SURFACE STUDIES WITH THE VACUUM MICROBALANCE[*]

A. W. CZANDERNA[**]

Department of Physics and Institute of Colloid and Surface Science, Clarkson College of Technology, Potsdam, NY 13676 (U.S.A.)

ABSTRACT

This paper is generally concerned with presenting a broad overview of the capabilities, limitations, and potential uses of the vacuum ultramicrobalance for surface studies. Determination of micromass changes of samples in vacuum and controlled gaseous environments at various temperatures is one of the powerful methods for studying surfaces. The traditional application of the vacuum microbalance and accompanying theoretical foundation for obtaining surface areas, activation energies of adsorption and desorption, the heat of adsorption and the initial stages of oxidation are reviewed. As with most physical measurements, the simultaneous measurement of mass change and other parameters greatly increases the ability to understand physical and chemical processes. Examples of the combined measurement of residual gases, infrared spectroscopy, and electrical properties as well as the mass change are presented. Recent progress in developing an automated ultramicrobalance for operation in a UHV system combined with RGA and AES is discussed. Information about specific gas–solid systems is presented to illustrate the utility of the microbalance.

INTRODUCTION

The solid, liquid and gas phases, non-infinite because of reality, form boundaries that are fundamentally different. Interface boundaries or *surface phases* can exist between the solid–solid, solid–liquid, solid–gas, liquid–liquid and liquid–gas phases. Since the widest application of the vacuum microbalance has been to study the solid–gas and solid–solid interface[1], this review will be confined to these subjects. Measurements of the surface area, kinetics of adsorption, absorption, and desorption, equilibrium adsorption, thermal desorption, sputtering yields, and mass changes during catalytic reactions are of interest for obtaining an understanding of the gas–solid interface. The study of the rate of oxidation and reduction can assist in under-

---

[*] Presented at the 14th Conference on Vacuum Microbalance Techniques, Salford, 27th–28th September 1976.
[**] Present address: Solar Energy Research Institute, 1536 Cole Blvd, Golden, CO 80401, U.S.A.

standing transport phenomena to and from the solid–solid interface. An understanding of mechanisms and/or processes related to catalysis, corrosion, adhesion, surface diffusion, sintering and degradation reactions is enhanced by microgravimetric studies, especially when combined with other measurements made in situ or in parallel studies.

A realistic view of the boundary at the solid–gas (vacuum) interface or a solid–solid interface is not the ideal atomically flat infinite plane. On an atomic scale, the solid–gas boundary includes crystal faces of different orientation, having imperfections such as impurities, a hole, an atom on the surface, an edge, a crevice, a step, a corner or dislocations. The composition, extent and orientation at the interface may be determined by the pretreatment of the solid, e.g., outgassing, chemical reduction, ion bombardment, annealing or thin film-deposition-parameters. Thus, the experimental effort for studying the manifold and fascinating surface phenomena requires utmost care.

For years, surface scientists have sought answers to the questions: What is the surface area of a material? How deep is the surface phase? What is the elemental composition of the surface? What is the nature of the gas–surface interaction, e.g., how much gas adsorbs and how fast, and how does the interaction depend on the surface composition and structure? What is the distribution of adsorption sites?

Until recently[2], the elemental composition of surfaces could not be measured directly. Now, surface probes such as ISS[3], SIMS[4], XPS (or ESCA)[5], and AES[6] are used routinely for this purpose, but none have been combined with a microbalance except for one apparatus under construction[7]. These modern surface probes do not provide the ultimate answer because, except for ISS, they are not uniquely sensitive to the surface monolayer. Chemisorption must of necessity occur at the outermost atomic plane, as recently reiterated by Sachtler[8]. With the advent of surface probes, procedures for obtaining clean surfaces by outgassing or chemical treatment have been established for a number of less-than-refractory metals. Since the microbalance can be used to carry out studies in situ at pressures well above regions inaccessible for study by electron and ion probes, careful microgravimetric studies may become fashionable for relating results obtained under the "ideal" conditions of UHV to those of the "real" conditions of practical environments. For example, a series of studies could be carried out to determine the differences or similarities of the adsorption of a specific gas on single crystalline, polycrystalline and supported platinum surfaces from UHV to atmospheric procedures.

To keep this review to within a manageable scope, the application of micro-weighing apparatus to obtaining an understanding of the gas–surface interaction will be considered. The reader is directed to recent and excellent review articles on oxidation reactions[9], catalytic reactions[10], sputtering phenomena[11] and degradation reactions[12] in which microgravimetric methods and procedures are connected with appropriate theory or models. Corrosion, catalysis and, frequently, degradation reactions are often controlled or limited by the chemisorption of a gas. Hence, the study of adsorption and desorption is fundamental to these areas of application.

EXPERIMENTAL

The vacuum microbalance is limited to measuring the *change in mass* (Δm) of a specimen, usually *to a limiting sensibility of 0.1 to 1 μg*. The mass change occurring as a function of time may be influenced by changing the temperature T, the pressure P of an ambient gas, and/or the composition Cg of the ambient gas surrounding the sample. Thus, $m(t, T, P, Cg)$ can be monitored with confidence as long as Δm is actually occurring on the sample and is not an artifact resulting from a buoyancy, static charge, magnetic, convection or Knudson force or from a differential temperature coefficient[1]. With appropriate theory, the determination of $m(t, T, P$ and/or $Cg)$ can be an extremely powerful method for studying the solid–gas interaction.

In addition to the vacuum microbalance, recorders, furnaces, dewars, pressure gauges, residual gas analyzers, and a vacuum system with sources of different gases are needed for the measurements. The simultaneous measurement of other physical parameters such as IR transmission, electrical conductance, elemental composition, optical reflectance, and the residual gas composition obviously requires the appropriate additional apparatus. Detailed descriptions of microgravimetric systems are available in the literature[13–15].

Materials chosen for study need to be vacuum worthy but may be of any size, shape or form that is compatible with the capacity of the balance (0.2–20g) and the design limitations of the vacuum enclosure. The solid form may be a single crystal, thin film, foil, slab, cylinder, or a powder, either on a support or in a container. For a chemisorbed layer, the amount of mass that can be gained by a specimen is directly related to the surface area. Combining this with the limiting sensibility and capacity of the balance provides an interesting limitation to studies with apparatus currently available. If each surface atom occupies 10 $Å^2$ of surface area, 10^{15} atoms cm^{-2} are exposed on a solid surface. If at the maximum coverage one adsorbate atom interacts

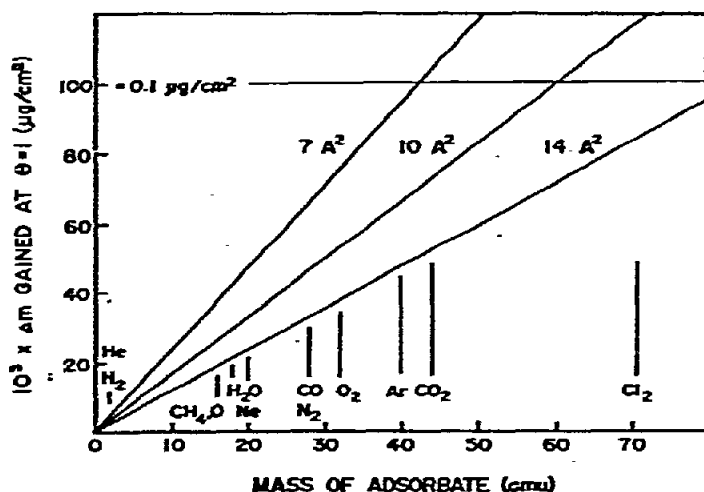Fig. 1. The amount of mass gained at monolayer coverage for adsorbates on adsorbent surfaces with effective surface areas of 7, 10 and 14 $Å^2$/adsorbent atom.

with a surface atom, then the mass of an adsorbed monolayer ($\theta = 1$) will be 0.00166M μg, where M is the mass of the adsorbate. The mass of an adsorbed monolayer is plotted in Fig. 1 for H_2, He, CH_4, H_2O, Ne, N_2, CO, O_2, Ar, CO_2 and Cl_2. As is seen, Δm ranges from 0.0033 to 0.112 μg cm^{-2} for a *monolayer of adsorbed gas*. Thus, studies of single crystals with $\sim$ 4 cm^2 of surface area are precluded with commercially available microbalances and most custom made units, where limiting sensibilities are typically 0.1 to 1 μg. Unless a unit with a sensibility of 0.01 μg, such as the Rodder balance[16] is used, studies of single crystals by ion bombardment and annealing are not feasible. However, many noble metals can be cleaned using outgassing and/or chemical treatments where much larger surface areas can be achieved by using a large number of wafers, discs, or supported thin films to achieve hundreds of square centimeters of surface. The power, limitation or unfeasibility of using a microbalance for a particular gas–solid system depends on the information desired. For example, determination of the amount adsorbed on a refractory metal single crystal, cleaned by ion bombardment and annealing cycles, or on an outgassed and/or chemically cleaned metal loaded zeolite with hundreds of square *meters* of active surface per gram of sample present considerably different requirements for the experimental apparatus.

When outgassing and chemical oxidation and/or reduction methods of surface cleaning are used, it is necessary to establish that the surface area remains constant, the chemisorption is reproducible, the cleaned surface is not poisoned by diffusion from the bulk and that neither the reactant *or product* gases involved in the cleaning cycle will adsorb onto the surface. All these criteria *can* be satisfied, as was demonstrated for the silver oxygen system using CO or H_2[17]. As repeated outgassing, adsorption, outgassing and chemical reduction cycles are carried out on a sample (OAOR cycling), the microbalance can be most useful for establishing if reproducible chemisorption behavior can be attained. The OAOR cycle is shown schematically in Fig. 2 for several cycles where *seven* parameters are monitored. These are the rate and
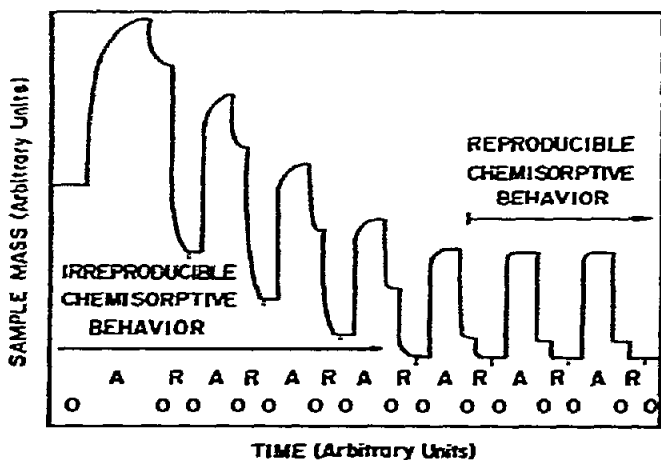

Fig. 2. Effect of outgassing, adsorption, outgassing and chemical reduction (OAOR) cycling in transforming a surface from irreproducible to reproducible chemisorptive behavior.

amount of adsorption, desorption and reduction and the change in sample mass. As is seen in Fig. 2, the seven parameters become constant or reproducible in the latter stages of cycling.

The methods for the measurement of $m(t)$ or $m(P)$ at different temperatures of adsorption, desorption, outgassing or equilibrium have been described[18]. The appropriate quantitative relationship for obtaining the surface area, activation energies for adsorption and desorption and isosteric heat of adsorption will be developed in the next sections and typical results presented.

SURFACE AREA

The surface area of a sample can be determined from an adsorption isotherm $\{m(P); T, Cg$ constant, as shown in the insert to Fig. 3$\}$ by using the BET theory for multilayer adsorption[19]. The two-parameter BET equation is:

$$\frac{x}{(1-x)m} = \frac{1}{m_m c} + \frac{(c-1)x}{m_m c}$$ (1)

where $x = p/p_0$, p is the pressure of the adsorbate, p_0 is the adsorbate vapor pressure at the isothermal temperature used, m is the mass of gas adsorbed at any pressure p, m_m is the mass adsorbed at monolayer coverage and c is a constant. The derivation of eqn (1) and an excellent discussion of the parameters c and v_m, the equivalent of m_m, are available[20].

A plot of $x(1-x)m$ versus x is linear from x of about 0.05–0.35, as shown in Fig. 3, with a slope S and intercept I (ref. 17). When a linear plot is obtained in this region of x, considerable care must be exercised because this range of x is not valid for all materials[21]. Since S is $c - 1/cm_m$ and I is $1/cm_m$, $m_m = 1/(S + I)$. The specific surface area SA is given in $m^2 g^{-1}$ by SA $= m_m K/m_s$, where m_s is the mass of the adsorbent and $K = A_m N/M$. Here, M is the gram molecular weight of the adsorbate, N is Avogadro's number and A_m is the area occupied by one adsorbate molecule. For nitrogen with $A_m = 16.2 \text{Å}^2$, $SA_{N_2} = 3.48 \, m_m/m_s$ when m_m is in μg and m_s is in mg. For the data in Fig. 3, $S = 0.0423 \, \mu g^{-1}$, $I = 0.00020 \, \mu g^{-1}$, $m_m = 23.5 \, \mu g$,
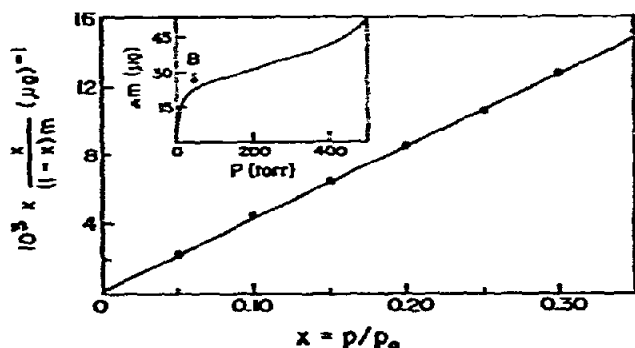

Fig. 3. BET plot of nitrogen adsorbed on silver powder at 78 K. The inset shows the original Type II isotherm obtained.

$m_s = 741.4$ mg yielding $SA_{N_2} = 0.110 \pm 0.004$ m^2 g^{-1} of silver powder after incomplete OAOR cycling.

The results of studies of the physical adsorption isotherms on porous and non-porous solids require a treatise on that subject alone, as is clear from reading the book by Gregg and Sing[22]. Numerous useful articles also appear in the proceedings of the *Conferences on Vacuum Microbalance Techniques*[14, 15], especially, since 1971[15]. For the surface scientist, the measurement of surface area answers one essential question: What is the surface area?

ADSORPTION KINETICS AND EQUILIBRIUM

The important quantitative parameters for an activated adsorption process are indicated in Fig. 4, where q is the heat of adsorption, E_A is the activation energy for adsorption, E_D is the activation energy for desorption and r_0 is the equilibrium displacement of the chemisorbed gas from the surface. The potential energy of the gas is usually chosen to be zero at infinite separation from the solid surface. More complex, and realistic, potential energy curves are shown in the inset where $q(\theta)$, $E_A(\theta)$, and $E_D(\theta)$ are indicated for two chemisorbed states. Numerous accounts of the theoretical basis for the potential energy diagrams are available[23-26]. The interest here is to indicate the utility of microgravimetric methods for determining E_A and E_D, the potential barriers to adsorption and q, the potential well for an adsorbed state. The methods used to measure the kinetics of adsorption apply as well to the initial and later stages of oxidation; for interpreting oxidation rates, the review chapter by Gulbransen and Brassart[9] is an excellent starting point for methods, techniques, literature references and a perspective of the field.

Adsorption equilibrium

At equilibrium between a specific gas and the solid, the mass m of the gas adsorbed per unit mass (or unit area) of the solid is a function of temperature and
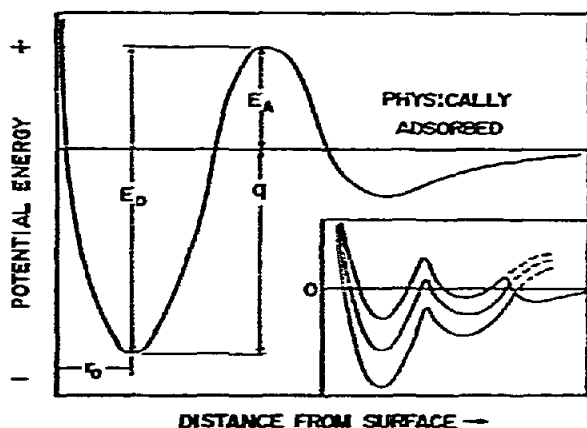

Fig. 4. Important adsorption parameters, E_A, E_D and q on a simple potential energy profile of a gas molecule at various normal displacements from the surface.
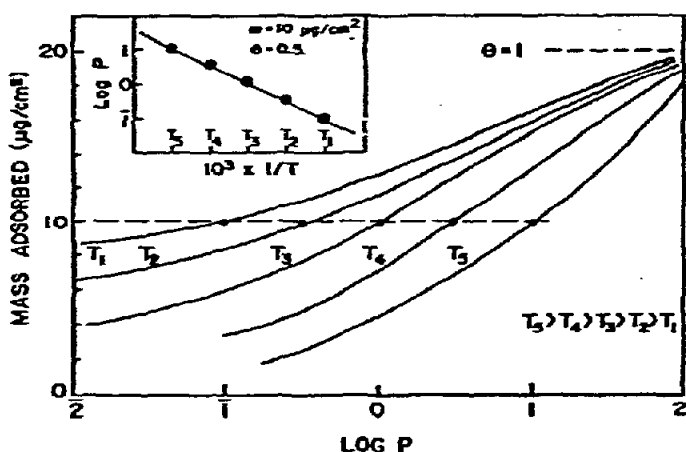
Fig. 5. Adsorption isotherms and their use (inset) to determine the isosteric heat of adsorption.

pressure, viz., $m(P, T)$. The necessary conditions that the surface area is constant, the measured amount of adsorption is the same at any given P and T, no absorption occurs, and the surface can be cleaned or at least returned to a reference state of controlled contamination apply here. A family of curves can be obtained by holding m, P or T constant. Thus, adsorption isotherms (T constant), isobars (P constant) and isosteres (m constant) are obtained from the determination of $m(P)$, $m(T)$ and $P(T)$, respectively. Isotherms and isobars may be determined directly by micro-gravimetric methods. Since any family of curves may be transformed to another by replotting[23], adsorption isosteres can be determined indirectly. From the data of adsorption isotherms, q may be determined at any particular mass of gas adsorbed from the relationship $(\mathrm{d}\ln P/\mathrm{d}T)_m = q/RT^2$, where q is the isosteric heat of adsorption. The slope of a plot of $\ln P$ versus $1/T$ is q/R, assuming q is independent of T. The mass adsorbed can be related to the surface coverage θ, from the measured surface area. If a specific crystal plane is known or assumed for the solid surface, the surface coverage will depend on the number of chemisorbed atoms assigned to each surface atom. Since q usually depends on θ, the plots of $\ln P$ vs. $1/T$ must be made at constant amounts adsorbed as illustrated in the set of isotherms shown in Fig. 5. Recent examples of obtaining $q(\theta)$ by microgravimetric methods have been published by Gandhi and Shelef[27] and Czanderna[28].

Adsorption kinetics

Chemisorption may occur at significantly different rates ranging from micro-seconds to weeks before the rate becomes too slow to be detectable. The rate of chemisorption u, where $u = \mathrm{d}m/\mathrm{d}t$, on a homogeneous solid surface depends on the factors given in eqn (2), viz.,

$$u = [P/(2\pi m k T)^{1/2}]f(\theta)\sigma(\theta)\exp - E_A(\theta)/RT \tag{2}$$

where $P/(2\pi m k T)^{1/2}$ is the number of impacts made by the gas atom or molecule per unit time per unit area, m is the mass of the adsorbate species, k and R are the Boltz-

mann and gas constants, $f(\theta)$ is the probability a collision will occur on an unoccupied site, and $\sigma(\theta)$ is the condensation coefficient. Since the exponential term is the fraction of gas atoms possessing the necessary activation energy, $\sigma(\theta)$ may be understood as the chance that a species with sufficient activation energy hitting an *unoccupied* site will adsorb rather than being reflected. Again, further detailed information on the theory of activated chemisorption is available[23-26].

For the experimental work, the unknowns $\sigma(\theta)$, and $f(\theta)$ can be eliminated by comparing u at a series of constant $PT^{-1/2}$ values. The slope on a plot of $\ln u$ versus $1/T$ at a particular θ yields E_A/R for the surface coverage considered. The values of u are obtained from the measurement of the mass gain as a function of time as illustrated in Fig. 6; the Arrhenius type plot obtained from the $\ln u$ at various T's, used to deduce E_A, is shown in the inset. The two activation energies correspond to two different potential barriers to the adsorption process, the lower one being rate controlling at lower temperature.
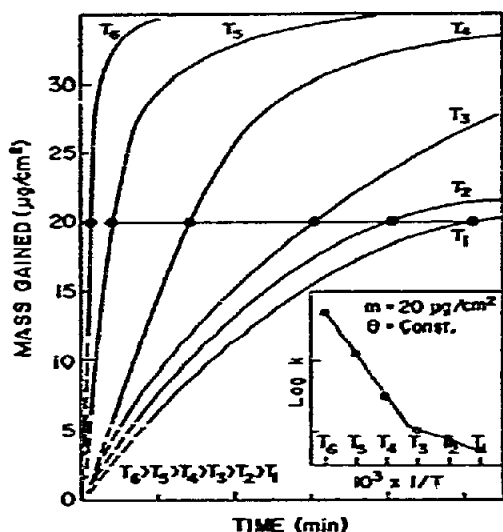

Fig. 6. The time dependence of the adsorption of a gas and its use on an Arrhenius plot to obtain E_A.

The necessity for having reproducible chemisorptive behavior can be easily understood from Fig. 6. For example, the curve at 60°C must be traced if the gas adsorbed is removed. The surface cleaning process must return the sample to the same mass, so the zero is established and the *rate* of adsorption as well as the amount must be reproduced on subsequent adsorption cycles at 60°C. Variations in the zero will shift the curves, so comparisons at the same θ are not possible and probably imply the surface is not reproducibly cleaned. Different rates and amounts of adsorption on repeated attempts probably result from changes in the distribution or rearrangement of the surface sites on the cleaned surface. A detailed determination of E_A versus θ for oxygen on silver, where the above criteria were all satisfied[17], has been published[29].

Desorption kinetics

The desorption of a gas from a surface is always activated and usually occurs at rates quite different from u. For a uniform surface where the variation in the desorption parameters results from surface interactions, the rate of desorption u' (dm/dt) will occur from occupied sites according to

$$u' = K(\theta)f'(\theta)\exp - [E_D(\theta)/RT] \qquad (3)$$

where $K(\theta)$ is a velocity constant, $f'(\theta)$ is the fraction of sites available for desorption and the exponential is the fraction of the adsorbed species with the necessary activation energy. In principle, a plot of $\ln u'$ versus $1/T$ at a constant amount adsorbed will yield a slope equal to E_D/R. In practice, the mass adsorbed may be in two or more adsorbed states and the ratios of these at any particular mass adsorbed is not known. Furthermore, when powders, stacked foils or stacked films are used, the desorption into vacuum may permit re-adsorption if the desorbing species can hit a different portion of the adsorbent surface. Thus, the determination of E_D depends on u' being the rate of desorption from the *same* initial coverage of a single state and a negligible re-adsorption probability, in addition to the requirements for reproducible chemi-sorptive behavior. From eqn (2), the re-adsorption probability is obviously smallest at high coverages, low pressures, high temperatures and where $E_D \sim E_A$, e.g., for a weakly bound state.

The interpretation of desorption is less ambiguous if one can assume the Wigner-Polanyi equation, e.g.,

$$-\frac{d\theta_s}{dt} = v_n \theta_s^n \exp - E_D/RT \qquad (4)$$

where θ_s is the fractional coverage of a single adsorbed state, v is the frequency factor, n is the order of the rate process and E_D is the activation energy of desorption. This equation has been applied successfully by Czanderna and his co-workers to the desorption of oxygen from silver. In ref. 31, the manipulations of eqn (4) into
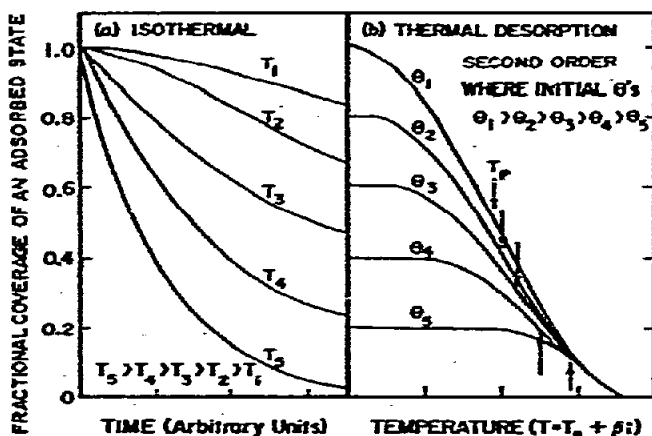

Fig. 7. The desorption of a gas from a solid surface. (a) At different isothermal temperatures; and (b) resulting from a linear increase in the sample temperature with time and different initial coverages.

appropriate forms are given for the analysis of isothermal desorption or a linearly programmed temperaturerise of the sample (thermal desorption). Typical data obtained for a series of isothermal desorption curves and thermal desorption of oxygen from silver are shown in Fig. 7. Using eqn (4), Kollen and Czanderna reported $E_D = 41.8 \pm 3.5$ kcal mol^{-1} from isothermal desorption and $E_D = 34.5 \pm 3.5$ kcal mol^{-1} for the thermal desorption of oxygen from the same silver sample[31]. Different ranges of v were also applicable[31].

Of the three adsorption parameters, E_D seems to be determined least satisfactorily by microgravimetric methods except for a few well-studied systems. Better sensibilities and UHV adaptation of ultramicrobalances may broaden considerably the solids that can be studied quantitatively in the future.

SIMULTANEOUS MEASUREMENT OF MASS AND OTHER PARAMETERS

The interpretation of dynamic micromass changes and equilibrium processes is enhanced considerably when additional physical parameters are measured simultaneously. Obvious possibilities include measurement of the residual gas composition in high and ultra-high vacuum[11, 33], the measurement of electromagnetic transmission and reflection, especially, in the infrared[18, 34, 35], magnetic susceptibility[36], electrical conductivity[37], and the elemental composition of the surface[38]. Since a complete review of the applicable literature in these areas is now being prepared[39], only a few examples will be cited.

Wolsky and Zdanuk[40] combined an omegation mass spectrometer with a bakeable ultramicrobalance to monitor the residual gases generated during the outgassing of germanium and silicon single crystals before and after oxidation. Later studies[11] by these investigators were concerned with sputtering phenomena and thin film studies. More recently, Fink and Merrill[41] used a quadrupole mass spectrometer with a Rodder ultramicrobalance in a study of the adsorption of carbon monoxide and ethylene on platinum foils. A direct coupling of the simultaneous measurement of mass change and desorbed gases was made by Brown et al.[33] during the oxidation of graphite in oxygen and subsequent desorption. A more qualitative combination of thermogravimetric and mass spectrometric measurements on the same system had been reported earlier by Wendlandt and Southern[42]. The path breaking efforts of combining a mass spectrometer with a microgravimetric system has been followed by a steady increase[15] in using this combined method.

Pioneering efforts to combine mass change with an infrared spectrometer with a quartz helix microbalance were carried out by Peri[43] and Amberg and Seanor[44]. The main results of these studies were concerned with the isomerization of butene on γ-Al$_2$O$_3$[43] and the adsorption of carbon monoxide on doped zinc oxide surfaces[44]. Angell[18] carried out a detailed investigation of the adsorption and desorption of carbon monoxide on zeolites using a beam microbalance and infrared spectrometer. More recently, Jacobs and Low[35] investigated the decomposition of dolomite in vacuum by also combining IR transmission measurements with a commercially

available microbalance. In most studies of this type, the investigators have used high area materials to secure enough IR absorption by the adsorbed materials from a single pass of the beam. The corresponding mass changes, as expected from the plot in Fig. 1, have been easy to detect. It is surprising to this reviewer that more combined investigations of infrared and mass change have not been carried out on high area catalyst materials. Here, the possibility exists for probing the gas–surface bonding *during* catalytic processes at operating temperatures and pressures, while monitoring the mass changes in flowing environments with a microbalance. The complications of interpreting the IR results are appreciated, but the in situ characterization of catalytic processes would seem to offer advantages over the wide-scale efforts of investigating catalytic materials in UHV and then extrapolating the observations to atmospheric or higher pressures.

The possibility of combining microgravimetric adsorption studies with magnetic susceptibility was explored by Czanderna[1] for oxygen on silver. A paramagnetic species was observed but very low levels of iron impurities with a strong temperature-dependence precluded carrying out a detailed quantitative investigation. Unfortunately, this promising project could not be continued after silver samples with low iron concentrations had been prepared.

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[46] but, to this author's knowledge, not simultaneously during adsorption or desorption. 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.[45] studied the adsorption of carbon monoxide and oxygen on thorium dioxide using simultaneous mass change and the luminescence of the adsorbent[45]. Their preliminary results indicate interpretation of the data will be challenging.

A combined measurement of mass change and the elemental composition of the surface was made by Levenson et al.[46] for phosphorus deposited on silicon using a crystal oscillator and Auger spectroscopy. His results demonstrated silicon signals could be detected even after $4.5 \cdot 10^{15}$ P atoms cm^{-2} ($\sim$ 3–6 atomic layers) were deposited. Furthermore, there was not a linear relationship between the phosphorus signal and amount deposited up to one monolayer, as is frequently assumed without concommitant mass-change data. There are well-known restrictions to using crystal microbalances for temperature-dependence studies[1]. Thus, the combination of an automated beam ultramicrobalance with one or more of the methods for surface analysis could have considerable impact for the study of surfaces if sufficient mono-layer sensibility is available with the balance.

Czanderna[38], 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. 8. A Rodder ultramicrobalance[47], automated with externally mounted photosensors to a sensibility of < 0.01 μg, was mounted on a UHV system. A suspended metal foil,
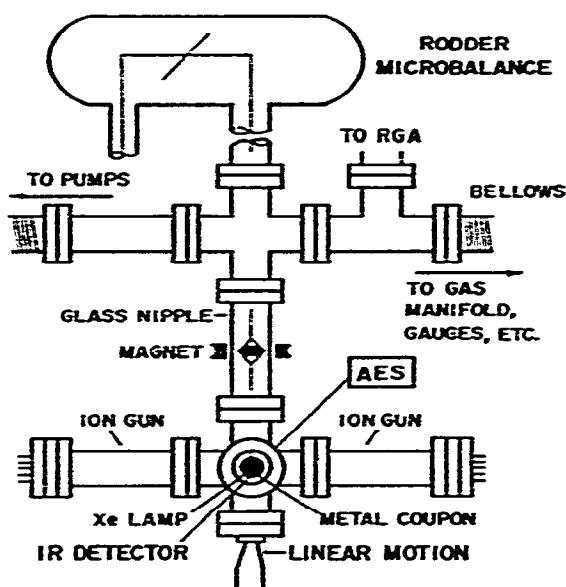
Fig. 8. Arrangement for the combined measurement of mass change, elemental composition of a metal surface and residual gas composition.

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 will 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 mono-layer of oxygen (as adions) adsorbed onto an 18-mm diam. metal disc, providing the area of each surface atom is 7 Å^2 and the short-range sensibility of 0.005 $\mu g^{\pm 1}$ of the Rodder balance is adequate for the time of the experiment.

The combination shown in Fig. 8 represents a significant capability for using the vacuum ultramicrobalance for adsorption studies on solid surfaces of known surface contaminations 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.

REFERENCES

1   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.
2   A. W. Czanderna (Ed.), *Methods of Surface Analysis*, Elsevier, Amsterdam, 1975, p. 1.
3   R. F. Goff and D. P. Smith, *J. Vac. Sci. Technol.*, 7 (1970) 72.
4   R. E. Honig, *J. Appl. Phys.*, 29 (1958) 549.

5 K. Larsson, C. Nordling, K. Siegbahn and E. Stenhagen, *Acta Chem. Scand.*, 20 (1966) 2880.

6 L. A. Harris, *J. Appl. Phys.*, 39 (1968) 1419.

7 G. F. Andrews, Jr., R. Alire and A. W. Czanderna, *J. Vac. Sci. Technol.*, 13 (1976) 552.

8 H. Verbeek and W. M. H. Sachtler, *J. Catal.*, 42 (1976) 257.

9 E. A. Gulbransen and F. A. Brassart, in S. P. Wolsky and E. J. Zdanuk (Eds.), *Ultra Micro Weight Determination in Controlled Environments*, Wiley, New York, 1969, Ch. 10.

10 D. A. Cadenhead and N. J. Wagner, in R. B. Anderson and P. Davison (Eds.), *Experimental Methods in Catalytic Research*, Part II, Academic Press, New York, 1976.

11 S. P. Wolsky and E. J. Zdanuk, in S. P. Wolsky and E. J. Zdanuk (Eds.), *Ultra Micro Weight Determination in Controlled Environments*, Wiley, New York, 1969, Ch. 12.

12 L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971.

13 S. P. Wolsky and E. J. Zdanuk (Eds.), *Ultra Micro Weight Determination in Controlled Environments*, Wiley, New York, 1969.

14 Eight edited books, *Vacuum Microbalance Techniques*, Vols. 1–8, Plenum, New York, 1961, 62, 64, 65, 66, 67, 70 and 71.

15 Three edited books, *Progress in Vacuum Microbalance Techniques*, Vols. 1–3, Heyden, London, 1972, 73 and 75 and the papers included in J. Vac. Sci. Technol., 11 (1974) 396–439 and 13 (1976) 541–560.

16 J. Rodder, in A. W. Czanderna (Ed.), *Vacuum Microbalance Techniques*, Vol. 8, Plenum, New York, 1971, p. 45.

17 A. W. Czanderna, *J. Phys. Chem.*, 66 (1966) 2120.

18 C. L. Angell and A. W. Czanderna, in S. P. Wolsky and E. J. Zdanuk (Eds.), *Ultra Micro Weight Determination in Controlled Environments*, Wiley, New York, 1969, Ch. 11.

19 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.

20 S. Brunauer, L. E. Copeland and D. L. Kantro, in E. A. Flood (Ed.), *The Solid–Gas Interface*, Vol. 1, Dekker, New York, 1967, p. 17 and 77.

21 D. L. Kantro, S. Brunauer and L. E. Copeland, in E. A. Flood (Ed.), *The Solid–Gas Interface*, Vol. 1, Dekker, New York, 1967, p. 413.

22 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1967.

23 D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, Butterworths, London, 1964.

24 V. Ponec, Z. Knor and S. Cerny, *Adsorption on Solids*, Butterworths, London, 1974 (English translation).

25 A. Clark, *The Chemisorptive Bond*, Academic Press, New York, 1974.

26 J. M. Thomas and W. J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, New York, 1967.

27 H. S. Gandhi and M. Shelef, *J. Catal.*, 24 (1972) 241.

28 A. W. Czanderna, *J. Vac. Sci. Technol.*, 14 (1977) 408.

29 A. W. Czanderna, *J. Phys. Chem.*, 68 (1964) 2765.

30 A. W. Czanderna, J. R. Biegen and W. Kollen, *J. Colloid Interface Sci.*, 34 (1970) 406.

31 W. Kollen and A. W. Czanderna, *J. Colloid Interface Sci.*, 38 (1972) 152.

32 A. W. Czanderna, S. C. Chen and J. R. Biegen, *J. Catal.*, 33 (1974) 163.

33 J. G. Brown, J. Dollimore, C. M. Freeman and B. H. Harrison, in A. W. Czanderna (Ed.), *Vacuum Microbalance Techniques*, Vol. 8, Plenum, New York, 1971, p. 17.

34 D. A. Seanor and C. H. Amberg, *Rev. Sci. Instr.*, 34 (1963) 917.

35 H. Jacobs and M. J. D. Low, *J. Colloid Interface Sci.*, 46 (1974) 165.

36 D. E. Soule, C. W. Nezbeda and A. W. Czanderna, *Rev. Sci. Instr.*, 35 (1964) 1504.

37 P. Schmider and H. Mayer, in C. H. Massen and H. J. van Beckum (Eds.), *Vacuum Microbalance Techniques*, Vol. 7, Plenum, New York, 1970, p. 207.

38 G. H. Andrews, Jr., R. M. Alire and A. W. Czanderna, *J. Vac. Sci. Technol.*, 13 (1976) 552.

39 A. W. Czanderna, *Progr. Surf. Sci.*, to be published.

40 S. P. Wolsky and E. J. Zdanuk, in M. J. Katz (Ed.), *Vacuum Microbalance Techniques*, Vol. 1, Plenum, New York, 1961, p. 35.

41 S. E. Fink and R. P. Merrill, in A. W. Czanderna (Ed.), *Vacuum Microbalance Techniques*, Vol. 8, Plenum, New York, 1971, p. 55.

42 W. W. Wendlandt and T. M. Southern, *Anal. Chim. Acta.*, 32 (1965) 405.

43 J. B. Peri, *Proc. Second Intern. Congr. Catalysis, Paris, 1960*, Edition Technip, Paris, 1961, p. 1333.

44   C. H. Amberg and D. A. Seanor, *Proc. Third Intern. Congr. Catalysis*, North Holland, Amsterdam, 1964, p. 122.
45   M. Breysse, L. Faure, B. Claudel and J. Vernon, in S. C. Bevan, S. J. Gregg and N. D. Parkyns (Eds.), *Progress Vacuum Microbalance Techniques*, Vol. 2, Heyden, London, 1973, p. 229.
46   L. L. Levenson, L. E. Davis, C. E. Bryson, III and J. J. Melles, *J. Vac. Sci. Technol.*, 9 (1972) 608.
47   J. Rodder, in A. W. Czanderna (Ed.), *Vacuum Microbalance Techniques*, Vol. 8, Plenum, New York, 1971, p. 43.