THEORY AND APPLICATIONS OF VACUUM MICROBALANCE TECHNIQUES

By JOHN M. THOMAS and BRIAN R. WILLIAMS*

(DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE OF NORTH WALES, BANGOR)

1. Introduction

EVERY chemist is familiar with the straightforward technique of weighing; and the advantages of using microbalances in routine operations ranging from chemical analysis to thermogravimetry, in which the course of a chemical reaction is followed by recording changes in weight, are well known. But the versatility of vacuum microbalance techniques, in which measurements of small forces are carried out *in situ*, does not seem to be generally recognised, although two outstanding examples—the determination[1] of atomic weights from the measurement of gaseous densities, and the direct experimental verification[2] of the theories of long-range forces of molecular attraction—have been discussed in previous *Quarterly Reviews*. This Review is intended (i) to survey the various types of thermodynamic, kinetic, and structural information which have been established using vacuum microgravimetry; (ii) to indicate other problems where similar techniques may profitably be applied; and (iii) to outline the theoretical principles which govern the operation of vacuum microbalances. Some attention will be given to the limitations and errors associated with the various types of microbalances now extant; but no attempt will be made either to trace the evolution of vacuum microbalances or to provide precise details concerning construction, manipulation, etc., since repositories of such information became available in 1953, when the uses of microbalances in the study of solid surfaces were surveyed by Rhodin[3] and Gulbransen.[4] Since that time, the scope and applications of vacuum microgravimetry have multiplied, as evidenced by the fact that international conferences dealing with the corpus of information on this topic have been held annually since 1960.

2. Definition of Terms

The term vacuum microbalance itself merits comment. It refers to balances, capable of detecting mass changes of down to a few microgrammes (μg), and which are either to be operated under vacuum conditions generally better than 10^{-6} torr. (10^{-6} mm. Hg.), or have been subjected to similar vacuum conditions during the course of sample pretreatment. The term is by no means precise, and is used as much to describe an ultramicrobalance capable of detecting 10^{-4} μg in an ultra high vacuum system

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* Present address: National Research Council, Ottawa, Canada.

[1] R. Whytlaw-Gray, *Quart. Rev.*, 1950, 4, 153.

[2] B. V. Derjaguin, I. I. Abrikosova, and E. M. Lifshitz, *Quart. Rev.*, 1956, **10**, 295.

[3] T. N. Rhodin, *Adv. Catalysis*, 1953, **5**, 39.

[4] E. A. Gulbransen, *Adv. Catalysis*, 1953, **5**, 119.

($< 10^{-9}$ torr.) as one that detects 10 μg in a soft vacuum of about 10^{-1} torr. The designation is also used to describe sensitive devices for measuring small forces (less than 10^{-5} dyn) not due to gravity.

Sensitivity and sensibility. The sensitivity of a balance is the ratio of the reversible response to the change of mass which produces that response. The latter is usually measured, especially for beam balances, by the deflexion of the beam-end and is expressed either in radians or in distance moved. Confusion may be avoided when reading microbalance literature if it is borne in mind that the inverse ratio of the sensitivity is frequently used to convey the precision of a balance (*sic.*). Moreover, in some articles, the sensitivity is quoted simply as a mass (*e.g.* 1 μg). even though such an expression is meaningless. Almost invariably, however, a closer enquiry will reveal that, elsewhere in the articles, a specified beam deflexion (usually 0·001 cm for beam-type vacuum microbalances) is quoted. The term sensibility, often a more useful quantity, stands for the minimum variation in mass that may be reproducibly measured with a given accuracy.

Two other factors are used to describe the performance of a microbalance: the *range*, which is the maximum variation in mass that the balance can take for a given load, and the *capacity* which is simply the maximum permissible load.

3. Types of Vacuum Microbalances

The ideal vacuum microbalance should have large capacity and range, be of high sensitivity (the magnitude of which should not vary with load), possess small temperature and pressure coefficients, have great zero point stability, be free from vibrational and electrostatic disturbances, and be capable of straightforward calibration. In addition, the material of the balance and other essential accoutrements, including the balance frame, suspensory fibres and cements, must be capable of withstanding baking, *in vacuo*, at temperatures high enough to remove chemisorbed and physically absorbed impurities, and be chemically inert to the gases used in subsequent studies. In view of these stringent requirements, it can be appreciated that most commercial balances cannot, with impunity, be used as vacuum microbalances. (There are a few notable exceptions: see, *e.g.*, refs. 5 and 6 where gold-plated and aluminium balances, respectively, are described). A very large number of special vacuum microbalances have been, and are continually being, evolved. Following a time-honoured practice, the vast majority of balances have been fashioned out of silica. This material certainly meets most requirements; but that there is nothing sacrosanct in this choice, and that a material such as duralumin is just as

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[5] J. J. Scholten, P. Zwietering, J. A. Konvalinka, and J. H. de Boer, *Trans. Faraday Soc.*, 1959, **55**, 2166.

[6] L. Cahn and H. R. Schultz, in "Vacuum Microbalance Techniques", vol. 3, ed. K. H. Behrndt, Plenum Press, New York, 1963, p. 29.

useable has recently been demonstrated theoretically[7] and experimentally[8].

As a general rule, vacuum microbalances have capacities that lie between 0·02 to 2 g., and sensibilities that are often as little as 10^{-2} μg but more customarily in the region of 1 μg. It can therefore be seen that the ratio of the capacity to the sensibility is not very different (*ca* 10^6) for conventional and vacuum microbalances. What is significant, however, is that vacuum microbalances have (i) the ability to cope with minute variations in the mass of *small* samples, such as single crystals and thin films, and (ii) a very considerable *range*.

It is instructive to consider the operation of vacuum microbalances by using the following, arbitrary, classification.

(*a*) **Cantilever Microbalances.**—The principle underlying the mode of operation of this type of balance is the bending of a thin beam when a weight is suspended from one end, the other end being fixed. As the movement of the beam-end is proportional to the *total* load, the ratio of the capacity to the sensibility will be limited. The sensitivity of such a balance is greatest for thin beams, which can take but small loads. Although this type of balance can be used to detect mass changes of 10^{-1} μg, it suffers from the disadvantage of being prone to errors arising from temperature inhomogeneities (the balance being unsymmetrical), and of requiring buoyancy corrections during operation.

(b) Spring Balances.—Helical springs, made of silica, have been extensively used,[9] especially by McBain,[9b] for a variety of vacuum studies. The extension of the spring is proportional to the total load, so that, again, high sensitivity is attainable only at the expense of reduced capacity. The sensitivity is itself dependent on the diameters of the fibre and the coil, the temperature of the helix and the number of coils per unit length. The necessity for buoyancy corrections and the notorious fragility of silica springs have tended to diminish the popularity of helical balances, but this trend has been offset by recent advances in the construction of springs made of tungsten[10] or copper–beryllium[11] alloy. Such springs have greater internal friction, so that oscillations are readily damped *in vacuo*, but they possess the undesirable property of metallurgical creep and require more stringent thermostatting. Spring balances, though not capable of the sensitivity of beam-type balances, have been used[12] for the study of gas–solid interaction at high temperature, and are amenable to electro-

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[7] C. H. Massen, J. A. Poulis, and J. M. Thomas, *J. Sci. Instr.*, 1964, **41,** 302.

[8] J. M. Thomas and B. R. Williams, in "Vacuum Microbalance Techniques", vol. 4, ed. F. A. Brassart, Plenum Press, New York, 1965.

[9] (*a*) F. Emich, *Monatsh*, 1915, **36,** 436; (*b*) J. McBain and A. Bakr, *J. Amer. Chem. Soc.*, 1926, **48,** 690.

[10] S. L. Madorsky, in "Vacuum Microbalance Techniques", vol. 2, ed. R. F. Walker, Plenum Press, New York, 1962, p. 47.

[11] P. J. Anderson and R. F. Horlock, *Trans. Faraday Soc.*, 1962, **58,** 1993.

[12] P. Connor, J. B. Lewis, and W. J. Thomas, "Proceedings of Fifth Conference on Carbon", Pergamon Press, Oxford, 1962, p. 120.

magnetic compensation,[13] which serves to increase their range for a given sensitivity.

(c) **Beam-type Balances.**—Although vacuum microbalances have been made[14] which are similar in design to conventional microbalances, both silica and agate knife-edges being utilised, the majority of those now constructed are beam-type gravity balances that are variants *either* of the classical Nernst–Donau apparatus later developed by Gulbransen[4] and Rhodin,[3] *or* pivotal balances of the kind made by Gregg[15] and others.[16] Torsional balances, which utilise the torsional moment of the wire constituting the primary fulcrum to restore the balance to an original setting, are also used.[17]

(*i*) *Gravity microbalances.* In this type of balance, the torsional contribution of the suspension wire that acts as primary fulcrum (Fig. 1) is made so small by using a very thin wire (*e.g.* 10μ diameter) that it is negligible compared with the "gravity" moment exerted by the sample and counterweight which are suspended from the two secondary fulcrums. To render the balance stable, and to produce the desired sensitivity, the beam is offset by a calculated amount at a computed distance either side of the primary fulcrum [Fig. 1 (b)]. Comparatively little manipulative skill is required to construct a balance of this type with a sensitivity such that a deflexion of 0·001 cm. of the beam-end corresponds to a mass change of 1 μg. Greater care in securing parity of arm length and uniformity of cross-section enables a sensibility of 10^{-1} μg to be reached, and a sensitivity that remains essentially independent of load (see Section 4).[18] By utilising thin silica beams, which sagged when loaded, Wolsky and Zdanuk[19] were able to arrange for the sensitivity to increase commensurately with increase

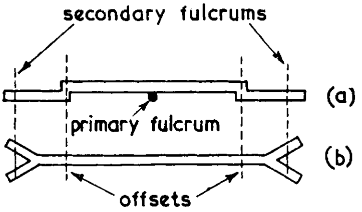

FIG. 1. *Schematic illustration of beam-type microbalance; (a) elevation, (b) plan.*

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[13] J. Hooley, *Canad. J. Chem.*, 1957, **35**, 374.

[14] B. D. Steele and K. Grant, *Proc. Roy. Soc.*, 1909, *A*, **82**, 580; S. Machin, Ph.D. Thesis, Rennselaer Polytech., 1961.

[15] S. J. Gregg, *J.*, 1946, 561; 1955, 1438.

[16] A. W. Czanderna and J. M. Honig, *Analyt. Chem.*, 1957, **29**, 1206.

[17] J. Strange, Ph.D. Thesis, Pennsylvania State University, 1964.

[18] B. R. Williams, Ph.D. Thesis, University of Wales, 1964.

[19] S. P. Wolsky and E. J. Zdanuk, in "Vacuum Microbalance Techniques", vol. 2, ed. R. F. Walker, Plenum Press, New York, 1962, p. 37.

of load. The limiting value for the sensibility of this type of balance appears to be *ca.* 10^{-2} μg; although it does seem possible to increase the capacity without sacrificing sensitivity.[20]

The prime advantage of this type of balance, which can readily be converted to a null-point instrument using electromagnetic adjustment,[21] is that, owing to its symmetry, disturbances arising from temperature and pressure gradients are minimised (but see Section 4), and buoyancy corrections need not be applied if the counterweight is so chosen that its density matches that of the sample.

(*ii*) *Pivotal balances.* In this modification, two fine points are employed instead of a knife-edge for suspending the balance beam at the primary fulcrum. Gregg[15] built a sturdy (capacity 20 g, reciprocal sensitivity 3×10^{-4} g./div.) pivotal balance using gramophone needles for the primary and secondary fulcrums. More sensitive* variants of this design have been constructed:[16] thus Czanderna[22] has recently developed an automatically operated pivotal balance that can take a load of 20 g. and has a sensibility of 2×10^{-1} μg.

(d) Quartz Crystal Microbalances.—Attempts to circumvent the disadvantages of the types of microbalances so far discussed, *e.g.*, difficulties associated with their usage in ultra high vacua ($< 10^{-9}$ torr.) and their tediousness in operation, have resulted in the successful development[23,24] of a new principle of weighing which utilises the fact that the frequency of a piezoelectric crystal is dependent on the total vibrating mass. Commercially available quartz crystals, which can be fitted with a gold plate to act as "sample holder", are made part of an oscillating circuit, and the change in frequency of the resonating crystal as a result of addition or loss of mass to or from the holder (by condensation or evaporation of adsorbed species) is monitored with an electronic counter. This kind of balance can be calibrated by evaporating a metal on to the holder and determining the mass of the deposit by subsequent spectrochemical analysis.[24] Frequency changes equivalent to 1×10^{-6} μg./cm^2 can now be measured: such precision implies that less than a thousandth of a monolayer of oxygen may be detected.

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* Some caution is required in interpreting the meaning of increased sensitivity. For convenience, the sensitivity is assessed by the smallness of the mass change corresponding to a fixed beam deflexion (Section 2). If ever-decreasing values of the deflexion can be detected (*e.g.*, electronically) then, for a fixed balance performance, the mass change decreases proportionally. Hence, it *appears* as if the balance densitivity is enhanced purely by the improvement in measuring deflexion.

[20] R. F. Hampson and R. J. Walker, *J. Res. Nat. Bur. Stand., Sect. A.*, 1961, **65**, 289; J. M. Thomas, E. L. Evans, and B. R. Williams, to be published.

[21] T. Gast, *Chem.-Ing.-Tech.*, 1957, **29**, 262.

[22] A. W. Czanderna, in "Vacuum Microbalance Techniques", vol. 4, ed. F. A. Brassart, Plenum Press, New York, 1965.

[23] (*a*) G. Sauerbrey, *Z. Physik.*, 1959, **155**, 206; (*b*) A. W. Warner and C. D. Stockbridge, in "Vacuum Microbalance Techniques", vol. 2, ed. R. F. Walker, Plenum Press, New York, 1962, p. 71; p. 93.

[24] I. Haller and P. White, *Rev. Sci. Instr.*, 1963, **34**, 677.

(e) Vertically Suspended Balances.—In measuring small forces, there is much to be gained by using an instrument that rotates about a vertical rather than a horizontal axis. The recording of very small forces exerted on samples placed in inhomogeneous magnetic fields can be accomplished[25] with great precision using what is, effectively, a vertically suspended torsion balance, advantage being taken either of modern electromagnetic means of operating the balance as a null-point instrument[25] or of recent refinements in the use of the Poggendorf optical lever[26] to measure the precise amount of deflexion.

It will emerge later that one of the most efficacious means of measuring the vapour pressures of solids involves what is nowadays designated the torsion–effusion technique [see Section 5(a)]. Introduced by Volmer[27] in 1931, this uses a vertically suspended torsion fibre attached to which there is a small concave mirror and, at the free end, a small cell with two orifices situated eccentrically on opposite faces [Fig. 2(a)]. The top view of a typical[28] sample holder used in a torsion–effusion balance is shown in Fig. 2(b), the axis of rotation passing perpendicularly to the plane of the paper through X. The type of assembly employed to measure the rate of growth or evaporation[29] of a crystal is illustrated by Fig. 2(c), and to record the intensity of a molecular beam[30] by Fig. 2(d).

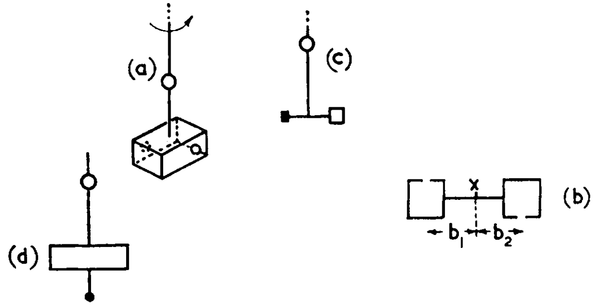

FIG. 2. *A selection of cells used with vertically suspended balances; (a) and (b) torsion–effusion cells, (c) arrangement for measuring growth or evaporation of crystals, and (d) arrangement for study of molecular beams.*

It is possible to devise systems that can, simultaneously, be operated both as vertically suspended torsion balances and horizontally mounted beam-type balances [see Section 5(a)].

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[25] J. A. Poulis, C. H. Massen, and P. van der Leeden, *Appl. Sci. Res., B.*, 1961, **9**, 133.

[26] R. V. Jones, *J. Sci. Instr.*, 1961, **38**, 37.

[27] M. Volmer, *Z. Physik Chem. Bodenstein Festband*, 1931, 836.

[28] R. S. Bradley and T. G. Cleasby, *J.*, 1953, 1681.

[29] (*a*) S. A. Kitchener and R. F. Stickland-Constable, *Proc. Roy. Soc.*, 1958, *A*, **245**, 93; (*b*) E. K. Rideal and P. M. Wiggins, *Proc. Roy. Soc.*, 1951, *A*, **210**, 291.

[30] D. W. Bassett and A. J. B. Robertson, *Brit. J. Appl. Phys.*, 1959, **10**, 534.

4. Theory of Microbalances

We shall, for heuristic purposes, briefly discuss the quantitative expression for the sensitivity of a beam-type gravity microbalance, and the deflexion of a vertically suspended balance. Then we shall consider the theoretical limitations of microbalances.

(a) **Beam-type Gravity Balances.**—If (see Fig. 3) C denotes the primary fulcrum (*i.e.* the suspension axis) and A and B the secondary fulcrums, then, if the length of the beam is $2l$, the masses of the sample, counterweight and beam are, respectively, $(M + m)$, M and G, the distance of the centre of mass below the primary fulcrum is s, and a is the distance of the primary fulcrum above the centre of the beam, we have, by taking moments about C:

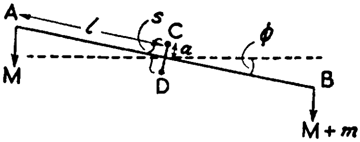

FIG. 3. *Illustration of theory of beam-type microbalances.*

$$\frac{d\phi}{dm} = \frac{l}{Gs + 2Ma + K} \tag{1}$$

$d\phi/dm$ being the sensitivity. K is the term that takes into account the torsional contribution of the main suspension wire: it is negligible for thin wires, so that equation (1) becomes identical with that which expresses the sensitivity of an ordinary knife-edge balance.[31]

If the sensitivity is to be independent of load, a must be zero; in other words all the fulcrums must be coplanar, and this is the main reason for offsetting the beams. Maximum sensitivity is reached when l is large and both G and s are small. Long thin beams are obviously desirable, but a compromise has to be made as sagging will be more pronounced with such beams. It is more prudent to construct a light sturdy balance, and to arrange for some means of preselecting a value of s, while still maintaining stability through having D lower than C, so as to permit the use of a range of sensitivities.* The sensitivity of a beam balance is improved† marginally if the beam has a rectangular, rather than a circular, cross-section.[8,33]

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* To this end, the procedure pioneered by Lambert and Phillips[32] of adding silica weights above the centre of the beam has often been adopted.

† The weight of the beam for a given moment of inertia is decreased by using a rectangular cross-section.

[31] Notes on Applied Science No. 7 (National Physical Laboratory), H.M.S.O., London 1954.

[32] B. Lambert and G. S. C. Phillips, *Phil. Trans., A*, 1950, **242**, 415.

[33] E. A. Gulbransen and K. F. Andrew in "Vacuum Microbalance Techniques", vol. 1, ed. M. J. Katz, Plenum Press, New York, p. 1.

(b) Vertically Suspended Torsion Balances.—If a vessel with two effusion holes is suspended in a vacuum on a fibre of torsion constant τ, the pressure p in the vessel in the neighbourhood of the orifices is related to the angle of twist θ by an equation which takes the form: $p = k\,\theta$, where k is an apparatus constant. The precise value of k can be evaluated by considering the recoil force arising from effusion through the holes of area a_1 and a_2 at distances b_1 and b_2 from the suspension axis X [Fig. 2(b)]. It transpires that:

$$p = 2\,\tau\,\theta/(a_1\,b_1 + a_2\,b_2) \tag{2}$$

However, since the effusion holes in any real cell must be of finite length, it has been found[34] necessary to incorporate a factor f into the expression on the right hand side of equation (2). In effect, f is the ratio of the force resulting from the effusion of molecules through an orifice of finite length to that expected for effusion through an infinitely thin orifice, and the value of f depends on the ratio of the length of the hole to its radius.

In general, if a force F acts normal to the surface of a vane suspended on a fibre, b being the distance from the suspension axis to the point at which the force acts, then:

$$F\,b = \tau\,\theta \tag{3}$$

Bassett and Robertson[30] showed how the force produced by a molecular beam of non-condensible gas could be calculated by assuming that the impinging molecules were first adsorbed and subsequently evaporated according to the cosine law.[35] By measuring the angle θ through which the vane was turned, and using equation (3), they could calculate the momentum carried by the molecules in the molecular beam.

(c) Theoretical Limitations.—We have now to consider two distinct types of limitations imposed on the performance of vacuum microbalances. One of these is totally unavoidable; the effect of the other can, however, be meliorated.

(*i*) *Influence of Brownian motion.* Since present-day improvements in the design and construction of microbalances are rendering them progressively more sensitive, it is pertinent to enquire where the theoretical limit to the sensitivity lies. A limit is imposed by the random fluctuations in the motions of the atoms of which the balance is composed and of the gas molecules which surround the balance when in operation. These fluctuations disturb the balance, so that any mass variation that is smaller than the background (Brownian motion) "noise" cannot be detected. Quantitative estimates of the magnitude of the spurious couple or force caused by Brownian motion have been made by several investigators.[36] Barnes and Silverman,[36a] in 1934, were under the false impression that the

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[34] A. W. Searcy and R. D. Freeman, *J. Chem. Phys.*, 1955, **23**, 88.

[35] M. Knudsen, *Ann. Physik.*, 1910, **31**, 205, 633.

[36] (*a*) R. Bowling Barnes and S. Silverman, *Rev. Mod. Phys.*, 1934, **6**, 162; (*b*) J. A. Poulis and J. M. Thomas, in ref. 6, p. 1.

limit of detection of microbalances was about 10 μg*, and hence regarded the magnitude of the "spurious mass" estimated by them (10^{-3} μg) as of academic interest only. Poulis and Thomas,[36b] in a recent assessment of the relevance of fluctuation theory[38] to the performance of beam-type and spring vacuum microbalances, concluded that, for the balance designs currently in vogue, the "spurious mass" arising from Brownian motion is likely to lie in the range 10^{-4} to 10^{-2} μg. It appears that we are not far from the state, already reached with galvanometers, where endeavouring to increase sensitivity is pointless because, by so doing, the fluctuations are simultaneously increased. (In "electronic" weighing, *e.g.* with quartz resonating crystals, it is possible to cope, to a certain extent, with the Brownian noise, by integrating the overall response in such a way as to neutralise the noise and so extract a meaningful signal).

(*ii*) *Disturbances arising from thermomolecular flow.* If the sample or counterweight, or even the fibres on which these are suspended, experience small temperature gradients when the ambient pressure is low, it is possible that spurious couples or forces several orders of magnitude as great as those to be measured may be registered. For example, Williams,[18] who used a beam-type gravity balance, found that when one limb, in which was suspended a sample of single crystals of graphite, was cooled in liquid air (the graphite counterweight suspended in the other limb being at room temperature), the apparent mass change *versus* pressure curve shown in Figure 4 was obtained. The apparent mass change is very considerable

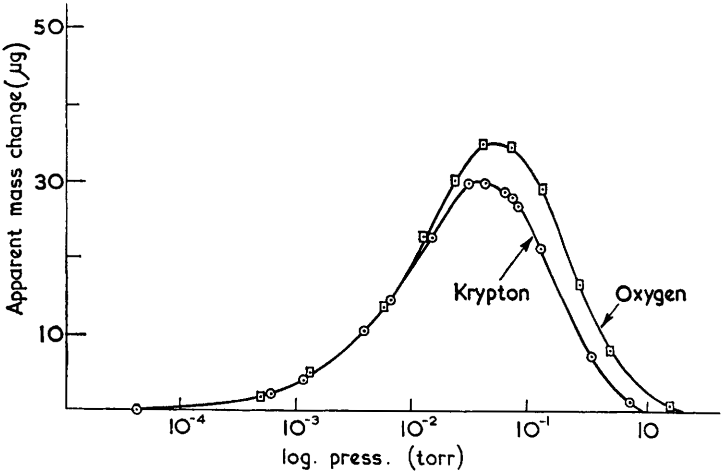

FIG. 4. *Apparent mass change, arising from thermo-molecular flow. Sample at* −193°C., *counterweight at room temperature.* (Reprinted, by permission, from B. R. Williams, Ph.D. Thesis, University of Wales, 1964).

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* In 1914, Petterson[37] had weighed 0·2 g. with an accuracy of 1 part in 10^9.

[37] H. Petterson, Dissertation, University of Göteborg, 1914.

[38] C. W. McCombie, *Reports Prog. Phys.*, 1953, **16,** 266.

and passes through a maximum in the Knudsen pressure range (10^{-2} to 10^{-1} torr.), where the mean free path of the gas molecules is comparable with the dimensions of the sample and annular space between sample and the balance limb. Spurious mass changes such as these can seriously impair the precision of vacuum microgravimetry* and can be minimised, but perhaps never completely eliminated, by diminishing the smallest of temperature gradients along sample, counterweight or suspension fibres. Thomas and Poulis[40] have formulated a theory which ascribes the occurrence of these spurious mass changes to thermomolecular flow (thermal transpiration). They use the well-known Knudsen equation:

$$p_1/p_2 = (T_1/T_2)^{\frac{1}{2}} \tag{4}$$

where p_1 and p_2 are the pressures associated with the temperatures T_1 and T_2, to evaluate the magnitude of the mass changes together with the pressures at which the changes are maximal for various gases. From their theory it emerges[40] that microbalances, when operating in the Knudsen pressure range, will, as has been borne out experimentally,[41] be prone to relatively large errors, unless unconscionably elaborate thermostatting is incorporated.

5. Applications of Vacuum Microbalance Techniques to Problems of Chemical Interest

Our discussion of the problems that can be tackled by vacuum gravimetry will be deliberately eclectic and our arrangement and sub-division of the topics unavoidably somewhat arbitrary. We exclude many notable applications such as the use of quartz microbalances to evaluate[32] the compressibilities and virial coefficients of gases, and adduce several that are not widely known and speculate upon others, as yet, untried.

In this section we shall concern ourselves with the measurement and use of vapour pressures of substances in the condensed phases.

(a) Vapour Pressure and Related Thermodynamic Data.—We recall that the enthalpy and entropy of vaporisation of solids and liquids may be obtained, *using the second law of thermodynamics*, from the variation of vapour pressure with temperature. The Clausius–Clapeyron equation relates the vapour pressure p to the absolute temperature T *via* the standard enthalpy of vaporisation ΔH°

$$\mathrm{d} \ln p/\mathrm{d}T = \Delta H^\circ/RT^2 \tag{5}$$

But the enthalpy, in general, varies with temperature and its value at a

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* It has been reported[39] that, with a sample held ostensibly at 1000°C., the spurious mass change arising from a largely unknown temperature difference was 10^3 μg in a pressure of 10^{-1} torr. of helium.

[39] A. W. Czanderna, ref. 33, p. 129.

[40] (*a*) J. M. Thomas and J. A. Poulis, ref. 6, p. 15; (*b*) J. A. Poulis and J. M. Thomas, *J. Sci. Instr.*, 1963, **40**, 95; (*c*) J. A. Poulis, B. Pelupessy, C. H. Massen, and J. M. Thomas, *J. Sci. Instr.*, 1964, **41**, 295.

[41] S. P. Wolsky, ref. 33, p. 143.

particular temperature, $\Delta H^\circ_{\mathrm{T}}$, can be written:

$$\Delta H^\circ_{\mathrm{T}} = \Delta H^\circ_0 + \Delta a\, T + \frac{\Delta b}{2} T^2 + \Delta c\, T^{-1} + \ldots\ldots \qquad (6)$$

ΔH°_0 being the enthalpy of the hypothetical vaporisation process at 0°K. All terms beyond the first on the right hand side of equation (6) arise from the change in heat capacity, ΔCp, for the vaporisation, since, for both the gaseous and condensed species the heat capacity may be written: $Cp = a + bT + cT^{-2} + \ldots\ldots\ldots$ If ΔCp is zero, equations (5) and (6) combined yield an equation of the form:

$$\ln p = -\,\mathrm{A}\,T^{-1} + \mathrm{B} \qquad (7)$$

where A is clearly equal to $-\Delta H^\circ_0/\mathrm{R}$ and B to $\Delta S^\circ/\mathrm{R}$, ΔS° being the standard entropy of vaporisation. If ΔCp is finite but constant, which is tantamount to saying that we may write $Cp = a$ for both the gaseous and condensed species, then:

$$\Delta H^\circ_{\mathrm{T}} = \Delta H^\circ_0 + \Delta a\, T \qquad (8)$$

so that substitution in equation (5) leads to:

$$\ln p = -\mathrm{A}T^{-1} + C \ln T + \mathrm{D} \qquad (9)$$

from which we may again extract the enthalpy and entropy of vaporisation. The enthalpy of vaporisation at 298°K., often required in thermodynamic calculations (see later), can be obtained from ΔH°_0 using equations (6) or (8). Note that whether ΔCp is zero or finite, and whatever the range of temperature employed, with the second law approach to the thermodynamics of vaporisation we obtain one value (an average) of ΔH°_0.

Using the third law approach, we may take advantage of tabulations of free energy functions and hence arrive at an independent value of ΔH°_0 (or $\Delta H^\circ_{\mathrm{T}}$) for every temperature at which vapour pressure is measured. This can be gleaned from the following equations which relate the Gibbs standard free energy of vaporisation $\Delta G^\circ_{\mathrm{T}}$ to the vapour pressure and to the free energy function change $\Delta(G^\circ_{\mathrm{T}} - H^\circ_0)/T$

$$\Delta G^\circ_{\mathrm{T}}/T = -R \ln p \qquad (10)$$

and

$$\Delta G^\circ_{\mathrm{T}}/T = \Delta(G^\circ_{\mathrm{T}} - H^\circ_0)/T + \Delta H^\circ_0/T \qquad (11)$$

Values of $(G^\circ_{\mathrm{T}} - H^\circ_0)/T$, also written as $f\,e\,f$, may be readily computed for the species in the vapour phase using statistical mechanical methods, provided the appropriate values of bond length, vibration frequency, etc., are known. For the condensed phase, $f\,e\,f$ values are obtainable from heat capacity measurements by using the following equation:

$$f\,e\,f = \frac{1}{T}\int_0^T C_{\mathrm{P}}\mathrm{d}T - \int_0^T C_{\mathrm{P}}\mathrm{d}\ln T \qquad (12)$$

Having seen how the enthalpy and entropy of vaporisation may be evaluated from vapour pressure data, we shall now outline the various ways in which vacuum microbalances can be used actually to determine the vapour pressure. The great advantage in using microbalances is that they enable pressures as low as 10^{-7} torr. to be determined, so that the technique can be used for metals, alloys and a vast range of organic and inorganic compounds at temperatures close to 298°K.

(*i*) *The Knudsen effusion method.* The rate of loss of mass, $\mathrm{d}w/\mathrm{d}t$, by effusion of vapour through a small hole (area a_1) and infinitely small thickness when the (low) pressure inside the effusion vessel is p and that outside is zero is given by:[35]

$$p = (-\mathrm{d}w/\mathrm{d}t)(2\pi RT/M)^{\frac{1}{2}}/a_1 \qquad (13)$$

where M is the molecular weight. The value of $\mathrm{d}w/\mathrm{d}t$ is readily determined using a beam-type or spring microbalance, the direction of effusion from the suspended cell being so arranged that the recoil force does not contribute to that recorded by the balance. The value of a_1 can be obtained either directly by measurement or by calibration using substances, such as benzophenone or sulphur, of known vapour pressure. Such a calibration will remove uncertainty concerning the effective, as opposed to the geometric, area of the hole. {No effusion hole is infinitely thin [see Section 4(*b*)] consequently the effusion area has to be multiplied by a so-called Clausing factor,[42] closely similar to the factor f previously mentioned}. This method has been used to determine the vapour pressures of paraffins,[43] aromatic hydrocarbons,[44] hydrogen-bonded organic crystals,[45] and a large number of metals, alloys and non-metallic elements.[46] However, when used for the determination of the enthalpy of vaporisation of ferrocene, misleading results were obtained[47] [probably because the coefficient of condensation, as defined in Section 5(a) (ii), was less than unity].

In a recent variant[48] of the method, the rate of effusion of Ag and Pd from a Knudsen cell has been measured by recording the mass increase of a collector plate, which was suspended on a microbalance directly above the effusion hole.*

(*ii*) *Langmuir free-evaporation method.*[50] The rate of loss of mass by vaporisation from a sample of area a_2 in a vacuum when none of the

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* This method is, however, not as sensitive as the analogous one, developed by Carson *et al.*,[49] using isotopically labelled solids.

[42] P. Clausing, *Ann. Physik.*, 1932, **12**, 961.

[43] A. R. Ubbelohde, *Trans. Faraday Soc.*, 1938, **34**, 282.

[44] R. S. Bradley and T. G. Cleasby, *J.*, 1953, 1690.

[45] R. S. Bradley and A. D. Care, *J.*, 1953, 1688.

[46] J. L. Margrave, in "Physicochemical Measurements at High Temperatures", ed. J. O'M. Bockris, J. L. White and J. D. Mackenzie, Butterworths, 1959, p. 225.

[47] J. W. Edwards and G. L. Kington, *Trans. Faraday Soc.*, 1962, **58**, 1323.

[48] P. D. Zavitsanos, *Rev. Sci. Instr.*, 1964, **35**, 1061.

[49] A. S. Carson, R. Cooper, and D. R. Stranks, *Trans. Faraday Soc.*, 1962, **58**, 2125.

[50] I. Langmuir, *Phys. Rev.*, 1913, **2**, 329.

gaseous molecules returns to the surface is related to the equilibrium vapour pressure by the equation:

$$p = (-\mathrm{d}w/\mathrm{d}t)(2\pi RT/M)^{\frac{1}{2}}/a_2\alpha \qquad (14)$$

The factor α, known either as the coefficient of condensation or the coefficient of evaporation, is the fraction of the gaseous molecules which would condense if they were to impinge on the vaporising surface under equilibrium conditions.[46] In measuring the vapour pressure of metals by this method it is often assumed that α is unity, although there are indisputable indications that α is fractional and tends to vary with temperature. Margrave and his co-workers[46,51] have shown that, for many metals, $\alpha = 1$ and the vaporising species are monatomic. A difficulty with this method is that the area a_2 is not easy to evaluate. For metals and alloys the roughness factor (true area divided by geometric area) is about two; for other substances it can be several hundreds, and its true value ought to be determined, as outlined in Section 6(*a*).

Beam-type microbalances have been used to study the vaporisation of metals and refractory substances up to 2000°C., and the reproducibility of the results can be judged from the following typical data for platinum. Using the second law approach adumbrated in the previous section, Dreger and Margrave[51b] found the slope of the ln p versus $1/T$ plot, together with tabulated heat capacity data to yield $\Delta H^\circ_{298} = 135 \pm 2$ kcal. mole^{-1}, the vapour pressure having been determined at eleven temperatures from 1638° to 1786°K. Using the third law [equation (11)], the same workers found $\Delta H^\circ_{298} = 135{\cdot}2 \pm 0{\cdot}85$ kcal. mole^{-1}. An independent determination[20] carried out using a similar microbalance gave $\Delta H^\circ_{298} = 134{\cdot}9 \pm 1{\cdot}0$ kcal. mole^{-1}. From these two "third law" values of ΔH°_{298}, the normal boiling point of platinum is estimated to be 4100 ± 100°K.

(*iii*) *The torsion–effusion or torque–Knudsen method.* We have already cited [equation (2)] the relationship between the vapour pressure within a cell which has two effusion holes arranged as in Fig. 2(*b*) and the angle of twist of the fibre on which the cell is suspended in vacuum. Equation (3) shows that the vapour pressure determined this way does not require a knowledge of the molecular complexity of the vaporising species, a point that was emphasised when the technique was first used[27] to measure the vaporisation of benzophenone, Hg and K at temperatures up to 200°C. The technique has been used, up to 1900°C., to measure the enthalpy of vaporisation of several elements[34,52] and compounds,[44,45,53] and, in association with the results from the Knudsen and Langmuir methods, to

[51] (*a*) Ke-Chin Wang, L. H. Dreger, V. V. Dadape, and J. L. Margrave, *J. Amer. Ceram. Soc.*, 1960, **43**, 509; (*b*) L. H. Dreger and J. L. Margrave, *J. Phys. Chem.*, 1960, **64**, 1323; (*c*) R. C. Paule and J. L. Margrave, *J. Phys. Chem.*, 1963, **67**, 1896.

[52] (*a*) K. Niwa and Z. Sibata, *J. Chem. Soc. Japan*, 1940, **61**, 667; (*b*) R. F. Barrow, P. G. Dodsworth, A. R. Downie, E. A. N. S. Jeffries, A. C. P. Pugh, F. J. Smith, and J. M. Swinstead, *Trans. Faraday Soc.*, 1955, **51**, 1354; (*c*) A. N. Nesmeyanov, "Vapour Pressure of the Chemical Elements", Elsevier, Amsterdam, 1963, p. 47.

[53] R. F. Barrow, E. A. N. S. Jeffries, and J. M. Swinstead *Trans. Faraday Soc.*, 1955, **51**, 1650; 1657.

determine the atomicities of Se and other elements in the vapour phase. It has recently been employed for the investigation of the vapour pressure of liquid alloys (such as Ag–Bi) and solid alloys (such as Ag–Mg).[54]

Wessel[55] and Bradley and Cleasby[28] ingeniously arranged for both the Knudsen effusion and the torsion–effusion methods to be employed simultaneously. A torsion effusion cell was suspended on a fibre from one end of a beam balance, so that both mass loss due to ordinary Knudsen effusion and the angle of twist arising from torsion–effusion could be measured. The operative equation for such an arrangement incorporates equation (13) into one of the form $p = k\,\theta$ (see Section 4(b)):

$$M = -(\mathrm{d}w/\mathrm{d}t)^2\, 2\pi RT/a_1{}^2(k\theta)^2 \tag{15}$$

Bradley *et al.*[28,56] used equation (15) to determine the molecular weight of the species produced during the vaporisation of a range of organic compounds. As an illustration the molecular weight of oxamide was determined to be 87·1 (actual value 88·05), proving that no decomposition or polymerisation occurs in the sublimate.

(b) A Summary of the Information Derivable from Vapour Pressure Measurements.

Quite apart from the fact that enthalpies and entropies of vaporisation are required for the compilation of trustworthy thermodynamic data for elements and compounds, much valuable information can be extracted from the direct use of the functions themselves.*

(*i*) *Bond energies.* The mean dissociation energy of the metal–carbon bonds in an organo-metallic compound MR_4, containing the quatervalent metal M and a monovalent organic radical R, is given by:

$$D(\mathrm{M{-}C}) = \tfrac{1}{4}\{4\Delta H_f^\circ(\mathrm{R},g) + \Delta H_f^\circ(\mathrm{M},g) - \Delta H_f^\circ(\mathrm{MR_4},g)\} \tag{16}$$

where $\Delta H_f^\circ\ (\ ,g)$ is the symbol representing the standard enthalpy of formation, from the elements, of the compound within the brackets. This equation includes the standard enthalpy of formation of the organo-metallic compound, MR_4, in the gaseous state. Calorimetry yields data which are applicable to that state of the compound which is stable at 25°C.; this is usually solid or liquid. The desirability of having reliable data on the enthalpy of vaporisation of the organo-metallic compound (and of the metals) is, therefore, evident.

The enthalpy of vaporisation of the dihalides of iron, determined by

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* An excellent example of the importance of precise measurement of calorimetric entropy is to be found in recent work concerning the entropies of the gaseous dihalides of Be, Mg and Zn. The discrepancies between the spectroscopic and calorimetric entropies of these compounds has now been tracked down to an error in the vibrational partition function.[57]

[54] J. N. Pratt and A. T. Aldred, *J. Sci. Instr.*, 1959, **36**, 465.

[55] G. Wessel, *Z. Physik.*, 1951, **130**, 539.

[56] R. S. Bradley and S. Cotson, *J.*, 1953, 1684.

[57] D. L. Hildenbrand, *J. Chem. Phys.*, 1964, **40**, 3438.

Sime and Gregory[58] using the torsion–effusion method, enabled the mean dissociation energies of the Fe–X bonds to be evaluated:

$$D(\text{Fe–X}) = \tfrac{1}{2}\{2\Delta H_f^\circ(\text{X},g) + \Delta H_f^\circ(\text{Fe},g) - \Delta H_f^\circ(\text{FeX}_2,g)\} \qquad (17)$$

It is interesting to note that, in principle, all the quantities on the right hand side of the last equation can be obtained from Knudsen effusion measurements. [Wise[59] determined the enthalpy of dissociation of F_2—hence $\Delta H_f^\circ(\text{F},g)$—by measuring the rate of effusion of the gas at different temperatures and thereby determining the degree of dissociation at each temperature: use of the van't Hoff isochore thence yielded the required enthalpy].

A far-reaching consequence of the availability of enthalpies of vaporisation is the demonstration, by Eley,[60] that the bond formed by the chemisorption of H_2 on metals is predominantly covalent. Eley arrived at a value of D(M–M), the strength of a metal–metal bond required for his calculation of the strength of the chemisorbed link, by writing, for face-centred cubic metals (which have twelve-fold co-ordination):

$$D(\text{M–M}) = \Delta H^\circ/6 \qquad (18)$$

(*ii*) *Lattice energies*. When the vapour pressure is low, the vapour behaves essentially as an ideal gas, and so the enthalpy of vaporisation of a solid may be equated to the lattice energy. The lattice energies of a large number of paraffins, hydrogen-bonded crystals, and aromatic ring compounds with or without functional groups have been tetermined by vacuum microgravimetry. Davies *et al.*[61a] have also determined the lattice energies of numerous hydrogen-bonded solids by precise weighing (but not involving vacuum microbalances).

The magnitude of the lattice energies of crystals of carboxylic acids, amides, etc. is determined[28] by contributions from electrostatic interaction energy, energy of repulsion and quantum-mechanical dispersion energy. But part of the lattice energy may be assigned to hydrogen-bonding between nearest neighbours. The following values of the hydrogen-bond energy, in kcal. mole^{-1}, in crystals of the specified compounds have been computed by Davies and Kybett[61b] from systematic measurements of the enthalpies of vaporisation:

straight-chain monohydric alcohols	6·8 ± 0·6
straight-chain even-carbon monocarboxylic acids	8·9 ± 0·4

Bradley and Cotson[56] found that the difference in lattice energy between the α-form of anhydrous oxalic acid, which crystallises in molecular sheets, and the β-form, which has a chain-like arrangement of the molecules, was small. But the difference in entropy of vaporisation was rather

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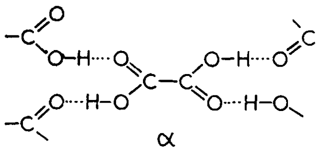
[58] R. J. Sime and N. W. Gregory, *J. Phys. Chem.*, 1960, **64,** 86.

[59] H. Wise, *J. Phys. Chem.*, 1954, **58,** 389.

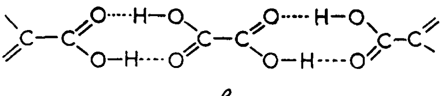
[60] D. D. Eley, *Discuss. Faraday Soc.*, 1950, **8,** 34.

[61] (*a*) M. Davies and J. I. Jones, *Trans. Faraday Soc.*, 1954, **50,** 1042; (*b*) M. Davies and B. Kybett, *Nature*, 1963, **200,** 776.

larger than might be expected from the packing in the two forms, and may be associated with the restricted rotation about the C–C axis of the eight-membered ring in the β-form, which has the higher entropy (lower entropy of vaporisation), whereas in the α-form this rotation is suppressed.



α



β

Little or no work appears to have been done, using vacuum microbalances, to determine the vapour pressure of essentially ionic solids: knowledge of the lattice energy of such solids aids quantitative intrepretation of absorption spectra and point-defect concentrations.[62]

(*iii*) *Phase diagram investigation and thermodynamic activities of alloys.* The torsion–effusion method offers a ready means of determining the vapour pressure of one component of an alloy system as a function both of temperature[54] and composition.[63,64] The composition is determined by using the equation:

$$\mathrm{R} = \mathrm{R}_0 - (M_2\,\Delta w/M_1 w_2) \tag{19}$$

where R_0 and R are the atom ratios of volatile to non-volatile component initially and at any particular stage when the total weight loss is Δw; M_1 and M_2 are the atomic weights of the volatile and non-volatile components, respectively, and w_2 is the weight of the non-valotile component in the effusion cell. This approach is being used to supplement (in some instances to supplant) the traditional methods, based on *X*-ray diffraction and metallography, of phase-diagram investigation.

Blackburn,[63] who was the first to use microbalances for this purpose, explored the oxygen dissociation pressures over uranium oxides an established that there are three stable oxides: UO_2, U_4O_9 and U_5O_{13}. Many alloy systems have been investigated by means of this technique.[64,65]

Progress is being made,[64] using microbalances, in the study of alloys from the standpoint of classical thermodynamics of non-electrolyte solutions. In an alloy AB, the component A alone being volatile, the thermodynamic activity a_{A} of component A, taking pure A as the standard state, is given by:

$$a_{\mathrm{A}} = p_{\mathrm{A}}/p^{\circ}{}_{\mathrm{A}} \tag{20}$$

where $p^{\circ}{}_{\mathrm{A}}$ is the pressure of pure A and p_{A} that of component A for a

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[62] P. Gray, *Quart. Rev.*, 1963, **17**, 441.

[63] P. E. Blackburn, *J. Phys. Chem.*, 1958, **62**, 897.

[64] (*a*) E. Veleckis, C. L. Rosen, and H. M. Feder, *J. Phys. Chem.*, 1961, **65**, 2127; 1962, 66, 362; (*b*) K. M. Myles and A. T. Aldred, *J. Phys. Chem.*, 1964, **68**, 64.

[65] K. M. Myles, *Acta Metallurgica*, 1965, **13**, 109.

particular alloy composition. The activity a_B of the non-volatile component can be computed[66] using the Gibbs–Duhem equation:

$$N_A \, d \ln a_A + N_B \, d \ln a_B = 0 \tag{21}$$

where N_A and N_B are the respective atomic fractions of the components. Pratt and Aldred,[54] upon computing the activities of bismuth in Ag–Bi alloys, found the systems to behave non-ideally (activities not synonymous with corresponding atomic fractions); and Myles and Aldred[64b] have shown that, in V–Fe alloys, iron exhibits fairly large negative deviations from Raoult's Law throughout the entire compositional range.

(*iv*) *Coefficients of condensation.* It has already been implied that the vapour pressure measured using the methods outlined above may differ from the true equilibrium value unless the coefficient of condensation α is unity. Values of α may be obtained either directly [Section 8(b)] or by taking the ratio of the pressures from Langmuir and Knudsen effusion experiments when every precaution has been taken (*e.g.* operating with a large ratio of sample area to orifice area) to ensure that the effusion method yields equilibrium pressures. It is possible[46,67] to draw conclusions about the mechanisms of the vaporisation and condensation process from the magnitude of α; and a plausible theory of the evaporation of metal crystals, involving the migration of surface species to and from monatomic ledges and the regions of emergence of dislocations, has been formulated.[67b] However, in view of some of the discrepancies reported by independent investigators[29,68] on identical systems, it seems that theory tends to be ahead of experiment in this particular branch. Many systems, notably the evaporation of droplets of certain esters and hydrocarbons are, on the other hand, well understood.[69]

6. Applications in Surface Chemistry

Irrespective of whether one is following the course of chemisorption of a gas on a solid surface in the sub-monolayer region, or the progress of physical adsorption in the multilayer region, or the embryonic stages of the oxidation of metals and alloys, there is much to commend the gravimetric over the manometric method of study. When the surface area of the solid in question is small (say a few hundred cm.^{2}) the advantages are overwhelming because, unlike the manometric method, which becomes progressively more insensitive as the total pressure of adsorbate or oxidant increases, the gravimetric method is potentially capable of being just as sensitive at 1 atm. pressure as at 10^{-10} torr. Moreover, when the dead-

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[66] L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals", McGraw-Hill Book Co. Inc., New York, 1953.

[67] (*a*) O. Knacke and I. N. Stranski, *Progr. Metal Phys.*, 1956, **6**, 181; (*b*) J. P. Hirth and G. M. Pound, "Condensation and Evaporation", Pergamon Press, Oxford, 1963.

[68] R. S. Bradley, *Proc. Roy. Soc.*, 1951, *A*, **205**, 553.

[69] (*a*) R. S. Bradley, M. G. Evans, and R. Whytlaw-Gray, *Proc. Roy. Soc.*, 1946, *A*, **186**, 368; (*b*) R. S. Bradley and J. Binks, *ibid.*, 1949, *A*, **198**, 226, 239.

space volume of the apparatus is large and the surface area of the solid very small (a few cm.^{2}), the manometric method is extremely inaccurate if not impracticable. Bearing in mind that if an area 1 cm.^{2} is covered by a chemisorbed layer of 0_2 molecules the mass increase is about 6×10^{-2} μg, we may appreciate that vacuum microgravimetry is ideally suited for the study of both the thermodynamics and kinetics of adsorption. Many applications of this type have already been cited by Rhodin,[3] Gulbransen[4] and Gregg.[70] The estimation from physical adsorption isotherms of the surface area and pore volume of solids using the B.E.T. and Kelvin equations, along with the determination of the heats and entropies of physical adsorption of gases and vapours using the Clausius–Clapeyron equation, will not be considered here (see refs. 70 and 71).

(a) Study of Chemisorption.—In the last decade it has become increasingly evident that extremely high precision may be attained in the study of the chemisorption of various gases on single crystal, thin film, and polycrystalline adsorbents by using microbalances under ultra-high vacuum conditions. Thus Wolsky and Zdanuk[72] were able to study the cleaning of Ge surface by ion-bombardment, record the sputtering rate as a function of ion energy, follow the subsequent chemisorption of gases on the "clean" surface, all in one microbalance assembly which could be evacuated to 10^{-10} torr. Stockbridge and Warner,[23b] using the resonating quartz microbalance, were able to follow the evolution and re-adsorption of gases during the fracture of quartz in vacua close to 10^{-12} torr. Further significant advances are represented (i) by the work of Bassett and Robertson[30] who studied the efficiency of exchange of translational energy in collision between cold gas molecules and a hot surface under conditions where the time of adsorption was small; (ii) by the study, carried out by Haller and White,[73] of the nucleation of molecular beams on surfaces prepared by evaporation in ultra-high vacuum; and (iii) by the kinetic study,[74] using the ultra-sensitive pivotal type beam balance, of the adsorption of O_2 on Ag, in which activation energies were obtained for the dissociative adsorption, molecular adsorption and surface migration of oxygen.

(b) Distinguishing Adsorption and Absorption.—Although it is, in principle, easy to distinguish between adsorption on the one hand from the various forms of absorption on the other, the distinction may, in practice, present difficulties. When, in gas–solid systems, the specific area of the solid is small, the difficulties are exacerbated, and vacuum microgravimetry constitutes one of the most satisfactory techniques to employ.

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[70] S. J. Gregg, "The Surface Chemistry of Solids", Chapman and Hall, London, 1961.

[71] J. M. Thomas, *Sci. Prog.*, 1962, **50**, 46.

[72] S. P. Wolsky and E. J. Zdanuk, ref. 33, p. 46.

[73] I. Haller and P. White, in "Proceedings of International Symposium on the Condensation and Evaporation of Solids", Dayton, Ohio, 1962.

[74] A. W. Czanderna, *J. Phys. Chem.*, 1964, **68**, 27.

Suppose that a small equilibrium uptake of oxygen by a single crystal of nickel at a fixed temperature had been recorded gravimetrically. If, after cleavage *in situ* the amount taken up by the nickel is increased by about 100%, it can be concluded that adsorption predominates.

It has been demonstrated[12] gravimetrically that, in contrast to the Br_2–graphite system where intercalation leads to the formation of lamellar compounds,[75] the I_2–graphite system involves chemisorption only. When H_2 and U or H_2 and Nb interact, the initial chemisorption is followed by extensive absorption, often with the formation of separate phases. Katz and Gulbransen[76] have studied the thermodynamics of such systems and the general phenomenon of occlusion of gases in transition metals with admirable precision. In their technique, phase-diagrams are constructed by noting amounts of gas uptake—the very reverse of the method pioneered by Blackburn[63] and described in Section 5(*b*) (*iii*).

(c) **Oxidation of Metals and Alloys and the Combustion of Solid Fuels.**— The systematic study of the kinetics of metal and alloy oxidation at high temperatures, and the influence of trace impurities on the pattern of behaviour has been pertinaciously executed over the last two decades by Gulbransen and his associates.[77] Apart from producing a wealth of technically useful data, such studies have added to our understanding of the mechanism of the oxidation process, and it is now possible to appreciate why, in one set of circumstances, the rate of oxidation is linear, and, in another, parabolic.

The microbalance technique is equally applicable to other gas–solid reactions that undergo mass changes, and the oxidation of solid fuels, notably the various forms of carbon and graphite, by a variety of oxidising gases typifies the niceties of the technique. Thorough outgassing of the sample in high vacuum, subsequent oxidation in either static or dynamic conditions at low pressures (to avoid troublesome diffusional effects), and the physical adsorption of an inert gas at low temperature (to yield surface areas and pore volumes), can all be carried out *in situ*.[78]

7. The Study of Decomposition Reactions

Since standard texts[79,*] on thermogravimetric analyses describe a wide range of chemical decompositions that can be followed by weighing, only

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[*] The "Thermal Analysis Reviews", ed. J. P. Redfern, published by the Chemistry Department, Battersea College of Technology in collaboration with Stanton Instruments Ltd., London, constitute excellent surveys of current literature on thermogravimetric analysis.

[75] R. C. Croft, *Quart. Rev.*, 1960, **14**, 1.

[76] O. M. Katz and E. A. Gulbransen, in "Non-Stoichiometric Compounds", ed. L. Mandelcorn, Wiley, New York, 1964, ch. 3.

[77] E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, 1963, **110**, 476 and references therein.

[78] E. A. Gulbransen, K. F. Andrew, and F. A. Brassart, Westinghouse Research Lab. Report, 1963, 63-139-120-P1.

[79] C. Duval, "Inorganic Thermogravimetric Analysis", Elsevier Press, Amsterdam, 1963.

a brief account will be given here of some reactions that are particularly well suited for study by vacuum gravimetry. There are two types of study which merit consideration.

The first of these embraces the decomposition of surface phases that extend to no more than a monolayer (*i.e.* chemisorbed phase) or to a thin film of a distinct phase consisting of several monolayers. Decompositions of such phases are conveniently studied by the analogue of the Langmuir free-evaporation method [Section 5(*a*) (*ii*)]. Both beam-type and helical balances have been used to (i) detect the presence and follow the breakdown of an integument of molybdic oxide on the surface of MoS_2;[80] and (ii) prove that a tenaciously held film of water is not removed from TiO_2 surfaces unless a temperature of 800°C. (at 10^{-6} torr.) is attained, and that point defects, consisting of TiO^{++} ions and quasi-free electrons, begin to be produced according to the reaction:

$$TiO_2(s) \rightleftharpoons TiO^{++}(s) + \tfrac{1}{2}\, O_2(g) + 2e \qquad (22)$$

at about 875°C.[81]

The formation and breakdown of surface oxides on graphite powders during oxidation;[82] the pyrolysis of carbonaceous materials in general;[83] and the photodesorption of chemisorbed phases on non-stoichiometric oxide catalysts[84] have also been elucidated by means of microgravimetry.

The second mode of studying decomposition reactions utilises the effusion cell technique either straightforwardly in the manner of Knudsen, or by employing the principle of torsion–effusion (see Section 5). The ordinary Knudsen method has been extensively used to accumulate thermodynamic data on the decomposition of metal halides, carbonates, hydrates, organic complexes, etc., which conform to the general reaction: A(s) → B(s) and C(g), the solid phases possessing low volatility. Gregory and his collaborators[85] have produced reliable enthalpy and entropy data for a diversity of thermal decompositions, some of which are quite complex reactions owing to the occurrence of simultaneous disproportionation or dimerisation of one of the participants. Thus a successful study has been made[85] of the vaporisation of Fe_2Cl_6 and the concomitant release of Cl_2 from solid $FeCl_3$ between 120° and 150°. Farber and Darnell[86] were able to study the decomposition of $TiCl_3$ (between 220° and 480°C.) according to

$$2\,TiCl_3(s) \rightleftharpoons TiCl_4(g) + TiCl_2(s) \qquad (23)$$

and, simultaneously, measure the vapour pressure of solid $TiCl_3$. However, the decomposition pressures, measured by effusion, in the system[87]

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[80] P. Cannon, *Nature*, 1959, **183**, 1612.

[81] A. W. Czanderna and J. M. Honig, *J. Phys. Chem.*, 1959, **63**, 620.

[82] E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, 1952, **44**, 1039.

[83] P. L. Waters, *Analyt. Chem.*, 1960, **32**, 852.

[84] R. Jongepier and G. C. A. Schuit, *J. Catalysis*, 1964, **3**, 464.

[85] (*a*) J. H. Stern and N. W. Gregory, *J. Phys. Chem.*, 1957, **61**, 1226; (*b*) R. R. Hammer and N. W. Gregory, *ibid.*, 1962, **66**, 1705; 1964, **68**, 314.

[86] M. Farber and A. J. Darnell, *J. Phys. Chem.*, 1955, **59**, 156.

$$Mg(OH)_2(s) \rightleftharpoons Mg\,O\,(s) + H_2O(g) \qquad (24)$$

were found to be seriously in error, a fact which can be ascribed[87,88] [*cf.* Section 5(*a*)] to an abnormally small coefficient of condensation.

In the kinetic study of thermal decompositions, the use of the tortion–effusion technique is advantageous. For example, the decomposition of polytetrafluoroethylene has been found to be first order, the activation energy being *ca.* 76 kcal. mole^{-1} and the molecular weight of the vaporising species 100 ± 6.[89]

8. Combined Study of Two or More Phenomena

Although combined measurements—such as the use of a mass spectrometer in Knudsen effusion experiments—have extended the range of information derivable from vapour pressure determinations, it is in the study of the surface chemistry of solids that combined or concurrent measurements utilising vacuum microbalances have proved most practicable. A selection of the information gained in this way will now be given.

(a) Magnetic Susceptibility Measurements.—In the study of solid catalysts, apart from measuring[90] the mass changes resulting from adsorption and desorption of intermediates formed on the surface, microbalances can be used to record changes in the magnetic susceptibility either of the solid itself or of the adsorbed species. Czanderna[91] has recently constructed a sensitive vacuum microbalance for determining the magnetic susceptibility of adsorbents and catalysts using the Faraday method. Extremely minute changes in susceptibility accompanying the processes of adsorption, desorption, oxidation and reduction of the specimens can be detected, and the apparatus has so far been used to (i) establish the valency of metallic ions buried substitutionally in alumina powders; (ii) study the magnetic properties of reduced cupric oxide; and (iii) measure the diamagnetic anisotropy of single crystals of graphite.

(b) The Study of Thin Films.—Fundamental studies of thin films of metals and alloys require a knowledge of their mass and thickness, optical transmission,[92] ease of deposition, and other properties, most of which can be obtained using vacuum microbalance techniques. The precision of mass measurements will be enhanced once the resonating quartz devices replace the beam-type balances, although the latter have proved remarkably successful in measuring the rates of deposition of thin films. Mayer *et al.*[93] have completed a particularly elegant study of the formation of thin films during the impingement of a beam of Hg atoms on a silica

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[87] E. Kay and N. W. Gregory, *J. Phys. Chem.*, 1958, **62,** 1079.

[88] K. Motzfeldt, *J. Phys. Chem.*, 1955, **59,** 139.

[89] C. L. Rosen and A. J. Melveger, *J. Phys. Chem.*, 1964, **68,** 1079.

[90] C. B. McCarty, *Diss. Abs.*, 1962, **22,** 2323.

[91] A. W. Czanderna, see ref. 8.

[92] A. W. Czanderna and H. Wieder, *J. Chem. Phys.*, 1961, **35,** 2259.

[93] H. Mayer, R. Niedermayer, W. Schroen, D. Stünkel, and H. Gore, ref. 6, pp. 75 and 87.

substrate maintained at low temperatures. At −133°C., the coefficient of condensation [Section 5(b) (iv)] was unity, but at higher temperatures α was no longer constant at any one temperature and was found to be dependent on the mass of deposit previously formed, the time of deposition and the thermal history of the substrate. Although some of the finer details are still obscure, the mechanism of thin film formation, which has long defied explanation, is now reasonably well understood, and the dependence of the rate of nucleation on surface temperature and beam intensity as well as the rôle of surface diffusion and time of adsorption are appreciated.

(c) Micrography and Microgravimetry.—Now that our knowledge of the nature of lattice imperfections has been considerably enlarged,[94] and the availability of single crystals of ultra-pure materials has increased, efforts can be made to investigate what relation, if any, exists between the chemical reactivity and the defective character of a solid. By combining the techniques of optical and electron microscopy on the one hand with microgravimetry on the other, Boggs and his coworkers[95] have established a *prima facie* case for believing that, in the oxidation of metals and alloys, oxide nuclei are formed preferentially at the regions of emergence of dislocations. The precise rôle of dislocations and point defects in thermal decomposition reactions has yet to be clarified. But it appears possible that vacuum microbalances may contribute in a special way to the understanding of the importance of such defects in, *e.g.* the thermal decomposition of carbonates, azides and hydroxides. The precision of microbalances is so great that it enables a very small percentage of decomposition to be detected, thus permitting a micrographic study to be made of the distribution of dislocations and point defects at the onset of decomposition or at the culmination of the induction period preceding decomposition.[96]

9. Future Possibilities

On the basis of previous work and current trends it is possible to enumerate several future uses of vacuum microbalances.

(*i*) *Study of polymorphic changes.* By obtaining the relevant vapour pressure data, Bradley and Cotson[56] showed which of the two anhydrous forms of oxalic acid was stable at room temperature; they also were able to compute the temperature at which the α and β forms were in equilibrium. It should be possible to locate transition temperatures by utilising the fact that a phase-transition is usually accompanied by a density change large enough to cause a readily measurable change in buoyancy when the sample (and "physically stable" counterweight) are suspended in

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[94] S. Amelinckx, "The Direct Observation of Imperfections", Academic Press, London, 1964.

[95] W. E. Boggs, R. H. Kachik, and G. E. Pellissier, *J. Electrochem. Soc.*, 1961, **108**, 6; 1963, **110**, 4.

[96] (*a*) J. M. Thomas and G. D. Renshaw, *Trans. Faraday Soc.*, 1965, **61**, 791; (*b*) G. D. Renshaw and J. M. Thomas, in the press.

a fixed pressure of an inert gas. (This principle has been employed to follow the crystallisation and melting behaviour of various polymers using a microdensity balance.[97])

(*ii*) *Molecular complexity of species in the vapour phase.* Margrave[46] has made the interesting suggestion that it ought to be possible to measure both the pressure and average molecular weight of a species by recording the apparent mass increase caused by the effusion of that species from a Knudsen cell in a direction which contributes to the force recorded by the microbalance. This procedure is quite distinct from the torsion-effusion method and it offers just as many rewards.

(*iii*) *Anisotropy of heats of chemisorption.* The resonating quartz balance and the more refined forms of beam-type microbalances offer the attractive possibility of determining the heats of chemisorption of certain gases on well-defined crystallographic planes of single crystal adsorbents. The quartz balance can be used[23b] directly as a calorimeter to measure the heat liberated; but in order to use the other balances the chemisorptions must be reversible. Such experiments would decide whether, as suspected, the bewildering range of different chemisorption bonds formed in a given system* are attributable solely to crystallographic factors.

(*iv*) *Study of adhesion.* Just as evaporation kinetics—as the reverse of crystal growth—can be studied using torsion-effusion techniques, so also could adhesion—as the reverse of condensation from molecular beams—be studied using either torsion-effusion plates[99] or resonating quartz crystals. In this way the strength of bonding between condensates (*e.g.* thin films) and substrates could be ascertained.

(*v*) *Miscellaneous studies.* Esoteric use of a vacuum microbalance has been made by Öhmann.[100] By utilising the thermo-magnetic properties of gadolinium metal, which has a Curie point close to 20°C., he measured the intensity of electromagnetic radiation using a microbalance. Calculations show[101] that the sensibility of present-day vacuum microbalances is already sufficient for them to be used in the precise measurement of the gravitational constant. And in view of their remarkable sensitivity to temperature gradients at low pressures [Section 4(c) (ii)] they may find use in some specialised aspects of thermometry.

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* For a system as simple as the W + CO one, it has been established[98] by the technique of flash-desorption that there are four distinct states of binding: α at 20, β_1 at 53, β_2 at 75 and β_3 at about 100 kcal. mole^{-1} (heat of adsorption).

[97] F. T. Simon and J. M. Rutherford, *J. Appl. Phys.*, 1964, **35**, 82.

[98] P. A. Redhead, *Trans. Faraday Soc.*, 1961, **57**, 641.

[99] L. M. Fitzgerald, private communication.

[100] Y. Öhmann and B. Rydgreen, ref. 6, p. 193.

[101] J. A. Poulis and C. H. Massen, private communication.