, T in K, and R is 62,364 cm^3 torr/mol K. This equation shows that the buoyancy effect on the mass is a

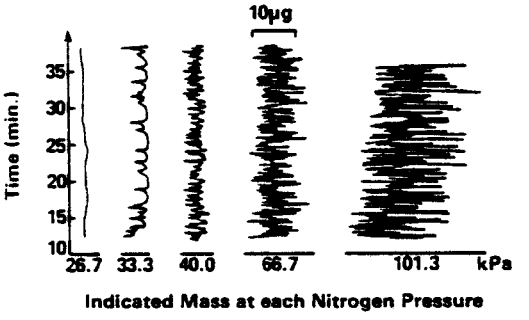

Fig. 12. Recorded time dependence of mass with a balance pan at -196°C and the beam at 27°C at various nitrogen pressures. (After Robens, ref. 199.)

function of four variables; viz. the pressure, temperature, gas, and net buoyancy volume. The advantage of a symmetric system is now evident since ΔV is the only parameter that can be designed to be zero, thus eliminating the correction for buoyancy. Arranging ΔV to be zero initially is a necessary but not complete solution; the *sample, counterweight, and heated or cooled* parts of the suspensions also must have the same volume to eliminate a temperature dependence of ΔV. Even then, Pierotti [202] has shown by an elegant statistical mechanical treatment that second order effects arise from a sample of large surface area. Thus, if the surface area of the sample and counterweight are different and if the surface area of the sample is greater than 1-100 m^2/g, a mass defect will be recorded. Pierotti [202] has shown that the mass defect arises because of the range of the van der Waals interaction between the surface and an ambient gas.

It is also evident that the first order buoyancy correction given by eqn. (1) is based on ideal gas behavior. When real gases are employed, care must be taken to use the equation of state that is appropriate for the gas, temperature, and pressure conditions of the experiment.

F. Radiometric Forces that Result from the Thermomolecular Flow of Gases

When a temperature gradient exists along a microbalance suspension fiber, sample, or counterweight, radiometric forces will be generated because of the thermomolecular flow (TMF) of gases at pressures which generally range from 10^{-2} to 266 Pa. The gas species arriving at a unit surface from regions of different temperatures, and hence with different momenta produce a net force on the fiber in the direction of decreasing temperature. The magnitude of the force depends on the pressure, gas, temperature, temperature gradient, and geometry of the system. The force may be minimized by employing identical suspension fibers, hangdown tubes, and temperature gradients about an identical sample and counterweight. With the ideal arrangement depicted in Fig. 13, TMF will produce compensating forces in opposite directions about the fulcrum of the balance. The net magnitude of the resultant "spurious" effect, then, is zero as a function of pressure. In practice, it is difficult to obtain ideal compensation and, therefore, there is a resultant force from TMF that is not a simple function of pressure. If all variables remain the same, it is reproducible and may be calibrated. The magnitude of the effect may not become submicrogram until the pressure is as low as 10^{-3} Pa or as high as 2.7 kPa if the geometry of the suspension fiber, sample, and hangdown tube is poor. Thus,

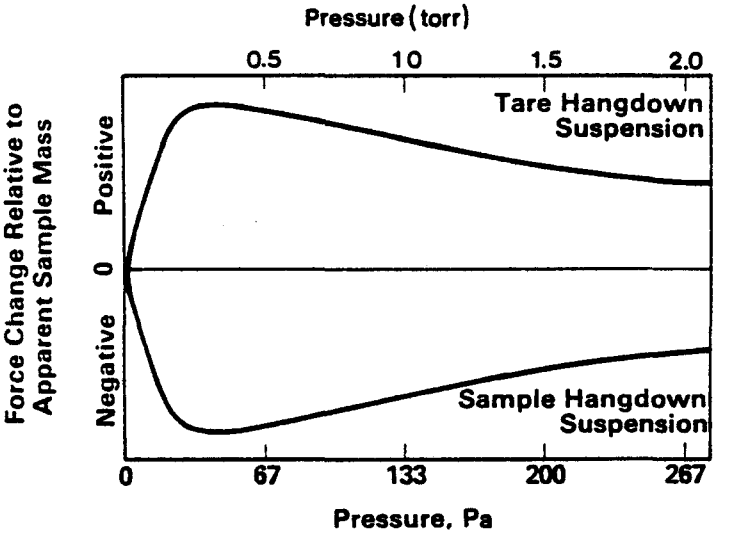

Fig. 13. Scheme for perfect compensation for the effect of thermomolecular flow of gases on a symmetrical balance hangdown, suspension, and sample geometry.

Czanderna [203] identified the origin of TMF and suggested an empirical scheme to correct for it. This qualitative explanation is simply an adaptation of the theory of the Knudsen or radiometer type pressure gauge [204]. The similarity between the composite plot of radiometric forces measured with a microbalance, shown in Fig. 14a, and the data shown in Fig. 14b taken from Fig. 5.36 of ref. 179 is striking. The latter data were taken from work by Bruche and Littwin [205].

Historically, the first identification of radiometric effects in thermogravimetry seems to be that of Eyraud and Goton [206] who detected forces equivalent to 5.0 mg at a pressure of 133 Pa. In his early work, the effect of TMF was simply termed a pressure effect by Gulbransen [27]. While the presence of TMF makes precision microgravimetry more difficult, it was probably the major thorn that led to Rhodin's development of the symmetrical housing and hangdown system [26,74] to minimize thermal eddy effects. Katz and Gulbransen [192] included the effects of TMF in a general empirical correction to the balance deflection because of pressure while others [156] accounted for it as an adsorption and desorption effect. Czanderna [131] and Czanderna and Honig [132] ascribed the pressure effect to thermomolecular flow; showed that the magnitude of the force depends on the gas, pressure, and temperature gradient of the system; and described techniques to correct for it [131,137,207].

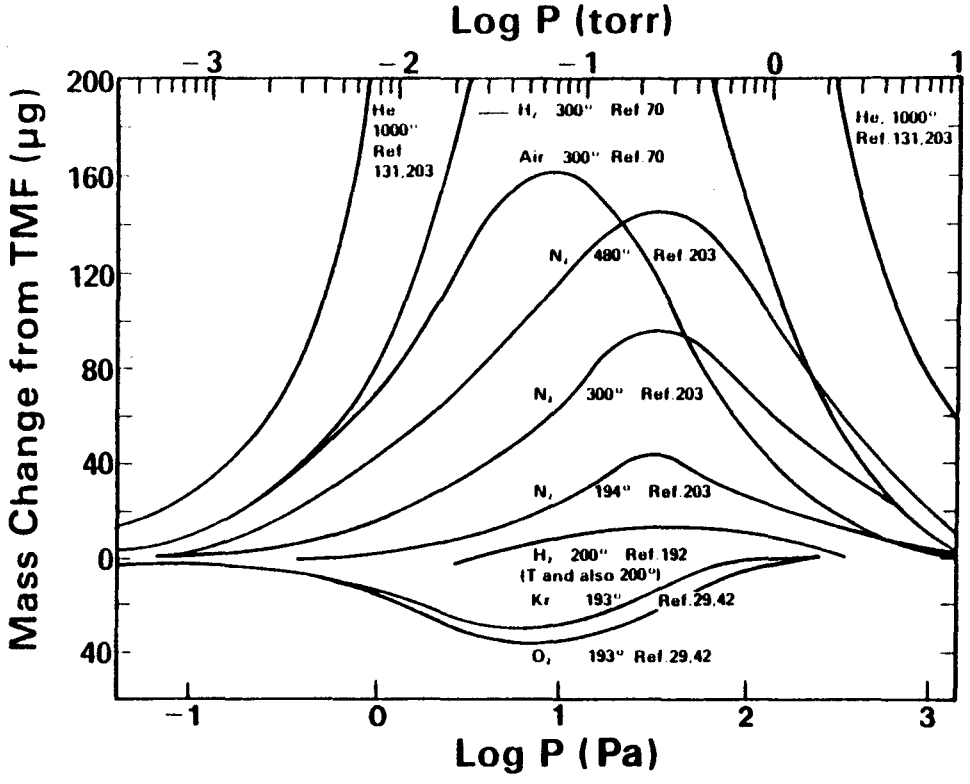

Figure 14a

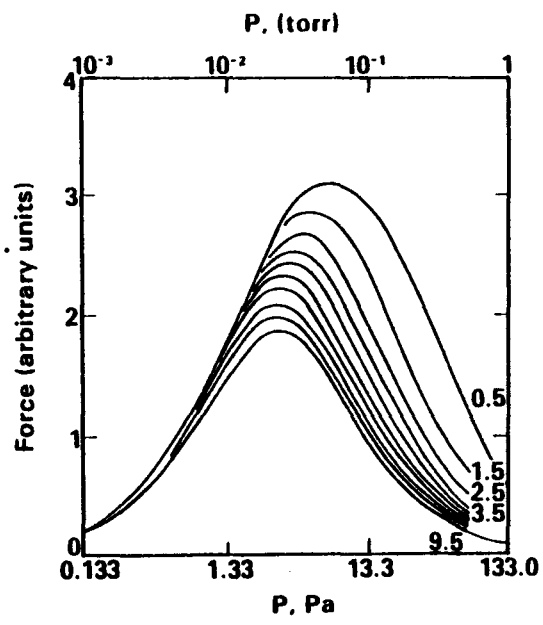

Figure 14b

Fig. 14. (a). Composite plot of thermomolecular flow effects published by a number of different workers. **(b).** The force on a movable vane in a Knudsen gauge, plotted against log P (Pa) for a series of values of the distance between the heated surface and the vane. (From observations by Bruche and Littwin, ref. 205.) (After Dushman and Lafferty, 2nd Ed., Scientific Foundations of Vacuum Technique, Wiley, 1962.)

The effect of thermomolecular flow was one of the three topics for discussion at the First Conference on Microbalance Techniques at Fort Monmouth, New Jersey, in January 1960 [3]. As a result of four papers [192,203,208,209], a discussion of TMF was initiated that involved practically every participant at the conference.

Thomas and Poulis [210,211], in pioneering the theoretical analysis of the problem, showed that the forces obtained experimentally by others [192,203] could be calculated approximately by modification and extension of Knudsen's theory, thus substantiating the qualitative description [203]. About the same time, Krupp et al. [212] reported the results of a detailed experimental study of the dependence of the magnitude of the radiometric force acting on one leg of a microbalance suspension. Using the methods described [3], they determined the pressure dependence of the force as a function of the temperature and geometry of the specimen and the ambient gas. They used modified quantitative expressions based on theories of Knudsen [179] and Hettner [213] to demonstrate that satisfactory agreement between calculated and measured values could be obtained in the high and low pressure regions (Fig. 14). Unfortunately, neither theoretical treatment [209-211] has been satisfactory in the transition pressure region; viz. the region of maximum force. Poulis et al. [214-217] and others [218,219] have not been able to develop a satisfactory equation, even a semi-empirical one [219], that will permit one to compute corrections for the force encountered in the transition pressure region. This approach is similar to that used by Liang [184] in dealing with thermal transpiration. It is indeed unfortunate that, after the most recent attempt [217], it was concluded that the best way to deal with the forces encountered in this region is to calibrate it experimentally. Thus, for equilibrium experiments requiring the greatest precision, the technique developed by Czanderna [220] using partial pressures of active gases may become increasingly important even though it is laborious, time consuming, and limited to balances of excellent long-term stability. For more routine work the methods described [131,132,137,196,203, 209,221] may deserve further study.

Since TMF is dependent on the presence of a temperature gradient, it is obvious that the effect will be encountered with a sample at temperatures below room temperature as well as above. This was reported in 1957 [131], 1962 [137,138], 1965 [42], and again in 1967 [221]. The general subject of thermal gas motion has also been reviewed in detail [199], mentioned in other recent review articles [31-33], and examined both theoretically [222] and experimentally [223].

Numerous encounters with TMF have been reported in the last two decades by a host of investigators [42,48,123,131,132,137,138,140,

185,186,196,203,207-209,212,220-230] in different types of pressure dependent studies. The observations made by Seanor and Amberg [48] and Freeman and Gwinup [123] deserve special mention because the TMF was noted using a quartz spring and vertical torsion balance, respectively, where no opportunity for at least partial compensation existed. All other reports were made by expermentalists using beam balances.

In a study of porous carbons, Thomas and Williams [42] have detected a disturbance they attributed to a high pressure TMF effect although further study seems warranted. These effects, which are attributed to temperature gradients as small as 0.01°C/cm at the gas-solid interface, have received further attention in the form of cavity forces [231,232]. Finally, new designs for furnaces have been postulated [233] to minimize the force from TMF by directing it orthogonally to the vertical hangdown suspension. These methods, however, will require not only considerable ingenuity to use in practice but also are of doubtful value because vertically directed temperature gradients have not been eliminated.

In a lucid paper Eschbach and Moret described a system to measure pressure using Knudsen flow [234]. This obviously is using the TMF of gases in reverse to achieve a desired goal.

G. Water Vapor Effects

In recent measurements of the sorption of water by polymers using a Cahn-RG, Vasofsky and Czanderna [168] found a "new" mass artifact of nearly 400 μg in 2.4 kPa of water vapor. Equivalent 0.8 g gold wires were suspended at the sample and tare positions, and the entire system was at room temperature. Since smaller artifacts had been previously reported using a Cahn-RG in water and nitrogen, it is possible that only the much larger magnitude is of interest. For example, Kollen [235] showed that mass artifacts as large as 10 μg exist for a Cahn-RG beam in the pressure range from 0.1 to 133 Pa of dry nitrogen. Fuller et al. [236] presented detailed curves showing mass artifacts in water vapor ranged from 4 μg at 0.01 Pa to 37 μg at 2.7 kPa, again with isothermal conditions about their Cahn-RG. Evans and White [237] found the mass artifact ranged from 4 to 30 μg with loads from 0.115 to 0.750 g. Thus, the effect measured by Vasofsky and Czanderna seems to be a combination of that seen by the researchers of refs. 236 and 237, but over *ten times as large*. The "new" mass artifact was tentatively ascribed to sorption by the polymer used to insulate the torque motor. As tabulated in the review article by Czanderna and Vasofsky [18], over 80 papers have been published in the last decade on water vapor sorption by various materials. It will be interesting

to see whether future work will show if their results [168] were obtained because of special circumstances related to their Cahn-RG or whether polymer insulated torque motors are to be generally distrusted.

VIII. APPLICATIONS

In this section the applications of microbalances for measuring mass changes attending kinetic and equilibrium processes will be arbitrarily categorized according to classic, simultaneous, and future use of the instruments. The bounds for classic operation include using the device to monitor a change in mass of a sample that results from altering the temperature and/or pressure of various gases about the sample, the measurement of a mass change of the sample such as in evaporation and sputtering, or the measurement of a force exerted on a sample or device suspended from a balance. Simultaneous use includes the measurement of the mass and at least one additional physical parameter simultaneously to enhance the analysis of the physical or chemical occurrences in or on the sample or specimen. Changes in the composition, but not the temperature or pressure, of the surrounding gases would be considered as an additional parameter. Obviously, there will be cases that are not clearly either "classic" or "simultaneous." Future applications will be suggested that appear to have potential; they represent areas of research where correlating mass changes in a specimen with other important physical parameters are considered to be of special importance.

A. Classic Operation

A mass change or a force change may be measured in classic operation of a microbalance. Mass changes that result from an increase or decrease in the pressure about a specimen occur in oxidation, reduction, adsorption, desorption, thermodesorption, photodesorption, surface area, deviations from stoichiometry, decomposition or degradation, and absorption studies. References in these categories in which mass changes have been measured by microweighing techniques are summarized in Table 3. Most of these papers were published prior to 1969 or have already been referenced for other reasons in this chapter. Over 400 papers in the categories listed in Table 3, published from 1969 to 1977, are included in the review entitled "Surface Studies with the Vacuum Microbalance" by Czanderna and Vasofsky [18]. In addition, Wolsky's long abstract [238] provides a good overview of classical applications of vacuum

TABLE 3

Selected References: Applications of Ultramicroweighing Techniques to Classical Studies

Applications	References
Oxidation	18, 25, 26, 35, 51, 63, 65, 79, 80, 82, 84, 85, 90, 91, 131, 135, 136, 137, 176, 189, 190, 226, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 273, 274, 275, 276, 277, 330, 331, 332, 335, 336, 347
Reduction	18, 25, 33, 35, 192, 250, 316, 328
Adsorption	18, 25, 33, 42, 48, 50, 74, 77, 89, 128, 141, 161, 169, 185, 202, 220, 225, 228, 235, 236, 237, 251-262, 325, 326, 327, 333, 334
Desorption	18, 33, 89, 169, 185, 195, 228, 235, 236, 237, 251, 253, 254, 256, 258, 259, 262
Thermodesorption and photodesorption	18, 141, 256, 258, 263, 264, 265
Surface Area	18, 25, 33, 42, 65, 106, 131, 137, 185, 199, 200, 201, 207, 221, 228, 237, 250, 255, 256, 259, 261, 266, 278, 279, 280, 281
Deviations from stoichiometry	131, 207, 250, 267, 268, 269, 277
Decomposition or degradation	18, 53, 55, 100, 131, 137, 207, 224, 270, 271, 272
Absorption	271
Superatmospheric pressure	144, 282, 283, 284, 285, 286, 287
Evaporation rates (for vapor pressure)	18, 91, 109, 114, 115, 120, 123, 124, 125, 271, 288, 289, 290
Evaporation rates (sputtering yields, thin film studies)	18, 55, 78, 79, 86, 90, 99, 113, 116, 117, 118, 119, 121, 160, 275, 291, 292, 293, 294, 295, 296, 345, 346
Gas densities	57, 126, 127, 129, 131, 132, 134, 137, 144, 297
Gas-solid, liquid-solid, solid-solid, gas-liquid interactions	18, 59, 157, 292, 298, 299, 300, 301
Magnetic susceptibility	18, 46, 77, 81, 97, 111, 112, 138, 143, 177, 178, 188, 269, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 333
Radioactive materials	315

microgravimetry. More detailed descriptions of the various applications are contained in refs. 239 to 277.

Additional references on oxidation are presented in Chapter 9 of this book while a considerable list of references on physical adsorption are given in Chapter 4 by Robens; special mention is made of four articles by Cutting [278-280] and Parkyns [280,281] dealing with the effect of the true sample temperature on the surface area. Additional references on chemisorption are given in Chapter 5 by Czanderna, in Chapter 7 by Angell, and in Chapter 8 by Fuller.

Of somewhat unusual interest are seven papers that employ a microbalance to determine mass changes at pressures of several or more atmospheres [144,282-288]. Force changes that result during use of the balance to measure evaporation rates; gas densities; gas-solid, liquid-solid, solid-solid, and gas-liquid interactions; and magnetic susceptibilities are also included in Table 3. References 288 through 316, which are included in these latter classifications, have been published in recent years. Surface tension, sedimentation, van der Waals interactions, etc., are included under the heading relating to bistate interactions.

The categories listed in Table 3 constitute the major fraction of classical use of balances. The diverse applicability of microgravimetric measurements is illustrated by reports of the determination of dust in flue gases [317,318], the measurement of liquid density [157,319], and the determination of molecular weight [320]. In the latter case [320], a gas density balance was substituted for a gas chromatographic detector in a flow system. Scott and Harrison [321] applied the principle of thermal gravimetric analysis and thermodesorption in a study of the "thermo" oxidation of several UO_2 mixtures. Finally, the impulse of a force has been measured to evaluate the microthrust of a dynamic electric engine [322].

As might be expected, a number of valuable *auxiliary* studies can be performed on microgravimetric specimens after classical treatment on the microbalance. These could include electron diffraction and electron microscopic investigations of the surface layers after kinetic and/or equilibrium studies. Recent representative studies that fall in this category have been reported by Boggs et al. [323] and Schwoebel [324]. Boggs concluded from his studies of the oxidation of polycrystalline tin and its alloys that oxide nuclei are formed preferentially at dislocations on the surface. Schwoebel used a bakeable ultrahigh vacuum ultramicrobalance to study the oxidation of magnesium single crystals. In this elegant study he has shown that the kinetics of oxide film formation on the basal and prismatic planes are consistent with the Wagner-Hauffe theory of oxide growth by the diffusion of lattice defects.

B. Simultaneous Measurement of Mass and Other Physical Parameters

The use of a horizontal beam balance combined with a vertically suspended torsion balance [114,116,123-125] was mentioned in Section IV.B.3.c. Balances of this type are frequently used with a mass spectrometer. This type of data has been included in the classic operation of balances. Although the use of a mass spectrometer and a microbalance in Knudsen effusion experiments has enhanced significantly the interpretation of vapor pressure determinations, the simultaneous measurement of mass and other physical parameters should be of greatest value in the study of surfaces of solids and thin films. The capability of resolving a mass change of one part in 10^8, discussed in Section III, in itself is suggestive of extensive application of microbalances to the fundamental investigation of gas-solid interactions, which are discussed in detail in ref. 18. The integration of combined measurements including mass is a natural extension of the advance in microbalance techniques [140]. Interpretation of the dynamic nature of micromass changes will be enhanced considerably if additional parameters are measured simultaneously. Some possibilities include the measurement of the ambient gas composition in vacuum and ultrahigh vacuum (Chapter 6), infrared transmission (Chapter 7), gas chromatography or mass spectrometry (Chapter 8), optical absorption, reflection or transmission, electron and optical micrography, thin film densities, magnetic susceptibility, magnetic resonance, electrical conductivity, thermoelectric power, work function, Auger spectroscopy, microcalorimetry, luminescence, and reaction rates. Although some of these involve considerable difficulty, it is surprising that more attempts have not been made.

Wolsky and Zdanuk [79] used an omegatron mass spectrometer during ultrahigh vacuum operation by a bakeable microbalance. Thus simultaneous information was generated during outgassing and oxidation of germanium and silicon single crystals. Subsequent use of the instrument, which has been related to the investigation of ion bombardment and thin film phenomena, has produced a steady flow of valuable information [78,251,253,254,293,295]. Gulbransen [189] reiterated the value of combining gas analyzer or mass spectrometer techniques with microbalance measurements for high temperature oxidation studies. The field has now grown to merit Chapter 6 by Kollen and Vasofsky.

Amberg and Seanor [48,325] combined a quartz spring balance with an infrared spectrometer to study the adsorption of carbon monoxide on doped zinc oxide surfaces. They showed that the integrated band intensities thus obtained were consistent with a proposed dipolar interaction between the weakly adsorbed CO spe-

cies and the adsorbent. Angell [326] has devised a similar combined measurement scheme employing an automatic recording balance and spectrometer for the study of gases adsorbed on zeolites. Ward [327] has carried out a similar study though the balance was not in the ultramicro range. In addition to the references in Chapter 7 by Angell, ref. 18 contains a listing of infrared and mass measurements, but in most cases the data were not collected simultaneously.

Czanderna and Wieder combined the measurement of the optical transmission and mass change in thin films [140] to discover a gross defect composition of cuprous oxide, $CuO_{0.67}$ [250]. The optical data, obtained simultaneously with mass, were then used to relate the auxiliary measurements of density, optical transmittance, electron diffraction and microscopy [250], and magnetic susceptibility [269] to the composition of the (partially) oxidized films. The combined measurement has been used effectively in the study of the reduction [328] and mobility [329] of thin films. It also enabled the optical constants of the gross defect composition to be determined [330]. Using the same apparatus, Czanderna and Clarke extended the method to the study of the oxidation of epitaxially grown single crystal films of copper [331,332].

Soule et al. [178] constructed an ultrasensitive Faraday susceptibility apparatus with the capability of studying magnetic susceptibility changes of a paramagnetic gas adsorbed on a diamagnetic solid. Thus Czanderna [196] was able to relate quantitatively the changes in susceptibility of oxygen adsorbed on a silver surface with the amount of oxygen adsorbed. A zenith of combined measurement was reached by Mertens and Eischens [333], who combined *magnetic susceptibility* as well as *infrared* with microgravimetry to study catalysts. Another study combining magnetic susceptibility and mass change for the study of catalysts was reported recently [334].

The use of an automatic recording balance in a flow environment by Gulbransen et al. [239,335,336] and others [337,338] could be classified as a simultaneous measurement because supplementary analyses of the reaction products are carried out. The flow system is effective in minimizing diffusion effects during fast reactions. Thus the authors can more reasonably expect the rate-determining step to be adsorption, reaction on the surface, or desorption. Various ways have been used to analyze gas compositions to assess reaction rates since the early studies by Gulbransen et al. [239]. They include using a gas chromatograph mass spectrometer [339] and gas chromatographs [339-341].

Considerable changes in electrical conductance occur during the adsorption of gases on semiconducting thin films. Measurements of the electrical conductivity and mass change have been made [342, 343]. At this time contemplated studies of this type appear to be

limited to semiconducting oxide films, where relatively large conductance changes could accompany the mass change from adsorption and desorption. Breysse et al. studied the adsorption of carbon monoxide and oxygen on thorium dioxide using simultaneous mass change and the luminescence of the adsorbent [344]. Their preliminary results indicate that interpretation of the data will be challenging.

The elemental composition of the surface has been measured using Auger spectroscopy (AES) and a crystal oscillator [345,346]; a design for AES with a beam microbalance has also been reported but no measurements were made [347]. The combined measurement of mass change and the elemental composition of the surface was made by Levenson et al. [345] for phosphorus deposited on silicon using a crystal oscillator and Auger spectroscopy. Their results demonstrated that silicon signals could be detected even after 4.5×10^{15} P atoms/cm^2 (3-6 atomic layers) were deposited. Furthermore, the relationship between the phosphorus signal and amount deposited up to one monolayer was not the linear one frequently assumed without concomitant mass change data. There are well-known restrictions to using crystal microbalances for temperature dependence studies. Thus, the combination of an automated beam ultramicrobalance with one or more of the methods for surface analysis could have considerable impact on the study of surfaces if sufficient monolayer sensibilty is available with the balance.

Czanderna [347], working with Alire and Andrews, has designed a system with the capability for combining the measurement of mass change, elemental composition, and residual gas analysis. The essential features of the design are shown in Fig. 15. A Rodder ultramicrobalance [88,89], automated with externally mounted photosensors to a sensibility of <0.01 μg, was mounted on a UHV system. A suspended metal foil with a mass of up to 150 mg can be cleaned on both sides by the simultaneous action of two ion guns. After rotating the sample 90°, a viewport is used to heat the sample with a xenon lamp, thus minimizing heating the chamber walls; temperatures above 55°C are measured with an infrared detector through the window. The elemental composition can be monitored by inserting an Auger spectrometer from the rear port of the six-way cross. The linear motion feed-through is used for grounding the sample during AES analysis. A residual gas analyzer is located off the manifold but could be easily located, with an appropriate UHV fitting, to have a line-of-sight to the sample. The unit described has a maximum capability for detecting 2.5% of a monolayer of oxygen (as adions) adsorbed onto an 18 mm diameter metal disc, provided the area of each surface atom is 7 Å^2 and the short-range sensibility of 0.005 μg [89] of the Rodder balance is adequate

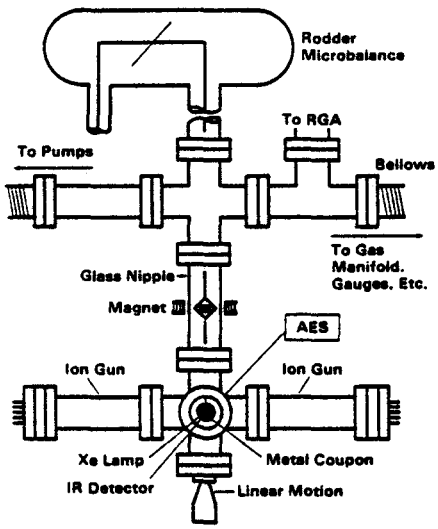

Fig. 15. Arrangement for the combined measurement of mass change, elemental composition of a metal surface and residual gas composition.

for the time of the experiment. The combination shown in Fig. 15 represents a significant capability for using vacuum ultramicrobalances for adsorption studies on solid surfaces of known surface contamination, for the study of the initial stages of oxidation, and for obtaining direct relationships between surface coverages and AES signal intensities, *in situ*, during desorption studies.

C. Future

The extensive application of precision microweighing to classical problems will undoubtedly continue at a high level of activity because of the existence of commercially available equipment and the fundamental nature of the measurement. Some of the most elegant studies should take place in surface science. For example, microbalances surely will be valuable in determining the mechanism of nucleation and growth of thin films. Little work has been done to study the physical properties of metal oxide thin films. Again, microweighing techniques will be used to obtain precise information.

It would be anticipated that the combined measurement of mass and additional parameters will increase by orders of magnitude. Many exciting unexploited possibilities exist for those methods mentioned in Section VIII.B., but there has been limited use of them. This seems particularly true for combining surface compositional analysis, residual gas analysis, and microgravimetry. The prospects

for studying single crystal surfaces are particularly promising for materials that can be cleaned by outgassing and/or reduction techniques. The advantages and limitations of beam microbalances for studying single crystals has been considered in quantitative detail in ref. 18.

Perhaps one of the greatest unexplored areas of gas-solid interactions is to determine the nature of a gas atom or molecule adsorbed on a well characterized surface. For this a combined study of adsorption, reaction on the surface, and desorption could be carried out by simultaneously employing a microbalance, infrared (or magnetic resonance) spectroscopy, a gas analyzer, and Auger or ion scattering spectroscopy. Further developments in the theory of thermodesorption and photodesorption will provide additional analytical parameters.

In the area of solid state science, the simultaneous measurement of mass change, conductivity, thermoelectric power, and magnetic susceptibility could be accomplished with appropriate pulsing techniques. Thus detailed correlation of the deviation from stoichiometry and carrier concentration could be achieved.

Finally, in all applications more sophisticated computerized data analysis and data reduction techniques should be considered. The conversion of strip chart records to digitalized data for analysis will attain greater significance as microweighing techniques are combined with several different parameters for simultaneous measurement.

D. Thermogravimetry

The fields of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) generally make use of microweighing apparatus, and indeed some overlap exists between the subject material of this book and TGA. Since entire volumes have been written on TGA [348,349], only brief mention will be made in this chapter. Quite obviously, many of the techniques developed and employed in TGA and DTA can be of value to the microgravimetric scientist. The primary difference is that many extraordinarily complex problems that arise in DTA and TGA can be greatly simplified for studies that carry into the microgram region of mass change as has been discussed for the case of thermodesorption of gases [264].

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REFERENCES

Code:
VMT - Vacuum Microbalance Techniques
PVMT - Progress in Vacuum Microbalance Techniques
RSI - Rev. Sci. Instr.
JVST - J. Vac. Sci. Technol.

1 S.P. Wolsky and E.J. Zdanuk (Eds.), Ultra Micro Weight Determination in Controlled Environments, Wiley, New York, 1969.
2 A.W. Czanderna, in S.P. Wolsky and E.J. Zdanuk (Eds.), Ultra Micro Weight Determination in Controlled Environments, Wiley, New York, 1969, p. 7.
3 M.J. Katz (Ed.), VMT, Vol. 1, Plenum, New York, 1961.
4 R.F. Walker (Ed.), VMT, Vol. 2, Plenum, New York, 1962.
5 K.M. Behrndt (Ed.), VMT, Vol. 3, Plenum, New York, 1963.
6 P.M. Waters (Ed.), VMT, Vol. 4, Plenum, New York, 1965.
7 K.M. Behrndt (Ed.), VMT, Vol. 5, Plenum, New York, 1966.
8 A.W. Czanderna (Ed.), VMT, Vol. 6, Plenum, New York, 1967.
9 C.H. Massen and H. Van Bechum (Eds.), VMT, Vol. 7, Plenum, New York, 1970.
10 A.W. Czanderna (Ed.), VMT, Vol. 8, Plenum, New York, 1971.
11 Th. Gast and E. Robens (Eds.), PVMT, Vol. 1, Heyden, London, 1972.
12 S.C. Bevan, S.J. Gregg, and N.D. Parkyns (Eds.), PVMT. Vol. 2, Heyden, London, 1973.
13 C. Eyraud and M. Escaubes (Eds.), PVMT, Vol. 3, Heyden, London, 1975.
14 D. Dollimore (Ed.), Thermochimica Acta, 24 (1978) 205-431; O.T. Sørensen (Ed.), 29, No. 2 (1979) in press.
15 Proceedings of the Eleventh Conference on Vacuum Microbalance Techniques, JVST, 11 (1974) 396-439.
16 Proceedings of the Thirteenth Conference on Vacuum Microbalance Techniques, JVST, 13 (1976) 541-560.
17 Proceedings of the Fifteenth Conference on Vacuum Microbalance Techniques, JVST, 15 (1978) 795-821.
18 A.W. Czanderna and R.W. Vasofsky, in S. Davison (Ed.), Progress in Surface Science, Vol. 9, No. 2, Pergamon, London, 1979, in press.
19 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, Interscience, 1964.
20 A. Warburg and E. Ihmori, Ann. Physik. Chem., 27 (1886) 481; 31 (1887) 145.
21 H. Pettersson, Proc. Phys. Soc. (London), 32 (1920) 209; Dissertation, University of Göteburg, 1914.
22 F. Emich, Abderhalden, 9 (1919) 55.
23 G. Gorbach, Mikrochemie, 20 (1936) 254.
24 G. Ingraham, Metallurgia, 39 (1949) 232; B.B. Cunningham, Nucleonics, 5 (1949) 62.
25 P.L. Kirk, Quantitative Ultramicroanalysis, Wiley, New York, 1950.
26 T.N. Rhodin, Advan. Catalysis, 5 (1953) 39.
27 E.A. Gulbransen, Advan. Catalysis, 5 (1953) 119.
28 K. Behrndt, Z. Angew. Phys., 8 (1956) 453.
29 J.M. Thomas and B.R. Williams, Quart. Rev. (London), 19 (1965) 231.
30 A.W. Czanderna, in S.P. Wolsky and E.J. Zdanuk (Eds.), Ultra Micro Weight Determination in Vacuum and Controlled Environments, Wiley, New York, 1969, p. 7.
31 Th. Gast, J. Physics E: Sci. Instr., 7 (1974) 865.
32 T. Takaishi, in B. Le Neindre and B. Vodar (Eds.), Experimental Thermodynamics, Vol. II. Experimental Thermodynamics of Non-Reacting Fluids, Butterworths, London, 1975, pp. 1023-1068.
33 D.A. Cadenhead and N.J. Wagner, in R.B. Anderson and P. Davison (Eds.), Experimental Methods in Catalytic Research, Vol. II, Academic Press, New York, 1976, pp. 223-255; Long Abstract: JVST, 13 (1976) 541.
34 R.O. Leonard, Anal. Chem., 48 (1976) 879A.
35 E.A. Gulbransen and K.F. Andrew, VMT, 1 (1961) 1.
36 H.S. Peiser, VMT, 2 (1962) 1.
37 R.L. Schwoebel, private communication.

38 G. Deamoley and D.S. Northrup. Semiconductor Surfaces for Nuclear Reactions. Spon Ltd.. London. 1966. p. 166.
39 C.H. Massen. J.A. Poulis. S.P. Wolsky. and E.J. Zdanuk. VMT. 6 (1967) 37.
40 C.H. Massen. J.A. Poulis. and J.M. Thomas. VMT. 4 (1965) 35.
41 Cahn Instrument Co., UHV Model RG.
42 J.M. Thomas and B.R. Williams, VMT. 4 (1965) 209.
43 B.L. Evans. J.M. Thomas, and B.R. Williams, J. Sci. Instr., 43 (1966) 263.
44 E. Salvioni. Dissertation, University of Messina, 1901.
45 S.L. Bonting and B.R. Mayron, Microchem. J., 5 (1961) 31.
46 J.O. Kessler and A.R. Moore, RSI. 33 (1962) 478.
47 J. Skelly, RSI, 38 (1967) 985; H. Patashnick and C.L. Hemeway, RSI. 40 (1969) 1008.
48 D.A. Seanor and C.H. Amberg, RSI, 34 (1963) 917.
49 F. Emich, Monatsh, 36 (1915) 407; Chem. Abstr., 9 (1915) 2997.
50 J. McBain and A. Bakr, J. Am. Chem. Soc., 48 (1926) 690.
51 P.L. Kirk and F.L. Schaffer, RSI, 19 (1948) 785.
52 M.J. Rand, RSI, 32 (1961) 991.
53 S.L. Madorsky, VMT, 2 (1962) 47.
54 S.S. Leshchenko, V.L. Karpov, I.K. Karpovich, V.N. Katyshev, and Zh.K. Krumin, Zavodsk. Lab., 29 (1963) 1016; Chem. Abstr., 59 (1963) 11679a.
55 M.M. Freundlich, Vacuum, 14 (1964) 293.
56 H. Kambe and S. Igarashi, Rept., Aeron. Res. Inst. Univ. Tokyo, 28 (1963) 145; Chem. Abstr., 60 (1964) 1891g.
57 R.M. Dell and V.J. Wheeler, U.K. Atomic Energy Research Estab., Gt. Brit., R 3424 (1960); Chem. Abstr., 55 (1961) 5046.
58 J. Duchene, Vortaege Originalfassung Intern. Kongr. Grenzflaechenaktive Stoffe, 3, Cologne. 1960, 1961; Chem. Abstr., 57 (1962) 8385a.
59 R.M. Joshi, J. Polymer Sci., 35 (1959) 271.
60 P. Barrett, Bull. Soc. Chim. (France), 1958, p. 376; Chem. Abstr., 54 (1960) 2828.
61 M.M. Vetykov, R.G. Chuvilyaev, and S.N. Shkolnikov, Zh. Fiz. Khim., 33 (1959) 2370; Chem. Abstr., 54 (1960) 12671h.
62 J. Westmoreland, Chem. Ind. (London), 1965, p. 2000.
63 C.T. Fujii, C.D. Carpenter, and R.A. Meussner, RSI. 33 (1962) 362.
64 J. Hooley, Can. J. Chem., 35 (1957) 374.
65 C. Moreau, VMT, 4 (1965) 21.
66 R.W. Harrison and E.J. Delgrosso, J. Sci. Instr., 41 (1964) 222.
67 B.D. Steele and K. Grant, Proc. Roy. Soc. (London), A82 (1909) 580.
68 W. Felgenträger, Feine Waagen, Wägungen und Gewichte, 2nd Ed., Springer, Berlin. 1933; Nature, 132 (1950) 730.
69 W. Weber, Werke (Berlin), 1 (1892) 497.
70 W. Nernst and E.A. Riesenfeld, Ber, 39 (1906) 381.
71 F. Emich and J. Donau, Handb. Biol. Arbeitsmeth., 1 (1921) 183.
72 J. Donau. Mikrochemi Emich Fest, 39 (1930) 10; 3 (1931) 1; Mikrochemie, 9 (1931) 1; 13 (1933) 155.
73 E.A. Gulbransen, RSI, 15 (1944) 201.
74 T.N. Rhodin. Jr., J. Am. Chem. Soc., 72 (1950) 4343.
75 P.L. Kirk, R.E. Craig, J.E. Gullberg, and R.Q. Boyer, Anal. Chem., 19 (1947) 427.
76 F. Edwards and R. Baldwin, Anal. Chem.. 23 (1951) 357.
77 T.J. Jennings, in T.J. Gray (Ed.), The Defect Solid State, Interscience, New York. 1957. p. 487.
78 S.P. Wolsky and E.J. Zdanuk, VMT, 2 (1962) 37.
79 S.P. Wolsky and E.J. Zdanuk, VMT, 1 (1961) 35.
80 R.F. Walker. VMT. 1 (1961) 87.
81 R.J. Kolenkow and P.W. Zitzewitz, VMT, 4 (1965) 195.
82 J.E. Whittle. J. Sci. Instr., 43 (1966) 150.
83 E.A. Gulbransen and K.F. Andrew. VMT. 2 (1962) 129.
84 R. Addiss, Ph.D. Thesis. Cornell University, Ithaca. New York. 1958.
85 R.L. Schwoebel, Ph.D. Thesis, Cornell University, Ithaca. New York. 1962.
86 R.L. Schwoebel. Surface Sci.. 2 (1964) 356.
87 W.E. Boggs. VMT. 6 (1967) 45.
88 J.A. Rodder. Brit., 851. 913: Chem. Abstr.. 55 (1961) P 8965d; VMT. 8 (1971) 45.
89 S.E. Fink and R.P. Merrill. VMT. 8 (1971) 55.

90 H. Mayer, R. Niedermayer, W. Schroen, D. Stuenkel, and H. Goehre, VMT, 3 (1963) 75.
91 N.J. Carrera and R.F. Walker, VMT, 3 (1963) 153.
92 H. Moret and E. Louwerix, VMT, 5 (1966) 59.
93 S. Fujiwara and H. Terajima, J. Phys. E.: Sci. Instr., 3 (1970) 695.
94 K.P. Zinnow and J.B. Dybwad, VMT, 8 (1971) 147.
95 J. Gouault, Compt. Rend., 256 (1963) 378.
96 V.P. Vetrov, N.I. Kokin, and A.N. Klassen, Nauchn. Soobshch. Aziatsk. Fil. Gos. Vses. Nauchn. Issled. Inst. Tsmentn. Prom., 1963, 66; Chem. Abstr. 63 (1965) 17942h.
97 J. Kaczer, Czech. J. Phys., 13 (1963) 386.
98 R. Niedermayer and W. Schroen, Vakuum-Tech., 11 (1962) 36.
99 P. Vast, Bull. Soc. Chim. France, 1965, 359.
100 E. Ericson and W.J. Kirsten, Microchem. J., 9 (1965) 82.
101 L. Cahn and H.R. Schultz, VMT, 2 (1962) 7.
102 L. Cahn, Dechema Monograph, 44 (1962) 45; Instr. Control Systems, 35 (1962) 107.
103 L. Cahn, H.R. Schultz, and P. Gaskins, Microchem. J. Symp. Ser., 2 (1962) 1027.
104 L. Cahn and H.R. Schultz, VMT, 3 (1963) 29.
105 J. Gouault, Compt. Rend., 256 (1963) 1455.
106 G. Gorbach, Anal. Chim. Acta, 29 (1963) 453; H.L. Gruber and C.S. Shipley, VMT, 3 (1963) 131.
107 H. Meiners, Dechema Monograph., 54 (1965) 131.
108 R.P. Cassiano and R.O. Leonard, PVMT, 3 (1975) 349.
109 M. Volmer, Z. Physik. Chem. Bodenstein Festband, 1931, 836.
110 M.C. Day, L.D. Hulett, and D.E. Willis, RSI, 31 (1960) 1142.
111 C.W. Fleischmann and A.G. Turner, RSI, 37 (1966) 73.
112 J.A. Poulis, C.H. Massen, and P. van der Leeden, Appl. Sci. Res. B, 9 (1961) 133.
113 W.T. Siegle and W.R. Beam, RSI, 35 (1964) 1173.
114 A.E. Wilson, J.H. Kim, and A. Cosgarea, Jr., RSI, 36 (1965) 1428.
115 E.K. Rideal and P.M. Wiggins, Proc. Roy. Soc. (London), A210 (1951) 291.
116 R.S. Bradley and T.G. Cleasby, J. Chem. Soc., 1953, 1681.
117 D.W. Bassett and A.J.B. Robertson, Brit. J. Appl. Phys., 10 (1959) 534; Chem. Abstr., 54 (1960) 11585e.
118 K.A. Becker, H.J. Forth, and I.N. Stranski, Z. Electrochem., 64 (1960) 373.
119 F.B. Humphrey and A.R. Johnson, RSI, 34 (1963) 348.
120 S. Pearson and N.J. Wadsworth, J. Sci. Instr., 42 (1965) 150.
121 A.R. Beavitt, J. Sci. Instr., 43 (1966) 182.
122 M. Peleg and C.B. Alcock, J. Sci. Instr., 43 (1966) 558.
123 R.D. Freeman and P.D. Gwinup, RSI, 37 (1966) 773.
124 G. Wessel, Z. Physik, 130 (1951) 539.
125 J.G. Edwards, JVST, 11 (1974) 400.
126 A. Stock and G. Ritter, Z. Physik Chem., 119 (1926) 333; 124 (1926) 204; 126 (1927) 172.
127 A. Stock and G. Ritter, Z. Angew. Chem., 39 (1926) 1463.
128 S.J. Gregg, J. Chem. Soc., 1946, 561; 1955, 1438.
129 E.W. Johnson and L.K. Nash, RSI, 22 (1951) 240.
130 J.H. Simons, C.L. Scheirer, Jr., and H.L. Ritter, RSI, 24 (1953) 36.
131 A.W. Czanderna, Ph.D. Thesis, Purdue University, W. Lafayette, Ind., 1957.
132 A.W. Czanderna and J.M. Honig, Anal. Chem., 29 (1957) 1206.
133 J. Richlin, M.S. Thesis, Purdue University, W. Lafayette, Ind., 1957.
134 J.M. Honig, VMT, 1 (1961) 55.
135 C.N. Cochran, RSI, 29 (1958) 1135.
136 C.N. Cochran, VMT, 1 (1961) 23.
137 P.A. Faeth, Vacuum and Adsorption Technique, Inst. Sci. Tech. Press, Univ. of Michigan, Ann Arbor, Michigan, TR-66100-2-X, 1962.
138 A.N. Gerritsen and D.H. Damon, RSI, 33 (1962) 301.
139 A. Langer, VMT, 4 (1965) 231.
140 A.W. Czanderna and H. Wieder, VMT, 2 (1962) 147.
141 A.W. Czanderna, VMT, 4 (1965) 57.
142 A.W. Czanderna, VMT, 4 (1965) 175.
143 D. Das, Indian J. Phys., 37 (1963) 582.
144 R.M. Tisinger, RSI, 38 (1967) 547.
145 A.F. Grigor and W.A. Steele, RSI, 37 (1966) 51.
146 A.W. Czanderna, U.S. 3,224,521 (to Union Carbide), 12-21-1965.

147 J.A. van Lier. RSI. 39 (1968) 1841.
148 A.W. Czanderna. W. Kollen. J.R. Biegen. and J. Rodder. JVST, 13 (1976) 556.
149 P.A. Faeth. J. Genco. J.A. van Lier. W. Kollen. P. Ficalora, S.P. Sharma. E. Grappun. and R. Vasofsky. private communications.
150 J.E. Wilson. private communication.
151 J.A. Poulis. W. Dekker. and P.J. Meeusen. VMT. 5 (1966) 49.
152 J.A. Poulis. P.J. Meeusen. W. Dekker. and J.P. de Mey, VMT, 6 (1967) 27.
153 R. Vieweg and Th. Gast. Kunststoffe. 34 (1944) 117.
154 Th. Gast, VMT 3 (1963) 45; 6 (1967) 59.
155 Th. Gast, private communication.
156 J.W. Beams. C.W. Hurlburt. W.E. Lotz. and R.M. Montague. RSI, 26 (1955) 1181.
157 J.W. Beams and A.M. Clarke. RSI, 33 (1962) 750.
158 New Instruments. RSI, 36 (1965) 1906.
159 W.H. Wade and D.E. Meyer, private communication.
160 K.H. Behrndt, VMT, 1 (1961) 69.
161 V.E. Vasserberg, Kinetika i Kataliz, 3 (1962) 556.
162 F.A. Chappell, VMT, 2 (1962) 19.
163 K. Angstrom. Oefversigt Kongl. Vetenskap Akad., (1895) 643.
164 D. Halliday and R. Resnick, Fundamentals of Physics, Wiley, New York, 1974, p. 565-567.
165 Sartorius Electrona Recording Balance, RSI, 28 (1957) 744.
166 Th. Gast, PVMT, 2 (1973) 105; 3 (1975) 108; JVST, 11 (1974) 418; 15 (1978) 813.
167 J.A. van Lier, unpublished private communication.
168 R. Vasofsky and A.W. Czanderna, JVST, 15 (1978) 818.
169 R.J. Hussey, M.J. Graham, and M. Cohen, JVST, 11 (1974) 397; S.P. Chauhan, J.C. Angus. and N.C. Gardner, JVST, 11 (1974) 423.
170 J.A. Poulis and J.M. Thomas, VMT, 3 (1963) 1.
171 J.A. Poulis. Proc. Phys. Soc. (London), 80 (1962) 918.
172 E.E. Pugh and G.H. Winslow, The Analysis of Physical Measurements, Addison-Wesley, Reading, Mass.,1966.
173 J.R. Biegen, Ph.D. Thesis, Clarkson College, Potsdam, New York, 1971.
174 L.B. Macurdy, VMT, 2 (1962) 165.
175 T.R.F.W. Fennell and J.R. Webb, Microchem. J. Symp. Ser., 2 (1962) 1003.
176 W.C. Tripp, R.W. Vest, and N.M. Tallan, VMT, 4 (1965) 141.
177 J.R. Singer, RSI, 30 (1959) 1123.
178 D.E. Soule. C.W. Nezbeda, and A.W. Czanderna, RSI, 35 (1964) 1504.
179 S. Dushman and J.M. Lafferty, Scientific Foundation of Vacuum Technique, 2nd Ed.. Wiley, New York, 1962.
180 G. Lewin, Fundamentals of Vacuum Science and Technology, McGraw-Hill, New York, 1965.
181 P.A. Redhead, J.P. Hobson, and E.V. Kornelsen, The Physical Basis for Ultra High Vacuum. Chapman-Hall, London, 1968.
182 American Vacuum Society, 335 East 45th St., New York, New York 10017.
183 W. Kollen and A.W. Czanderna, VMT, 8 (1971) 145.
184 S.C. Liang, Can. J. Chem., 33 (1955) 279.
185 E.L. Fuller, H.F. Holmes, and C.H. Secoy, VMT, 4 (1965) 109.
186 W. Schoeniger, Mikrochim. Acta, 3 (1959) 382; Chem. Abstr., 56 (1962) 8498a.
187 E. Kissa. Microchem. J., 4 (1960) 89; Chem. Abstr., 54 (1960) 8162f.
188 A.W. Czanderna, VMT, 4 (1965) 159.
189 E.A. Gulbransen, VMT, 4 (1965) xi.
190 H.C. Graham and W.C. Tripp, VMT, 6 (1967) 63.
191 M.J. Laubitz, Can. J. Phys., 37 (1959) 1114.
192 O.M. Katz and E.A. Gulbransen, VMT, 1 (1961) 111.
193 E. Prince. R. Vasofsky, and A.W. Czanderna, to be published.
194 M.J. Kennedy and S.C. Bevan, PVMT, 2 (1973) 91; M.A. Day, PVMT, 2 (1973) 197.
195 R.P. Merrill, C.R. Arnold, and A.J. Robell, VMT, 8 (1971) 131.
196 A.W. Czanderna. unpublished results.
197 S.P. Wolsky, unpublished results.
198 R.E. Hawley and C.J. Williams, JVST, 11 (1974) 419.
199 E. Robens. VMT, 8 (1971) 73.
200 J.W. Schürman. C.H. Massen, and J.A. Poulis. PVMT. 1 (1972) 189.

201 M.G.C. Cox, B. McEnany, and V.D. Scott, PVMT, 2 (1973) 27.
202 R.A. Pierotti, VMT, 6 (1967) 1.
203 A.W. Czanderna, VMT, 1 (1961) 129.
204 See ref. 179, for example pp. 277-278 and Fig. 5.36.
205 E. Bruche and W. Littwin, Z. Physik, 52 (1928) 318.
206 C. Eyraud and R. Goton, Bull. Soc. Chim. France, 1953, 1009; Chem. Abstr., 48 (1954) 4898g.
207 A.W. Czanderna and J.M. Honig, J. Phys. Chem., 63 (1959) 620.
208 S.P. Wolsky, VMT, 1 (1961) 143.
209 W.E. Boggs, VMT, 1 (1961) 145.
210 J.M. Thomas and J.A. Poulis, VMT, 3 (1963) 15.
211 J.A. Poulis and J.M. Thomas, J. Sci. Instr., 40 (1963) 95.
212 H. Krupp, E. Robens, G. Sandstede, and G. Walter, Vacuum, 13 (1963) 297.
213 C. Hettner, Ergebn, Exakt. Naturwiss., 7 (1928) 209.
214 J.A. Poulis, B. Pelupessy, C.H. Massen, and J.M. Thomas, J. Sci. Instr., 41 (1964) 295.
215 J.A. Poulis, Appl. Sci. Res., A14 (1965) 98.
216 C.H. Massen, B. Pelupessy, J.M. Thomas, and J.A. Poulis, VMT, 5 (1966) 1.
217 J.A. Poulis, C.H. Massen, and J.M. Thomas, J. Sci. Instr., 43 (1966) 234.
218 T. Steensland and K.S. Førland, VMT, 5 (1966) 17.
219 K.H. Behrndt, C.H. Massen, J.A. Poulis, and T. Steensland, VMT, 5 (1966) 33.
220 A.W. Czanderna, VMT, 4 (1965) 69.
221 J.D. Ferchak, RSI, 38 (1967) 273.
222 J.A. Poulis and F.N. Hooge, JVST, 15 (1978) 795.
223 E. Robens and Th. Gast, JVST, 15 (1978) 805.
224 S.D. Bruck, VMT, 4 (1965) 247.
225 H.L. Gruber, Monatsh. Chem., 95 (1964) 1017; Chem. Abstr., 62 (1965) 3389c.
226 P. Kofstad and P.B. Anderson, J. Phys. Chem. Solids, 21 (1961) 280.
227 G. Sandstede and E. Robens, Chem. Ing. Tech., 32 (1960) 413.
228 G. Sandstede and E. Robens, Chem. Ing. Tech., 34 (1962) 708.
229 C.J. van Duyn, C.H. Massen, and J.A. Poulis, PVMT, 3 (1975) 45.
230 L. Leisztner, S. Gál, and P. Timár, PVMT, 3 (1975) 51.
231 C.H. Massen and J.A. Poulis, VMT, 6 (1967) 17.
232 J.A. Poulis and C.H. Massen, J. Sci. Instr., 44 (1967) 275.
233 J.A. Poulis, C.H. Massen, and B. Pelupessy, VMT, 4 (1965) 41.
234 H.L. Eschbach and H. Moret, Vakuum Technik, 17 (1968) 29.
235 W. Kollen, Ph.D. Thesis, Clarkson College, Potsdam, New York, 1969.
236 E.L. Fuller, Jr., H.F. Holmes, R.B. Gammage, and C.H. Secoy, PVMT, 1 (1972) 235.
237 B. Evans and T.E. White, VMT, 6 (1967) 157.
238 S.P. Wolsky, JVST, 11 (1974) 417.
239 E.A. Gulbransen, K.F. Andrew, and F.A. Brassart, VMT, 4 (1965) 127.
240 P.E. Blackburn, J. Weissbart, and E.A. Gulbransen, J. Phys. Chem., 62 (1958) 902.
241 I. Rusznak, D. Levai, and M. Toth, Vysokomolekul., Soedin., 5 (1963) 449; Chem. Abstr., 59 (1963) 1831c.
242 E.A. Gulbransen and K.F. Andrew, J. Electrochem. Soc., 110 (1963) 476, and refs. cited.
243 P.A. Faeth and A.F. Clifford, U.S. Atomic Energy Comm. Conf-20-16 (1963) 22; Chem. Abstr., 61 (1964) 10302d.
244 R.W. Harrison and E.J. Delgrosso, J. Sci. Instr., 41 (1964) 222.
245 R.J. Sorenson, U.S. Atomic Energy Comm., HW 79141 (1963); Chem. Abstr., 60 (1964) 11601g.
246 J.M. Thomas and K.M. Jones, J. Nucl. Mater., 11 (1964) 236.
247 I. Stamenkovic and I. Blagojevic, Chem. Abstr., 62 (1965) 15742e.
248 E.A. Gulbransen, K.F. Andrew, and F.A. Brassart, J. Electrochem. Soc., 113 (1966) 1311.
249 W.C. Tripp, R.W. Vest, and H.C. Graham, VMT, 6 (1967) 107.
250 H. Wieder and A.W. Czanderna, J. Phys. Chem., 66 (1962) 816.
251 S.P. Wolsky and A.B. Fowler, Semiconductor Surface Physics, Univ. of Pennsylvania Press, Philadelphia, Pa., 1957.
252 P.L. Cannon, RSI, 29 (1958) 1115.
253 S.P. Wolsky and E.J. Zdanuk, Vacuum, 10 (1960) 13.
254 S.P. Wolsky and E.J. Zdanuk, 6th Nat'l. Symp. Vacuum Tech. Transact., Pergamon Press, Oxford, 1960; S.P. Wolsky and A.B. Fowler, p. 401.

255 G. Sandstede and E. Robens. Chem. Ingr. Tech., 32 (1960) 413: Chem. Abstr., 54 (1960) 19081i.
256 A.W. Czanderna. J. Phys. Chem., 68 (1964) 2765.
257 M.R. Harris. J. Sci. Instr., 41 (1964) 163.
258 A.W. Czanderna. J. Coll. Inter. Sci., 22 (1966) 482.
259 A.W. Czanderna. J. Phys. Chem., 70 (1966) 2120.
260 J. Barto, J.L. Durham, V.F. Baston, and W.H. Wade, J. Coll. Inter. Sci., 22 (1966) 491.
261 R.A. Pierotti and R.E. Smallwood, J. Coll. Inter. Sci., 22 (1966) 469.
262 Th. Gast. Archiv. Technisches Messen, 361 (1966) R31.
263 A. Winkel, Staub, 22 (1962) 77; Chem. Abstr., 57 (1962) 4488a.
264 A.W. Czanderna. VMT, 6 (1967) 129.
265 R. Jongepier and G.C.A. Schuit, J. Catalysis. 3 (1964) 464.
266 J.M. Thomas. E.E.G. Hughes, and B.R. Williams, Nature, 189 (1961) 134.
267 A.W. Czanderna and J.M. Honig, J. Phys. Chem. Solids. 6 (1958) 96.
268 J.M. Honig, A.F. Clifford, and P.A. Faeth, Inorg. Chem., 2 (1963) 791.
269 A.W. Czanderna and H. Wieder, J. Chem. Phys., 39 (1963) 489.
270 P.D. Garn, Anal. Chem., 33 (1961) 1247.
271 E. Robens, G. Robens, and G. Sandstede, Vacuum, 13 (1963) 303.
272 P.L. Waters, Anal. Chem., 32 (1960) 852.
273 B.E. Deal and H.J. Svec, J. Electrochem. Soc., 103 (1956) 421.
274 H.J. Svec and T.J. Rider, J. Less Common Metals, 14 (1968) 103.
275 R.E. Pawel, J. Electrochem. Soc., 114, (1967) 1222.
276 J.E. Antill and J.B. Wharburton, J. Electrochem. Soc., 114 (1967) 1215.
277 M.G. Hapase, M.K. Gharpurey, and A.P. Biswas, Surface Sci., 9 (1968) 87.
278 P.A. Cutting, VMT. 7 (1970) 71.
279 P.A. Cutting, PVMT. 2 (1973) 147.
280 P.A. Cutting and N.D. Parkyns, JVST, 13 (1976) 543.
281 N.D. Parkyns, PVMT, 3 (1975) 93.
282 W. Bierman and M. Heinrichs, Can. J. Chem., 40 (1962) 1361.
283 B. Boehlen, W. Hausmann, and A. Guyer, Helv. Chim. Acta, 47 (1964) 1821.
284 B. Boehlen and A. Guyer, Helv. Chim. Acta, 47 (1964) 1815.
285 K.M. Laing, VMT, 6 (1967) 149.
286 P.E. Blackburn, J. Phys. Chem., 62 (1958) 897.
287 C.G. Gachet and J.Y. Trambouze, PVMT, 3 (1975) 144.
288 N.E. Heyerdahl, VMT, 5 (1966) 121.
289 A. Block-Bolten, Arch. Hutnictwa, 8 (1963) 81; Chem. Abstr., 60 (1964) 2387f.
290 P.D. Zavitisanos, RSI, 35 (1964) 1061.
291 H. Mayer, R. Niedermayer, W. Schroen, D. Stuenkel, and H. Goehre. VMT, 3 (1963) 87.
292 I. Haller and P. White, RSI, 34 (1963) 677.
293 E.J. Zdanuk and S.P. Wolsky, J. Appl. Phys., 36 (1965) 1683.
294 H.H.A. Bath, J. Sci. Instr., 43 (1966) 374.
295 E.J. Zdanuk and S.P. Wolsky, VMT, 5 (1966) 111.
296 R.G. Hart and C.B. Cooper, JVST, 13 (1976) 553.
297 E.A. Johnson, D.G. Childs, and G.H. Beaven, J. Chromatog., 4 (1960) 429.
298 P. Schatzberg, VMT, 6 (1967) 89.
299 B.V. Derjaguin, LI. Abikosova, and E.M. Lifshitz. Quart. Rev., 10 (1956) 295.
300 J.A. Mann, Jr., and R.S. Hansen, RSI. 34 (1963) 702.
301 K. Edelmann and K. Wulf, Faserforsch. U. Textiltech, 12 (1961) 461; (1961) 466.
302 K.N. Korovkin, N.A. Oks, E.A. Bylyna, and V.B. Evdokomov, Zh. Fiz. Khim., 35 (1961) 677; Chem. Abstr., 55 (1961) 17109g.
303 E. Wachtel, Mem. Sci. Rev. Met., 59 (1962) 416; Chem. Abstr., 57 (1962) 10889a.
304 A. Blaise and M.A. Peuch. Comm. Energie At. (France), Rappt. No. CEA-2187 (1962); Chem. Abstr., 58 (1963) 8506c.
305 R. Havemann, Z. Chem., 4 (1964) 121.
306 R. Kohlhaas and H. Lange, Z. Angew. Phys., 17 (1964) 448.
307 L.N. Mulay and L.K. Keys. Anal. Chem., 36 (1964) 2383.
308 A. Van den Bosch. VMT, 5 (1966) 77.
309 A. Van den Bosch. VMT, 7 (1970) 9.
310 R. Cini and M. Torrini, VMT, 7 (1970) 37.
311 R.T. Lewis, JVST, 11 (1974) 404.
312 V.J. Perrichon, J.P. Candy, P. Fouilloux. PVMT. 3 (1975) 18.

313 A. Van den Bosch, PVMT, 3 (1975) 361; 3 (1975) 398.
314 J.D. Kulick and J.C. Scott, JVST, 15 (1978) 800.
315 W.J. Kerrigan, J.S. Byrd, and P.D. Halloway, VMT, 8 (1971) 215.
316 D. Hofmann, W. Hirschwald, and M. Grunze, JVST, 13 (1976) 542.
317 Th. Gast, Dechema Monograph, 31 (1959) 9; Chem. Abstr., 54 (1960) 9375c.
318 Th. Gast, Staub, 20 (1960) 266; Chem. Abstr., 55 (1961) 25113a.
319 C.W. Hargens, RSI, 28 (1957) 921.
320 C.S.G. Phillips and P.L. Timms, J. Chromatog., 5 (1961) 131.
321 K.T. Scott and K.T. Harrison, J. Nucl. Mater., 8 (1963) 307; Chem. Abstr., 60 (1964) 10153.
322 P. Malherbe, T. Vogt, and C. Boebel, VMT, 5 (1966) 97.
323 W.E. Boggs, R.H. Kachik, and G.E. Pellissier, J. Electrochem. Soc., 108 (1961) 6; 110 (1963) 4.
324 R.L. Schwoebel, J. Appl. Phys., 34 (1963) 2776; 34 (1963) 2784.
325 C.H. Amberg and D.A. Seanor, Proc. Third Intern. Congr. Catal., North-Holland, Amsterdam, 1964, p. 122.
326 C.L. Angell, VMT, 6 (1967) 77.
327 J.T. Ward, J. Catalysis, 9 (1967) 225.
328 H. Wieder and A.W. Czanderna, J. Chem. Phys., 35 (1961) 2259.
329 A.W. Czanderna, VMT, 5 (1966) 135.
330 H. Wieder and A.W. Czanderna, J. Appl. Phys., 37 (1966) 184.
331 A.W. Czanderna and E.G. Clarke, Jr., PVMT, 2 (1973) 9.
332 E.G. Clarke, Jr., and A.W. Czanderna, Surface Sci., 49 (1975) 526
333 F.P. Mertens and R.P. Eischens, in G.A. Somorjai (Ed.), The Structure and Chemistry of Solid Surfaces, Wiley, New York, 1969, p. 53-1.
334 T. Iwaki, M. Komuro, K. Hirosawa, and M. Miura, J. Catalysis, 39 (1975) 324.
335 E.A. Gulbransen, K.F. Andrew, and F.A. Brassart, Carbon, 1 (1964) 413.
336 E.A. Gulbransen and F.A. Brassart, J. Less Common Metals, 14 (1968) 217.
337 Th. Gast, Thermal Analysis, Proc. 3rd ICTA DAVOS, Vol. I, 1971, p. 235.
338 W.B.A. Sharp and D. Mortimer, PVMT, 1 (1972) 101.
339 H. Förster and V. Meyn, PVMT, 3 (1975) 371.
340 A.J. Tench, D. Giles, and J.F.J. Kibblewhite, Trans. Faraday Soc., 67 (1971) 854.
341 L. Forni, L. Zanderighi, C. Cavenaghi, and S. Carrá, J. Catal., 15 (1969) 153.
342 P. Schmider and H. Mayer, VMT, 7 (1970) 209.
343 J. Merey and A. Cointot, PVMT, 3 (1975) 380.
344 M. Breysse, L. Faure, B. Claudel, and J. Vernon, PVMT, 2 (1973) 229.
345 L.L. Levenson, L.E. Davis, C.E. Bryson, III, and J.J. Melles, JVST, 9 (1972) 608.
346 S. Sinharoy, M. Smith, and L.L. Levenson, JVST, 14 (1977) 475.
347 G.F. Andrews, Jr., R. Alire, and A.W. Czanderna, JVST, 13 (1976) 552; A.W. Czanderna, Thermochim. Acta, 24 (1978) 345.
348 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
349 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 1974.

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