Hydraulic-Leverage Principles for Magnification of Sensitivity of Gas Change in Free and Fixed-Volume Manometry

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BIOCHEMICAL, biophysical, and other users of conventional types of manometers have often wished to measure volumes of gas changes with a sensitivity far greater than the commonly obtained order of a cubic millimeter, without having to resort to extensive changes in apparatus, to microscope cathetometers, or to esoteric instrumentation. Small sensitivity gains up to onefold or so have indeed been attained with conventional manometers by the use of tilted manometer arms, confining fluids of low-weight density (for example, hydrocarbons or oils of $D \sim 0.7$ g/cm^3), small experimental vessels, or, what comes to the same, vessels filled with relatively large volumes of liquid.

This paper shows how, with or without the aforementioned minor devices, additional sensitivity gains of 10- to 100-fold may readily be achieved with little or no change in widely available commercial manometers by appropriate use of hydraulic-leverage principles (amplification by fluid geometry rearrangement) combined with unusual moving-boundary indices. The procedures to be described are remarkably simple in both theory and practice and may be applied to both constant-(fixed) volume manometry and free manometry (volume and pressure variable), including volumetry. The open-arm, fixed-volume manometer made classic and universal by Otto Warburg (*1–5*) is chosen to provide a basis for illustrating the application of the hydraulic-leverage principles involved and to provide an arbitrary standard of reference by which to judge the sensitivity magnification obtained. Applications to a wide range of manometer types will be readily evident, including differential and compensation manometers and Cartesian diver techniques (*6–8*). Finally, several new types of hydraulic manometers are described, including a general-purpose manometer and a one-arm free manometer of unique advantages in which paradoxically an increase in the amount of confined gas results in a decrease in pressure of the gas (*sic!*).

In the Warburg manometer (Fig. 1) a change in amount, x (mm^3) N.T.P., of a given gas in the reaction vessel is equal to hk, where h (mm) is the resulting, experimentally observed, vertical displacement of the meniscus of the fluid in the manometer arm open to the atmosphere when the meniscus of the confining fluid in the closed arm is maintained at a fixed level (by means of the adjustable screw and fluid-filled sac at the base of the manometer), and k (mm^2) is the standard vessel constant parameter $[(v_G \cdot 273/T) + v_F\alpha]/P_o$, v_G (mm^3) being the volume of gas space in the vessel to the level of the confining fluid in the closed arm, v_F the volume of liquid in the vessel itself, α the Bunsen absorption coefficient of the given gas in the liquid in the vessel, T the average absolute temperature of the confined gas, and P_o the pressure of 1 atm expressed in millimeters of confining fluid (for example, 10,000 mm Brodie's fluid of weight density $D = 1.034$ g/cm^3, equivalent to 760 mm-Hg of weight density $D = 13.60$ g/cm^3).

In the standard arrangement for operating the Warburg manometer, h (mm) of confining fluid is a measure of the change in pressure Δp induced by a change of x (mm^3) gas kept at constant volume and other conditions implied in the formula just given for k. In the hydraulic-leverage arrangement described here, for given values of x and k, h is further magnified to a larger value H, with a corresponding and reciprocally decreased smaller value of K, such that $x = hk = HK$. The theoretical sensitivity magnification may then be defined as $M = H/h = k/K$, so that $H = hM$ and $K = k/M$. M thus defined is, for constant-volume manometry, independent of the attributes and events of the manometer vessel (v_G, v_F, α, T, P_o, x) and depends in principle only upon the leverage events and arrangements in the manometer measuring arms (*9*). In this last connection it is important to observe that the upper end of the open manometer arm of virtually all present-day commercial Warburg manometers consists of, or may be readily made to hold, a wide and even-bore *reservoir* 30 to 40 mm long, whose area A (30 to 50 mm^2) is some 10 to 100 times the area a (0.5 to 3 mm^2) of the narrow, even-bore capillary with which it is contiguous below (corresponding ratio of radii, $R/r \cong 3$ to 10).

Sensitivity magnification with constant-volume manometry. To set up the desired hydraulic-leverage arrangement, two operations, each requiring a few seconds, must be carried out: (i) the upper level of the manometer fluid in the open arm is raised from its normal position in the capillary into the even-bore section of the reservoir and maintained there throughout the experiment; and (ii) a bubble of room air (or bubble of any suitable and convenient gas or immiscible liquid) of length slightly greater than the diameter of the arm capillary, is inserted into the fluid in this capillary by means of a long and narrow needle attached to a syringe or medicine dropper bulb (Fig. 2). Short of gross mishandling, the static position of the bubble in the capillary fluid is indefinitely stable in accordance with the IXth Hydrostatical Paradox of Robert Boyle. Such a bubble moves freely and reversibly in response to changes in Δp or to turning of the adjustable screw pressing on the sac at the base of the manometer. The movement of the bubble is an accurate measure of both the volume and distance displacements of the confining fluid in the capillary.

Any change in height h $(=\Delta p)$ of the air-fluid interface meniscus in the reservoir taking place as a result of change x of gas in the experimental vessel held at constant volume and temperature will be magnified A/a times in the movement H of the bubble-fluid interface in the capillary below, for the *volumes* of fluid displaced in the capillary and in the reservoir must obviously be identical. Hence $M = A/a$; $h(=\Delta p) = Ha/A$; $H = \Delta pA/a = hA/a = hM$; and $K = ka/A = k/M$.

To calculate x by the proposed reservoir-bubble leverage arrangement, one merely multiplies the observed displacement H by K, that is, $x(=hk) = Hka/A = HK$. Although a and A may be determined separately by mercury calibration in the usual manner, only the ratio a/A need actually be known for the purpose indicated. The ratio a/A may be ascertained most directly, and in the course of only a few seconds, by measuring the ratio of height change in the bubble level in the capillary compared with that of the air-fluid level in the reservoir when both levels are altered simultaneously by turning the adjustable screw, preferably over as wide a range as possible, or by particular parts if need be. Such a determination of a/A can obviously be carried out completely independently of any attributes of, or events occurring in, the other manometer arm or the reaction vessel—even during an experiment if need be—and indeed may be determined in the complete absence of the other arm and vessel if one employs the original Barcroft-Haldane form of Warburg manometer constructed with separable arms (Fig. 3) (*10–12*).

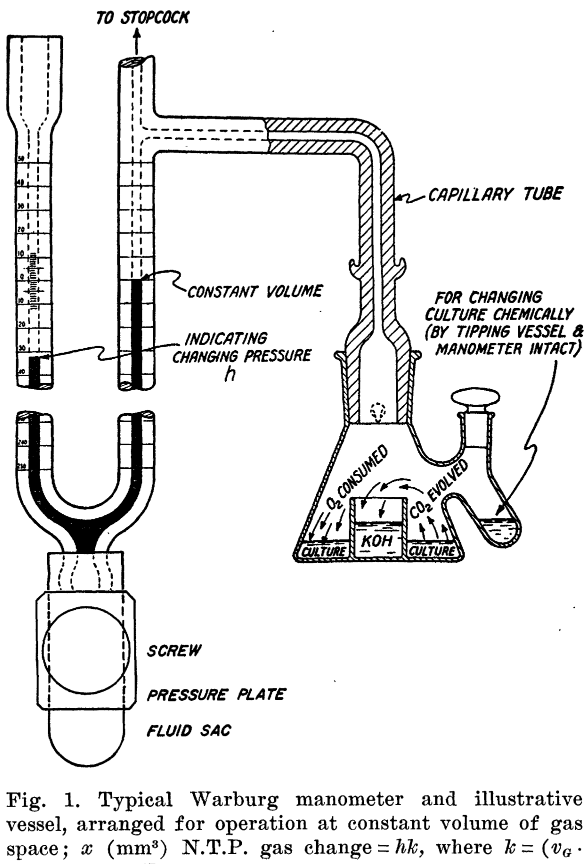

Fig. 1. Typical Warburg manometer and illustrative vessel, arranged for operation at constant volume of gas space; x (mm^3) N.T.P. gas change $= hk$, where $k = (v_G \cdot 273/T + v_F\alpha)/P_o$.

The increased sensitivity of the reservoir-bubble leverage arrangement calls for adequate thermobarometric control in order to achieve full theoretical sensitivity magnification in practice, with minimization of "noise." Especially with extreme values of magnification M it may be desirable, just as in conventional manometry, to connect the open ends of the manometer arms of the thermobarometer and all experimental vessels via a manifold with pressure tubing or plastic connections to a single 1- or 2-lit flask filled with water-vapor saturated air and immersed in the thermostat bath in order to eliminate sudden large or variable atmospheric pressure changes that may occur in some laboratories. In any event the thermobarometer H correction must, at least where large, first be multiplied by its relative a/A value with respect to the a/A value of each experimental vessel, for H values obtained by the reservoir-bubble arrangement are not equal to, but only proportional to, h and Δp values, the proportionality constant being A/a. For this reason, when manometers on hand are significantly variable with respect to their a/A values, it is desirable to choose for a thermobarometer a manometer whose a/A value is mean or modal.

Although there is no theoretical limit to M short of infinity, the chief practical limitation is set by the closeness with which the meniscus of the inner-arm confining fluid can be brought each time to the same constant-volume level. For conventional level setting by hand and eye (with or without hand lens), the effective limit of M is reached at values of ~ 15 to 30, depending upon the manometric fluid employed, cleanliness of the arm's inner glass wall, setting speed required, replication of settings permissible, and so forth. To obtain practicable M values above this limit, it is necessary to set the closed-arm confining-fluid level with the aid of optical, electric, or other devices. One such device is the adjustable screw at the base of the manometer, which can be used as an approximating vernier; the angular turn of the screw may be calibrated, with a suitable scale, against the fluid movement in the outer arm, and then be employed to compensate for the latter movement, by a series of approximations if necessary.

It may well be that M values somewhat less than those provided by the a/A values of manometers on hand will be desired, especially where a is very small ($r = 0.4$ to 0.2 mm for $R = 3$ to 5 mm). Such intermediate magnification, or in effect "demagnification," can be attained and regulated at will by the use of glass rods of known cross section appropriately suspended into the fluid in the open-arm reservoirs, with consequent decrease in effective A values and, hence, a/A values. Capillarity considerations here, as throughout this paper, offer no problem, since only changes in capillarity dependent on x would be involved and these are, or should be, zero.

Sensitivity magnification and demagnification can also be regulated conveniently by appropriate use of a second manometer fluid of density d, smaller than the density D of the main manometer fluid. The lighter fluid, immiscible with the denser and preferably nonvolatile, nontoxic, and odorless, is floated on top of the denser fluid in the capillary of the open arm up into the even-bore section of the reservoir. The change in height H' of the boundary between the two fluids is now observed instead of H of the bubble employed before. In this two-fluid method, Δp, for given values of x and k, is no longer equal to the change in height of the fluid in the reservoir but is given by $\Delta p = H'D - H'd + H'(a/A)d = H'[D - d(1 - a/A)]$. From this, and the fact that correspondingly in the one-fluid method $\Delta p = hD$, it can readily be shown that for $x = hk = HK = H'K'$, $K' = k[D - d(1 - a/A)]/D$, and $M = k/K' = D/[D - d(1 - a/A)]$.

Thus M increases, not only as a/A decreases, but also as $(D - d)$ decreases. In the limit of $d = D$, $K' = K = ka/A$, as with the bubble method before, so that, whether one employs the bubble method with one fluid or the boundary method with two different fluids of equal density, the theoretical result of complete dominance of sensitivity magnification by a/A remains the same. In the limit of $d = 0$, $M = 1$, which must be true since there is then no liquid in the reservoir. In the limit of $a = A$, $M = 1$ also, and there is likewise no sensitivity magnification, because the diameters of the capillary and the reservoir are the same, and a difference between a and A is a *sine qua non* for sensitivity magnification of $M > 1$, regardless of any relationship D/d.

Finally, in the limit of a/A approaching zero (attained by either decreasing a or increasing A indefinitely), M approaches $D/(D - d)$. This is important because it indicates that with even reasonably small values of a/A (0.05, 0.02, 0.01), sensitivity magnification can also be regulated in a quite practical way, over a very wide range, virtually by density difference alone. Thus, if $d = 0.99D$ (which is easy to arrange, experience shows), then $M \cong 100$; if $d = 0.9D$ (as with Brodie solution-isocaproic acid combination), then $M \cong 10$; and if $d = 0.66D$ (as with Brodie solution-hydrocarbon combination), then $M \cong 3$, the exact M values being determinable in any event by the empirical method indicated earlier for the bubble method.

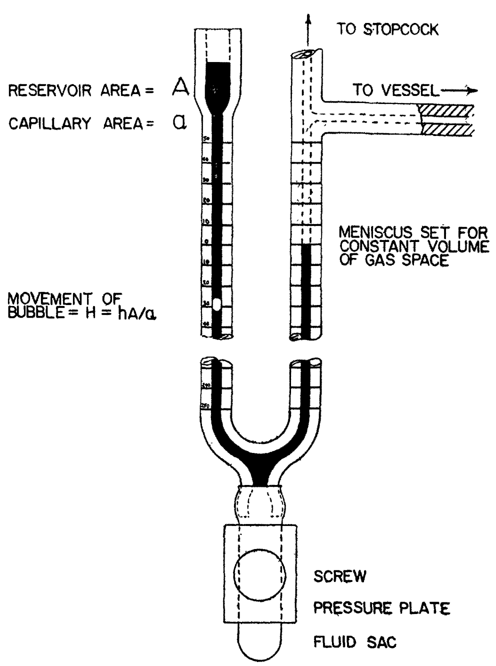

Fig. 2. Warburg manometer arms with reservoir-bubble arrangement for hydraulic magnification of sensitivity at constant volume of gas space: x N.T.P. gas change $= hk = Hk \cdot a/A = HK$, where $K = ka/A$, and the sensitivity magnification $M = H/h = A/a = k/K$.

Sensitivity in conventional free manometry (equal capillary areas, no reservoir bubble). In conventional free manometry with the Warburg-type manometer, the confining fluid in the closed arm is not maintained at a constant level but is allowed to move freely against constant external pressure, atmospheric or otherwise. The volumes of manometric fluid displaced in the capillary sections of the open and the closed arms are exactly equal. The respective distances of fluid displacement are also equal if the areas a and a^* of the open- and closed-arm capillaries are also equal, as they usually are, to a close approximation (otherwise the respective heights would obviously be in inverse ratio as the areas). The adjustable screw below the capillaries is left untouched throughout the experiment, often in its most extended position, where it then exerts no pressure on the sac containing the reserve supply of confining fluid.

A change of x (mm^3) N.T.P. gas in the vessel causes not only a change of gas pressure Δp^* but also a change of volume of confined gas space ah^*, where h^* (mm) is the displacement of confining fluid in either of the equal-arm capillaries. Owing to the gas-space volume change in free manometry, Δp^* is never as great as, and often much less than, Δp in constant-volume manometry, for given values of x and k. When the fluid movement is confined, conventionally, to the (equal) capillary sections of the manometer arms, $\Delta p^* = 2h^*$. The corresponding conventional free manometry "vessel constant," k^*, may readily be shown [following partly Warburg (*1*, pp. 9–12) and Dixon (*3*, pp. 26–32) but necessarily deviating therefrom when Δp^* of free rather than ΔP of differential compensation manometry is involved (*13*)] to be $k^* = x/h^* = 2k + (a \cdot 273/T')[(P + 2h^*)/P_o]$, where T' is the absolute (room) temperature and P the initial pressure of dry gas confined in the closed-arm capillary just above the manometric fluid level; P is as a rule so nearly equal to P_o and the term $2h^*$ so small compared with P and P_o that the expression in brackets may be neglected with usually much less than 1-percent change in the calculated value of k^*, so that the vessel constant normally employed reduces to simply $k^* \cong 2k + (a \cdot 273/T')$.

Since k^* thus always exceeds $2k$ (by the quantity $a \cdot 273/T'$) and $hk = h^*k^*$, $2h^*$ is thus always less than h, and $\Delta p = 2h^*$ is always less than $\Delta p = h$. This means that in conventional free manometry (that is, without adjuvant use of the reservoir-bubble arrangement) there is usually a considerable loss or demagnification of sensitivity as compared with constant-volume manometry carried out under otherwise identical conditions, the more so when a is made large compared with k; a and k are commonly of the order of 1 mm² each, so that frequently $k^* \cong 3k$ and therefore $h^*/h \cong 1/3$, and then if one reads one manometer arm capillary only, the sensitivity in conventional free manometry, as judged by the observed fluid displacement per change in amount of gas, h/x, will be $\sim 1/3$ as great as in conventional constant-volume manometry, for given values of x and k, and if one reads both arms, 2/3 as great. Frequently employed values of a and k different from 1 mm² could obviously readily make the respective values 1/3 and 2/3 either much smaller or somewhat greater but obviously never greater than 1/2 and 1 as respective maximum limits. To obtain these limits of maximum sensitivity, a must be made very small compared with k, so that $k^* \cong 2k$, and $\Delta p^* \cong \Delta p$, and therefore $2h^* \cong h$. Since values of a as small as 0.05 mm² (capillary diameter $\sim$ 0.25 mm) are feasible of construction and workable in laboratory practice, k^* can thus be made to equal $2k$ within a few percent, and similarly $2h^* \cong h$.

The usually considerable decrease in sensitivity in conventional free manometry, which has always been qualitatively evident to the bench experimentalist even without the algebraic working out of the simple vessel constant k^* given in the preceding paragraphs, is the chief reason why free manometry has so seldom been employed and indeed rarely been taken cognizance of without unnecessarily complicated formulation (*14, 15*). Nevertheless, free manometry possesses several very definite advantages not possessed by constant-volume manometry that would be highly desirable to retain if possible. Frequent resetting of the closed arm fluid to constant level—with attendant error, uncertainty, inconvenience, and time requirement—is no longer required in free manometry, and a given experimental observation requires a single reading taken on one arm only. Free manometry thus lends itself much better to automatic and continuous recording [long a desired but seldom attained object in constant-volume manometry (*16*)] and also to following time courses of rapid reactions (*17, 18*) without the disturbance of leveling adjustments. It is worth while, therefore, to examine whether simple hydraulic-leverage arrangements may be devised for free manometry that will overcome the disadvantage of usual lowered sensitivity and yet retain the other marked advantages.

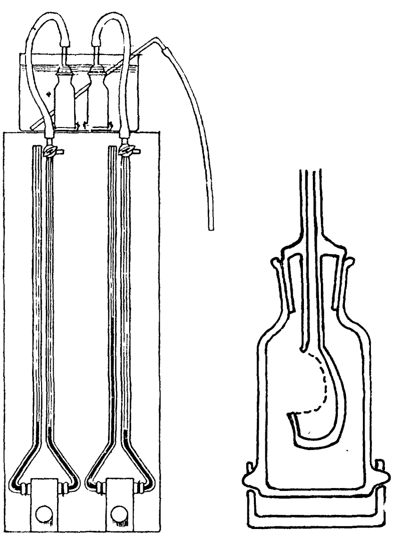

Fig. 3. The historic (1902) Barcroft-Haldane manometer and vessel type (*10*).

Free manometry with equal capillaries and open-arm reservoir. If to conventional free manometry with equal capillaries is added the open-arm reservoir-bubble arrangement described earlier in connection with constant-volume manometry, then the fluid-volume displacements are equal not only in the capillary sections of each arm but also in the reservoir, whereas the fluid-distance displacements will vary inversely with the area a of the capillaries and the area A of the reservoir. For given values of a, x, and k the fluid-distance displacements in the capillary sections will be greater than those obtained in conventional free manometry without the employment of the reservoir, by, as shown here, a maximum limit of twofold, and therefore likewise (as indicated in the preceding section) twofold the sensitivity obtained in conventional constant-volume manometry. The mathematical formulation with the open-arm reservoir arrangement is similar to that given in the preceding section for the case without the reservoir, with substitution of H^*, K^*, and A for h^*, k^*, and a (H^*, like h^*, referring to the equal fluid-distance displacements obtained in either the closed- or the open-arm capillary, being observed in the latter instance by means of the bubble movement). The pressure change ΔP^* no longer equals $2h^*$ but now equals $H^*(1 + a/A)$, whence $K^* = x/H^* = k(1 + a/A) + (a \cdot 273/T')\{[P + H^*(1 + a/A)]/P_o\} \cong k(1 + a/A) + a \cdot 273/T'$. When a/A is very small, $K^* \cong k + a \cdot 273/T'$, and, when a itself is very small compared with k, then $K^* \cong k$. This means that in free manometry with adjuvant use of the open-arm reservoir-bubble system the sensitivity, as judged by total fluid displacement per x change in amount of gas, can be made to approach as a maximum limit *twice* that obtained in constant-volume manometry ($K^* \cong k$, $K^*H^* = kh$, $2H^* = 2h$), if one reads both arms (bubble displacement in the open arm and gas-fluid interface displacement in the closed arm), just as one reads two arms in constant volume manometry. On the other hand, reading the closed arm only, the sensitivity of free manometry with the reservoir approaches as a maximum limit the sensitivity of the constant-volume manometer ($H^* \cong h$). Experience shows that both of these manometric procedures (use of open-arm reservoir, with or without bubble) represent very practical types of free manometry that can satisfactorily replace conventional constant-volume manometry without any constructional change in widely available manometers, without disadvantage with respect to order of sensitivity (in fact with some real gain if the open-arm bubble is also observed), and with retention of the afore-mentioned advantages of free manometry over constant-volume manometry!

The open-arm reservoir-bubble procedure with equal capillary free manometry still fails, however, to produce the great gains in sensitivity magnification M that have been shown to be possible when applied to constant-volume manometry. To accomplish this, several hydraulic-leverage arrangements are proposed, all of which require small modifications in the standard Warburg manometer. The modifications may, as one chooses, be temporary or permanent, and laboratory- or commercially-made. The sensitivity magnification obtained will be intermediate (up to one order) or high (beyond one order) depending upon whether, respectively, different-sized capillaries or two reservoirs are employed. The last-named device is considered first since equal capillaries are still involved.

High-sensitivity magnification in free manometry with equal capillaries and two (equal) reservoirs. The general condition of Boyle, $PV =$ a constant, must be satisfied for any given value of x at constant temperature. To obtain maximum sensitivity magnification in constant-volume manometry, one must maximize ΔP by minimizing the change in gas volume so that $\Delta V \sim 0$. To obtain maximum sensitivity magnification in free manometry, it is conversely necessary to maximize the volume change by minimizing the pressure change so far as possible. This can be most effectively accomplished by constructing, as in the Braun-Fritzsching duplex manometer (*19*), a second reservoir at the top of the closed arm of area and height the same as that of the reservoir at the top of the open arm. The greatly increased area A of the added closed-arm reservoir, compared to the area a of the capillary contiguous below, will then operate in such a manner that a given change in amount of gas x will induce equal displacement of volumes of manometric fluid in the reservoirs and in the capillaries of both arms; but the total pressure change indicated by the algebraic sum of the fluid-distance displacements in the two reservoirs will be very small, even though not reducible to zero. At the same time the fluid-distance displacements in the capillaries, which may be readily followed and measured in either or both capillaries by means of inserted air bubbles, will be relatively large but will involve of themselves no net change in pressure since the heights and amounts of fluid in the capillaries will remain unchanged, even though the bubbles are moved. The fluid-distance displacements in the capillaries and in the reservoirs will vary inversely with their respective areas a and A, for given values of x and k.

To obtain greatest minimization of pressure change clearly requires the employment of both reservoirs, since if use is made of only one, a considerable and undesirable change in total height of fluid will occur in the other arm and, hence, a considerable change in pressure of the confined gas per change in x. Reservoirs in free manometry may be regarded as devices to reduce or minimize the positive magnitude of $\Delta P/x$ and, for maximum effect, must obviously be present and active on not just one but both arms. In constant-volume manometry the use of a closed-arm reservoir is superfluous and cannot provide any gain in sensitivity magnification M, since upon continued resetting of the bubble to a constant mark no pertinent change in the closed arm is ever developed (*19*).

The change in gas pressure ΔP^{**} induced by a change x, with the two-reservoir arrangement, may be measured and expressed in terms of the two observed equal-capillary fluid-distance displacements H^{**} and the two different areas a and A involved: $\Delta P^{**} = H^{**}a/A + H^{**}a/A = 2H^{**}a/A$. Then, similarly as before, $K^{**} = x/H^{**} = 2ka/A + (a \cdot 273/T')[(P + 2H^{**}a/A)/P_o] \cong (2ka/A) + (a \cdot 273/T')$, and if a/A is made very small then $K^{**} \cong a \cdot 273/T'$, and when a itself is made very small, K^{**} approaches zero and the theoretical sensitivity magnification, $M = k/K^{**} = H^{**}/h$, approaches infinity! In practice, however, capillaries of diameter less than 0.25 mm, corresponding to area values of a less than 0.05 mm^2, are too difficult or (in accordance with Bernoulli's theorem) too slow to work with (*20, 21*), so that sensitivity magnification values reach a practical limit in equal-reservoir, equal-capillary free manometry of $M = k/(0.05) \cong 20$ per each manometer arm (40 per both together), for normal k values of the order of unity, and greater or less than 20 (or 40) when k is greater or less than unity—that is, greater when v_G/v_F is increased and less when α, P_o, and T are increased. In any event practical, high M-values are readily attainable in suitable two-reservoir free manometry that equal or even surpass those earlier indicated as obtainable in practice in constant-volume manometry, namely, 15 to 30. Such magnifications will frequently be far more than desired and more than adequate to uphold the maxim of science that to increase sensitivity by an order of magnitude ($\sim$10-fold) is to open new worlds for study.

Experience and calculation show that, for maximum practical effect in any type of hydraulic-leverage magnification arrangement applicable to ordinary commercially available manometers, the arm reservoir area A need seldom be greater than the areas obtainable with diameters of 6 to 10 mm ($A = 30$ to 75 mm^2) unless a is exceptionally large ($>$ 3 mm^2; diameter $>$ 2 mm). With small values of a (which are preferable in order to obtain small values of a/A), the heights of the even-bore sections of the reservoirs need be only a few millimeters, and the total volume of the reservoirs less than 1 cm^3. Calculations based on the equations for K^{**} given in the preceding paragraph will also show that capillaries of area a 1 mm² and greater will seldom yield high magnification ($M \gg 1$) in two-reservoir free manometry, no matter how large the reservoir area in the expression for K^{**} is made, since the $a \cdot 273/T'$ component of K^{**} then always amounts to at least ~ 1 and, hence, values of $k/K^{**} = M \sim 1$ (*19*), except in the unusual cases when $k \gg 1$.

Ordinarily, therefore, for *high M* values with equal-capillary free manometry, not only are two reservoirs required but also values of a somewhat less than 1 mm² down to a practical limit of, say, 0.05 mm². However, there yet remains another series of hydraulic-leverage arrangements whereby it is possible in free manometry to obtain intermediate, even if not high, values of M, and these arrangements do not definitely require either of the two particular reservoirs just described or any permanent alteration of the glass construction of available manometers such as is involved when one adds the second reservoir to the closed arm of a manometer at hand. In the three-arm manometers described here, use is made of ordinary unaltered commercial Warburg manometers of large capillary bore to which is added a third arm of either of two types (vertical or horizontal), of very small capillary bore, in a form that is optionally removable or permanent and can be made in the laboratory or commercially.

Free manometry with unequal capillaries. Although in fixed-volume manometry a difference in capillary area between the open and closed arms is of no notable consequence for fluid-distance displacement changes observed in the open arm, the scope of free manometry can be greatly extended by the use of capillaries with markedly unequal areas in conjunction with either one or two reservoirs. The use of one reservoir alone with two unequal capillaries can be made to yield high-sensitivity magnifications nearly as striking in practice as those obtained with two reservoirs and equal capillaries already described. This is true because marked inequality between capillary areas is algebraically equivalent, and therefore under properly chosen conditions nearly numerically equivalent, to inequality between reservoir and capillary areas. This situation makes the construction of the second reservoir unessential to obtaining large M values in free manometry of some form or other and leaves as alternative the construction of a manometer with one fine capillary arm, preferably the open arm since a reservoir is more easily mounted thereon, and a bubble inserted therein.

With the manometer arrangement just indicated—open-arm reservoir, small capillary, and bubble—the change of gas pressure in the confined space is given by the sum of the algebraic fluid displacements in the open-arm reservoir and in the closed-arm capillary, thus, $\Delta\overline{P} = \overline{H}a/A + \overline{H}a/a^* = \overline{H}(a/A + a/a^*)$, where $\overline{H}$ is the measured bubble distance displacement in the open capillary, a and A are (as before) the areas of the open-arm fine capillary and reservoir, respectively, and a^* is the area of the closed-arm capillary. Then $\overline{K} = x/\overline{H} = k(a/A + a/a^*) + (a \cdot 273/T')\,\{[P + \overline{H}(a/A + a/a^*)]/P_o\} \cong k(a/A + a/a^*) + (a \cdot 273/T')$. (This equation also covers the more general situation of *two* reservoirs and *unequal* capillaries if a^* is regarded as the area A^* of the confining fluid in the closed-arm reservoir rather than the closed-arm capillary to which it is algebraically equivalent).

With practical values of $a = 0.05$ mm² (diameter, 0.25 mm), $a^* =$ 3 mm² (diameter, 2 mm), and $A = 50$ mm² (diameter, 8 mm), $\overline{K} \cong k(0.05/50 + 0.05/) + 0.05 \cong 0.066$ for k of unity, so that a sensitivity magnification value of $M = \overline{K} \cong k/0.066 \cong 16$ is readily feasible, based on reading the bubble movement in the one arm only and without any resetting to fixed volume in the other arm. Since a^* could be made still larger, and hence M also, the practical limit of sensitivity magnification is largely governed, under these conditions, by the single magnitude $a \cong 0.05$, or $M \cong 20$! One has attained here, in essence, a volumeter operating at virtually constant pressure.

Warburg-type manometers with markedly unequal capillaries of the order of the dimensions just indicated would make excellent general-purpose manometers for both free and fixed-volume manometry, either with or without high-sensitivity magnification (with or without actual use of the reservoir-bubble arrangement). The unequal capillaries would offer no essential disadvantage for ordinary, conventional fixed-volume manometry but would open up a whole field of heretofore unenvisaged possibilities for free manometry. The widespread scientific utilization of such a type of all-purpose hydraulic manometer with two reservoirs (Fig. 4) deserves highest recommendation.

In the absence of such manometers at hand, it is possible to convert, in the laboratory or otherwise, the

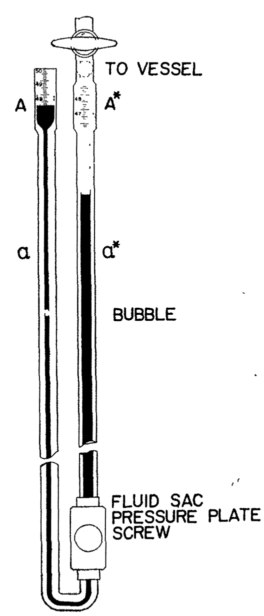

Fig. 4. Hydraulic general-purpose manometer designed for equally efficient use in either constant-volume manometry, free manometry, volumetry, or (Fig. 5) one-arm manometry, with either high-sensitivity magnification or conventional sensitivity: A and A^* are areas of outer and inner-arm reservoirs, ~ 30 mm² (diameters ~ 6 mm); a is area of outer-arm capillary of diameter optionally variable between, say, 0.25 to 2 mm; and a^* is area of inner-arm capillary of diameter optionally variable between, say, 1 to 2 mm. The customary graduations (not shown) of the capillary arms are extended to the tops of the reservoirs, and manometers with outer arms graduated over the range 0 to 500 mm may be mounted on standard commercial manometer backs normally supporting standard Warburg manometers of conventional range 0 to 300 mm. Outer and inner arms are readily separable and interchangeable at the fluid-sac juncture, permitting a wide range of K values dependent upon variable values of a/a^*, a/A^*, a^*/A^*, and so forth.

conventional, equal-capillary Warburg manometers into volumeter forms (three-arm manometers) that are equivalent to those with capillary inequality, two types of which are briefly described and analyzed.

To the open arm of an ordinary Warburg manometer filled to the top of the reservoir with manometric fluid, there is attached (by pressure tubing, plastic tubing, or glass ground jointing) an inverted, graduated, fine capillary U-tubing that rises and then descends, as a third manometer arm, the parallel length of the two other arms, to dip into an open reservoir filled with manometric fluid whose level is conveniently about that of the bottom of the two other arms. By means of the adjusting screw (or otherwise) the fluid in all three arms is made continuous except for insertion of a small air bubble in the U-tubing. This bubble may be inserted by lowering the reservoir fluid level momentarily below the end of the U-tubing and allowing a short length of air column to enter, with the aid of regulation by means of the adjustable screw.

The mathematical treatment is the same as is given in the preceding section, with a and A referring now to the areas of the capillary U-tubing and the test-tube reservoir, respectively. A can be made so large (several centimeters in diameter), if desired, that the term a/A in the formula for $\overline{K}$ drops out. The U-tubing can be made to extend far above the top of the manometer, and the bubble movement can be followed and measured over the entire length of both sides of the U-tubing, so that the scale length of fine capillary can be increased to several times the conventional scale length of 300 mm. It is possible to arrange for a series of machine-drawn capillary U-tubes of different areas, in order to obtain different values of sensitivity magnification desired (for example, 20, 10, 5).

A horizontal three-arm manometer variant consists merely of a long, graduated, fine capillary, attached to the second arm reservoir, as in the foregoing instance, but mounted horizontally. Fluid-distance displacement $\overline{H}$ readings are made simply at the end of the manometer fluid column in the fine capillary of area a, or optionally with an air bubble, or even with a small liquid bubble in an air column. The horizontal arrangement is perhaps geometrically less satisfactory, but experience shows that it is not without interest for the manometric hobbyist. Mathematically the term a/A in $\overline{K}$ is eliminated altogether, since the only hydrostatic pressure change involved occurs in the confining arm only and no longer at all in the middle or open arms, as is otherwise the case to some degree in all other arrangements previously described. $\overline{K}$ is now simply $\overline{K} = ka/a^* \div (a \cdot 273/T')$, and a more than ever is the main determinant of sensitivity and sensitivity magnification. This brings us to the most remarkable type of hydraulic free manometry, in which neither a nor k alone, nor the sum of these invariably positive quantities, is the main sensitivity determinant, but their *difference* is.

One-arm, "paradox" free manometer. In all the manometric procedures considered so far, either with or without hydraulic leverage, an increase in amount of confined gas has caused an increase in pressure in practice, and never less than zero change in theory (volumetry), regardless of the number of arms per manometer or whether any of the arms are vertical or horizontal. When, however, an odd number of arms per manometer is involved (1, 3, or 5, and so forth), with the confining meniscus area A^* greater than area a^* of the open, terminal arm capillary declined at any angle greater than zero, preferably 90° for maximum effect, a truly astounding paradox and exceedingly useful result is obtained, invariably occasioning upon first acquaintance therewith by orectic hearers, temporary total disbelief: increases in amounts of confined gas cause notable *decreases* in pressure (Δp negative!), and vice versa. The vertical, one-arm, manometer with hydraulic confining reservoir (Fig. 5), but no terminal reservoir, is the most striking and simplest example to consider in detail.

In such a manometer, initially adjusted with manometric fluid in both the reservoir and capillary sections of the arm, a positive production of gas x in the vessel causes an increase in volume of confining gas space $H^\dagger a^*$, where $H^\dagger$ is the observed vertical lengthening (mm) of the fluid column in the capillary section of the arm as measured by the downward movement of the lower (hanging) meniscus in the capillary. Had there been, initially, fluid in the capillary portion only and none in the reservoir, there would have been column displacement without lengthening, and the increase in gas space would have been smaller than $H^\dagger a^*$, and the pressure change in the confined gas would have been, as in ideal volumetry, zero. The observed lengthening takes place as a result of the effect of the hydraulic factor A^*/a^*, but, contrary to all manometric arrangements considered previously, it does so not against, but in the same direction as (*with*), gravity, which acts as an added force to increase the gas space change. Since the opposing upward and downward pressures at the level of the hanging meniscus in the capillary section are always equal, atmos-

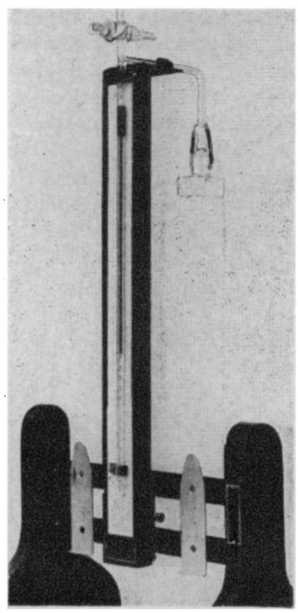

Fig. 5. Working model of the hydraulic, one-arm, "paradox" free manometer derivable from the hydraulic general-purpose manometer (Fig. 4) merely by removal of outer arm therefrom.

pheric (P_A), and unchanged by any change in x, and since the column length has been increased by a depth (not height) $-f\mathrm{H}^{\dagger}$, it follows that the final pressure P_f of the confined gas has been decreased compared with the initial pressure P_i, and that the change in pressure $\Delta P^{\dagger}$ has been negative, $\Delta P^{\dagger} = (P_A - P_i) - (P_A - P_f) = P_f - P_i = -fH^{\dagger} < 0$, where the terms $(P_A - P_i)$ and $(P_A - P_f)$ refer to the initial and final hydrostatic pressures of the column (*22*). Obviously, with allowance for the shortening of the column in the reservoir, whose movement is opposite in sign from that in the capillary, $\Delta P^{\dagger} = -H^{\dagger} + Ha^*/A^* = -H^{\dagger}(1 - a^*/A^*)$.

From this expression for $\Delta P^{\dagger}$ it follows that the vessel "constant" of the one-arm manometer is $K^{\dagger} = x/H^{\dagger} = -k\ (1 - a^*/A^*) + (a^* \cdot 273/T')\{[P - H^{\dagger}(1 - a^*/A^*)]/P_o\}$, and no longer represents a sum but a difference of the two terms in a and k, as earlier adumbrated. This circumstance allows $\mathrm{K}^{\dagger}$ to become smaller than the a term previously limiting high-sensitivity magnification in free manometry. Positive values for $K^{\dagger}$ may decrease to zero and $M = k/K^{\dagger}$ may approach infinity. This yields the important practical result of eliminating the necessity for very small values of a, which may now be of the same order as k (say 1 to 2 mm^2), with the very important added advantage of eliminating the slow response involved with small capillaries and at the same time retaining the main merit of free manometry, namely, no requirement for continual resetting to constant volume.

It is evident from the expression given for $K^{\dagger}$ that a wide range of possibilities, impossible to detail here but interesting to work out numerically and algebraically, offer themselves for obtaining any desired value of $K^{\dagger}$ and of $M = k/K^{\dagger}$ by varying the main components of $k(v_G, v_F, D)$, or A^* and a^* (relative and absolute values), or the initial height of the capillary-reservoir column that will affect the value of P, which is obviously always slightly below the prevailing atmospheric pressure P_A, and which must, like $H^{\dagger}$, be given due consideration when $K^{\dagger}$ is small. The initial height and stability of the capillary-reservoir column may be governed technically by means of a sac and screw clamp attached to the stopcock at the top of the manometer, or in various other ways unnecessary to detail here (*23*).

The eventual limitation to the use of the one-arm manometer is reached at high $M = k/K^{\dagger}$ values where small $K^{\dagger}$ values may not retain sufficient constancy over a wide range of observed $H^{\dagger}$ values. Since the exact formula given for $K^{\dagger}$ contains the then no longer minor variable $H^{\dagger}$ term, at small value of $K^{\dagger}$ (small differences between the terms in a and k), the expression within $K^{\dagger}$ in the braces can no longer be neglected as it could be in all previously reported approximation formulas for free manometry vessel constants, where a and k were additive in a positive sense only. This eventual limitation becomes especially significant when a^*/A^* is made small so that values of $H^{\dagger}/P_o$ for values of $H^{\dagger} = 100$ to 300 mm may then amount to an appreciable fraction of the entire term in a and, hence, in $K^{\dagger}$ when the latter is, say, 0.05 or less ($M \sim 20$). At this extreme range, the evaluation of $K^{\dagger}$ as a function of $H^{\dagger}$ will obviously require careful attention, involving some form of calibration (calculated or empirical), but this will be well worth while in view of the high speed of manometric fluid response to changes in x obtainable with one-arm manometry as compared with other highly sensitive forms of free manometry. Moreover, since high sensitivity is involved here, small values of $H^{\dagger}$ will frequently be sufficient for problems at hand; indeed the $H^{\dagger}$ values obtained may alternate plus and minus in sequence, as is commonly the case in problems such as photosynthesis, where $H^{\dagger}$ values of ± 10 mm per light-dark cycle may be entirely adequate, so that values of $M \sim 100$ could be obtained with satisfactory constancy of $K^{\dagger}$ as a function of $H^{\dagger}$.

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References and Notes

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5. J. J. Perkins, *Ind. Eng. Chem.* **15**, 61 (1943).
6. K. Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg* **24**, 334 (1943).
7. H. Holter, *ibid.* **24**, 399 (1943).
8. D. Glick, *Techniques of Histo- and Cyto-Chemistry* (Interscience, New York, 1949), p. 342.
9. The reference standard of *sensitivity* may be regarded as "millimeters of displacement of manometric fluid observed per cubic millimeter N.T.P. gas change," that is, $h/x = 1/k$; and for any given set of values of v_G, v_F, a, T, P_o; sensitivity *magnification* M is regarded in this paper as any form of amplification of h/x values, or reduction of k values, effected by various arrangements of hydraulic leverage-moving boundary index devices to be outlined. *Demagnification* may be regarded as any device or procedure for decreasing M, even to values below unity.
10. J. Barcroft and J. S. Haldane, *J. Physiol.* (*London*) **28**, 232 (1902).
11. The determination of vessel constants k, K, and various others (K', k^*, K^*, K^{**}, $\overline{K}$, $K^{\dagger}$) described throughout this paper are often better determined entirely empirically rather than by combinations of conventional mercury calibrations. The methods of Scholander, Niemeyer, and Claff (*12*) are very suitable, and their apparatus may readily be modified (and even simplified) to handle the smaller amounts of gas (smaller vessel constants) involved with high M values. It is recommended, however, that their procedure of calculation by formula be replaced by a procedure of direct comparison with a given standard manometer and vessel already accurately calibrated with mercury, carried out in such a manner that upon addition of identical quantities of gas to the standard and to the unknown manometer-vessel systems, the observed manometric fluid displacements will bear exactly inverse ratios to the desired respective vessel constants. This procedure has the advantage that it is not even necessary to know the quantity of gas added. Surprisingly accurate results, to within less than 1 percent, may be obtained when the gas is added at room temperature by means of an ordinary, tight-fitting, satisfactorily greased hypodermic syringe attached by pressure or plastic tubing to the manometer above the stopcock Eminently satisfactory instruments for accurate delivery of small quantities of gas are available on the market. The indicated empirical methods have been found in practical experience to be especially convenient and suitable to the needs of hydraulic manometry.
12. P. F. Scholander, H. Niemeyer, and C. Lloyd Claff, *Science* **112**, 437 (1950).

13. $x = \Delta p^* \{k + (a \cdot 273/T') [(Ph^*/\Delta p + h^*)/P_0]\}$.
14. A. Goldstein, *Science* **110**, 400 (1949).
15. ———, *Proc. Am. Acad. Arts Sci.* **77**, 237 (1949).
16. W. Arnold, E. W. Burdette, and J. B. Davidson, *Science* **114**, 364 (1951).
17. High shaking rates are often essential when using the standard rectangular Warburg manometric apparatus undergoing horizontal reciprocating motion, and it is often desirable or necessary to make readings without stopping the shaking. We have found (*18*) that by suitably mounting an ordinary hand lens, such as a standard equiconvex magnifying glass, on the carriage that supports and moves the manometers, any given manometer appears to the eye or camera to be *stationary* even though it may be shaking at a rate of 250 cy/min or more where unaided visual observations are unfeasible. This phenomenon is the result of an optical effect that reduces apparent motion to zero when the lens is mounted at approximately its principal focal length away from the manometer and moving with it in unison and in parallel, so as to produce collimated light. Whereas in principle any lens of ample size can be used, one with a focal length of 8 to 12 in. and a diameter of 3 to 4 in. has been found satisfactory (Fig. 6). The diameter of the lens should, of course, be as large as the shaking amplitude of the manometer, otherwise the image will disappear during part of the cycle. A lens with ample diameter will also increase the field of view, so that the manometers may be read when there are large changes in the displacements of the fluid indices observed, or where two adjacent manometers are to be observed simultaneously. For photography it is preferable that the lens employed be of a type corrected as in a telescope or binocular objective.
18. G. Hobby, V. Riley, and D. Burk, *An Optical Device for Reading a Rapidly Shaking Manometer or Other Reciprocating Apparatus*, in preparation.
19. The Braun-Fritzsching manometer has on each arm a reservoir of about 20 mm inside diameter and a capillary of about 1 mm inside diameter. This arrangement cannot provide notable sensitivity magnification in free manometry (see text) but only in constant-volume manometry, in which case the inner-arm reservoir is superfluous.
20. At least without making use of special wetting agents and of manometric fluids of exceptionally low viscosity and surface tension (*21*).
21. B. Kok, G. W. Veltkamp, and W. P. Gelderman, *Biochim. et Biophys. Acta* **11**, 10 (1953), Fig. 5.
22. Regarded in another way, since the sum of the hydrostatic pressure of the column and the pressure of the confined gas must always equal the prevailing atmospheric pressure (P_A), and since a positive increase in x causes a positive increase in hydrostatic pressure, it follows (by difference) that the pressure of the confined gas must decrease with positive values of x, and the change in pressure must be negative. Such *a priori* considerations can readily be confirmed experimentally by means of a conventional manometer connected in tandem with the one-arm manometer via vented plugs in the vessels of the two manometers. If gas is added to the one-arm manometer through its stopcock, the already described lengthening of its fluid column will be accompanied by a registered decrease of pressure in the conventional manometer operated either at free or fixed volume in the conventional manner without use of hydraulic magnification devices; that is, the column in the outer arm will fall. If, however, enough gas is added to the one-arm manometer to force all the liquid out of its reservoir down into the capillary below, then, from this point on, the column in the open arm of the conventional manometer will reverse its direction and rise, indicating now the customary increase in pressure with an increase of x in the system when the hydraulic factor A^*/a^* is no longer operating in the one-arm manometer.
23. Demonstrated at the meeting of the Society of General Physiologists, Woods Hole, Mass., 9 Sept. 1954.

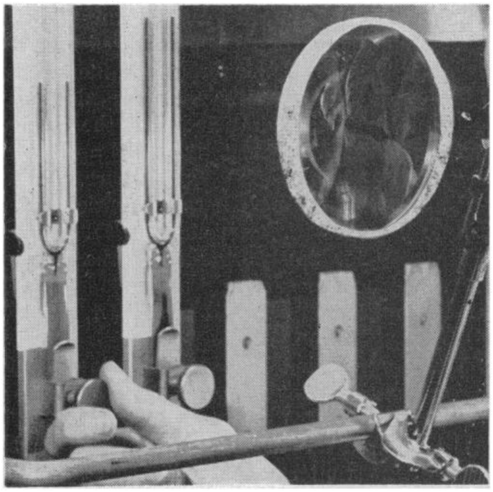

Fig. 6. Illustrative, simple arrangement for obtaining a stationary optical effect (zero apparent motion) with an equiconvex lens mounted at its focal distance and shaking in parallel and unison with a rapidly reciprocating manometer (*17*, *18*).

News and Notes

International Instrument Congress

The wide scope and large size of the 1st International Instrument Congress and Exposition, held under the auspices of the Instrument Society of America in Philadelphia, 13–24 Sept., afforded more than 23,000 persons a unique opportunity to view at first hand the intensive activity that characterizes the present-day field of instrumentation, to observe trends and to evaluate the impact of these trends on individual areas of interest. Although this was actually the ninth in an annual series of instrument conferences and exhibits of the Instrument Society of America (the 1st Instrument Conference and Exhibit was held in Pittsburgh in 1946), it was the first in which foreign countries were especially invited to participate. More than 70 foreign firms were represented in the exhibit; the number of foreign visitors is not yet known but was certainly well into the hundreds.

Official recognition and encouragement of this international participation was provided by two resolutions passed in the U.S. Congress and approved by the President. One resolution permitted articles imported from foreign countries for the purposes of this exhibition to be admitted without payment of tariff, and the other authorized the President of the United States to invite the states of the Union and foreign countries to participate in the congress and exposition. In accordance with this resolution, President Eisenhower issued a proclamation and then went further to signify his endorsement of the congress and exposition by sending a letter to the president of the Instrument