[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

THE UPPER RANGE OF THE QUARTZ-FIBER MANOMETER

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As recently pointed out by Carver,[1] the ordinary forms of micromanometer are not suited for use with organic vapors, either because they demand that the gases whose pressures are being measured shall obey the perfect gas laws, which these vapors do not, or else because they involve the use of hot wires, etc., which might decompose them. Carver solves the problem with the aid of a very elaborate optical-lever mercury manometer. However, it would seem that a much simpler and equally satisfactory solution is offered by the quartz-fiber manometer of Haber and Kerschbaum.[2]

This instrument, as originally described, consists of a moderately thin quartz fiber sealed at the top into a glass bulb. By gently tapping the bulb, the fiber is set swinging, and the amplitude of its vibration can be determined at any instant with the help of a suitable telescope with micrometer eye piece. This amplitude will decrease with time, at a rate depending upon various factors, but constant under given conditions. Let $\frac{-dA}{Adt} = C$, the damping constant, where A is the amplitude. Then, by a simple integration, it follows that

$$C = 1/T \ln A_1/A_2 \qquad (1)$$

where T is the time (measured by a stopwatch) which elapses while the amplitude decreases from A_1 to A_2.

Three cases now arise. If the tube is completely vacuous, no damping will occur except that due to the inelasticity of the quartz itself; let this be represented by $C = a$, where a depends only on the dimensions of the fiber and its temperature. If, however, gas is present, but at such low pressure that the mean molecular free path is large compared to the diameter of the fiber, additional damping will occur, proportionally to the pressure and to the square root of the molecular weight, so that

$$C = a + bp\sqrt{M} \qquad (2)$$

where b likewise depends only on the dimensions and temperature of the instrument. Finally, with increasing pressure, the mean free path becomes comparable to or smaller than the diameter of the fiber and Equation 2 ceases to hold; instead, C increases more and more slowly with increasing pressure, and soon reaches a limiting value unchanged by further increase in pressure. This limit is proportional to the viscosity of the gas in the tube and is, therefore, different for different gases. In fact, this differ-

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[1] Carver, THIS JOURNAL, **45**, 59 (1923).

[2] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

ence in the behavior of gases having different viscosities applies over the whole range just considered.

Obviously the instrument is most useful in its "lower" range, where its behavior follows a simple law, the same for all gases. However, this range extends only up to about 0.01 or 0.02 mm., and leaves a large gap to be filled before the range of the simple mercury manometer is reached. This gap roughly corresponds with the "upper" range of the quartz-fiber gage, that is, the range within which the damping still changes with the pressure, but in a different way with different gases, and can, therefore, be used to measure the pressure only after calibration with another type of gage, with the particular gas in question.

In order to investigate the usefulness of the upper range, two such gages were constructed as shown in Fig. 1. The simple fiber is replaced by a system of 2 fibers supported at their tops about 1 cm. apart, and having their lower ends joined by a small glass tip. The whole being made out of Pyrex, no difficulty was found in attaching the quartz to the glass, the ends of the fiber being first sealed into small glass armatures, which were in turn attached to the supporting stem. The fibers are about 9 cm. in length and 0.004 cm. in diameter. The tip of Gage B is heavier than that of Gage A. The glass guard ring *g* serves to limit the travel of the tip and prevents the fiber from ever coming into contact with the walls; it has proved invaluable in preventing breakage. The little glass points $p_1p_2p_3$ in the figure are used in reading the gage. The cross hairs of the micrometer telescope are set vertically in contact with the images of two of these points (p_1 and p_3 for a high pressure; p_1 and p_2 for a low pressure, in order to save time), the system set in vibration by suitable shaking, and the time noted during which the extreme position of the tip relapses from coincidence with the cross hair set on p_1 to coincidence with that set on p_3 or p_2. This time, together with twice the distances of the points from the position of the tip when at rest, is then substituted in Equation 1 to give *C*. The distances mentioned are found once for all with the aid of the micrometer, and will not change so long as the gage remains mounted in the same position, so that the telescope may be removed and reset as often as desired without introducing additional measurements or computations. During a reading, the top part of the gage is covered with a cap of snow, in order

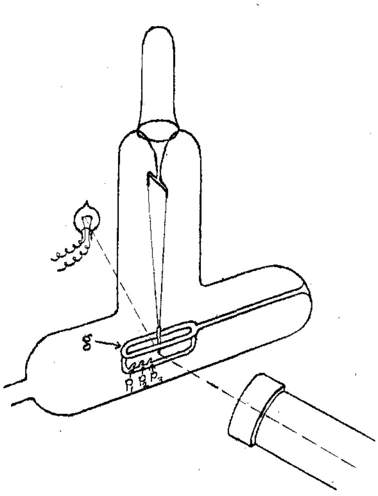

Fig. 1

to prevent temperature variations of the constants. It was found that cooling from room temperature to zero reduced the constant a by more than half.

Two advantages accrue from this bifilar construction. First, the system can vibrate only as a whole, and in only one plane, namely, that normal to the line joining the points of support, to which the axis of the telescope should be parallel. In the simple fiber gage, especially with fibers less than 0.01 cm. in diameter, much trouble is experienced from elliptical and harmonic vibrations. Second, the mass of the glass tip serves to decrease the frequency and therewith the rate of damping of the vibrations, so that accurate measurements of the damping time can be made at pressures so high that the simple fiber would be brought to rest in one or two seconds.

The quartz-fiber gages were tested by comparison with McLeod gages, using a variety of gases and vapors. Gold foil was introduced to keep mercury vapor out of the quartz gages. No account was taken of the difference in pressure which must have been caused, at the lowest pressures, by the temperature differences in the system (273° K. at the quartz, about 290° at the McLeod; at very low pressures, where $\Delta p/p = {}^1/_2 \Delta t/t$ this would amount to about 4%). In interpreting the results it must be kept in mind that the readings on the McLeod gage are not reliable except in the case of the permanent gases. With easily condensible gases and vapors the readings are too low, not because of failure to obey the gas laws during the last stages of compression, but because of adsorption on the walls during the early stages, the adsorbed gas failing to be carried up by the rising mercury. The fraction adsorbed will be the greater, the lower the pressure and the less volatile the vapor in the gage. In an effort to reduce the resulting error by recovering and estimating the adsorbed gas, a McLeod gage was constructed having a main chamber of 500 cc. capacity, and a "capillary" of 15 mm. diameter in which the volume and pressure of the trapped gas could be read after compression (100 times) by a micrometer microscope to 0.05 cc. and 0.01 mm., respectively. After the reading was taken, the gas was expelled through an electromagnetically-operated mercury-sealed glass valve at the top of the capillary, after which the mercury was lowered until it just continued to close the intake-port. Into the vacuum so produced the greater part of the adsorbed gas escaped and was estimated by once more raising the mercury and reading pressure and volume, the amount so found being added to the main portion in calculating the pressure. Even with this correction, it was found that no confidence could be placed in the readings below, say, 0.05 mm. in the case of benzene vapor. On the other hand, the behavior of the quartz gage with this vapor cannot be predicted from Equation 2 much above 0.005 mm., since the mean free path of the benzene molecules is exceptionally short. In the intermediate range an interpretation of the readings with the quartz gage in terms of pressure can be found, if at all, only indirectly, by analogy from the behavior of permanent gases in the same range.

This behavior is shown by the dashed lines in Fig. 2. The letters A and B refer to the quartz gages A and B, respectively. For the sake of simplicity the observed points are not put down on these curves; furthermore, the hydrogen and air curves for each gage are drawn somewhat closer together than they should be, in order to avoid overlapping. The abscissas are values of *C*, the damping constant, in reciprocal seconds, while the ordinates represent $p\sqrt{M}$ in millimeters of mercury. A logarithmic scale is used so that a great range may be covered. It will be seen that in the lower range, below about $p\sqrt{M} = 0.1$, the curves for both gases coincide, but that above this value they separate, air giving greater damping than hydrogen, in keeping with its higher viscosity. However, the curves for the two gases have the same shape, and can be brought into coincidence by displacement along their common asymptote. If this relation holds for all gases, and if the required displacement for each gas can be determined by other means, we have evidently a method of interpreting the gage readings with any gas, which does not rely upon the McLeod gage except for a single calibration curve with a permanent gas. A clew as to the amount of displacement required is given by the consideration that the upper limiting values of *C* should be proportional to the viscosities of the gases. If, therefore, $C \times \eta^{-1}$ or $C \times k\eta^{-1}$ be plotted instead of

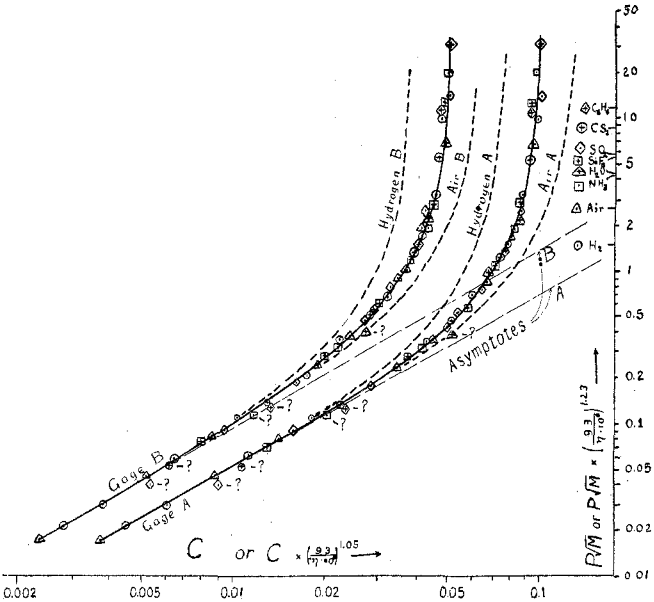

Fig. 2

C (where η is the viscosity of the gas in question, and k is any constant, the same for all gases) against $p\sqrt{M}$, the upper limits of the curves for all gases will coincide. In order that the lower portions of the curves may coincide, a vertical displacement also is necessary; inspection of the logarithmic graph shows that this should bear to the horizontal displacement the ratio which measures the slope of the asymptote, namely, 1.17. It turns out, however, that the displacement necessary to bring the air and hydrogen curves together is 5% greater than that calculated from the viscosities given in Landolt Börnstein "Tabellen" by the same reasoning. We shall therefore take, as our displaced variables, (arbitrarily setting $k = (93 \times 10^{-6})^{1.05}$), $C \times \left(\frac{93}{\eta \times 10^6}\right)^{1.05}$ for abscissa, and $p\sqrt{M} \times \left(\frac{93}{\eta \times 10^6}\right)^{1.23}$ for ordinate.

These variables are plotted in Fig. 2. It is evident that the points for hydrogen and for air actually lie on the same curve within the errors of measurement. (The probable error seems to be about 1% except in the highest range, where it increases because of the smallness of the time intervals measured.) The entire hydrogen curve can, therefore, be derived from the air curve (or *vice versa*) with the aid of knowledge of the viscosity of the two gases, or by a single measurement at a relatively high pressure, in order to determine the displacement required. This latter method, of course, is tantamount to determining the relative viscosity of hydrogen. It is reasonable to hope that in the same way curves for other gases and vapors can be derived, without reliance on the McLeod gage except for one orientating measurement at a relatively high pressure; in the orientating measurements slight errors in the McLeod gage would be unimportant, as C is here almost independent of $p\sqrt{M}$.

This hope appears to be justified. In Fig. 2 are collected observations on 6 additional gases and vapors, having a wide range of viscosities, molecular weights, and volatilities. The viscosities (η_c), calculated from the necessary displacements of the points, are listed in Table I, together with those (η_1) given in Landolt, and the molecular weights.

TABLE I

VISCOSITIES AND MOLECULAR WEIGHTS OF GASES

Gas	$\eta_c \times 10^6$	$\eta_1 \times 10_6$	M	Gas	$\eta_c \times 10^6$	$\eta_1 \times 10^6$	M
C_6H_6..............	71	70.9	78	OS_2............	93	92.4	76
H_2................	[87]	87.0	2.02	SO_2............	117	122.5	64
H_2O..............	93	90.4	18	SiF_4............	147	...	104.3
NH_3..............	93	95.7	17	Air.............	[175]	175.0	29

In Fig. 2, the symbols used to distinguish the different gases are shown at the right, at positions on the scale of ordinates corresponding to actual pressures of 1 mm. All points lie on the same curves except the 10 points marked "?," which lie too low; but this is exactly what we should expect, because the McLeod gage reads too low at low pressures, especially with slightly volatile vapors such as those of benzene and water. It will be noticed that these vapors begin to deviate at higher pressures than the others which are more volatile. We may, therefore, safely conclude that the solid curves represent the true relations between pressure and quartz-gage readings over the entire range, and can be used to read pressures for any gas whose viscosity and molecular weight are known, from the lowest detectable pressure up to the point where the slope becomes too steep for accurate reading. This extends the useful range from about 0.1 on the axis of ordinates (the limit of the lower range) to about 1 on the same axis, thus carrying us well into the range of the McLeod gage.

An approximate explanation of this relationship can be evolved as follows. An ideal gas, with infinite molecular free path, would presumably follow the asymptote over the entire range of pressures. Actual gases will begin to deviate from the asymptote at pressures at which their free paths become smaller than some definite value. Taking $L = 3\eta/\rho\omega$, where L is the mean free path, ρ, the density of the gas $= \frac{Mp}{RT}$, and ω, mean molecular velocity $= \sqrt{\frac{8RT}{\pi M}}$, we have $L = \sqrt{\frac{\pi RT}{8}} \times \frac{\eta}{p\sqrt{M}}$.

It follows that different gases will begin to deviate from the asymptote at the same values of $p\sqrt{M}/\eta$. We may also suppose that at still higher pressures, different gases will deviate by the same amount when their mean free paths and, therefore, the values of $p\sqrt{M}/\eta$, are equal, so that their curves will remain coincident when $p\sqrt{M}/\eta$ is plotted against C/η. The presence of exponents different from unity is not explained.

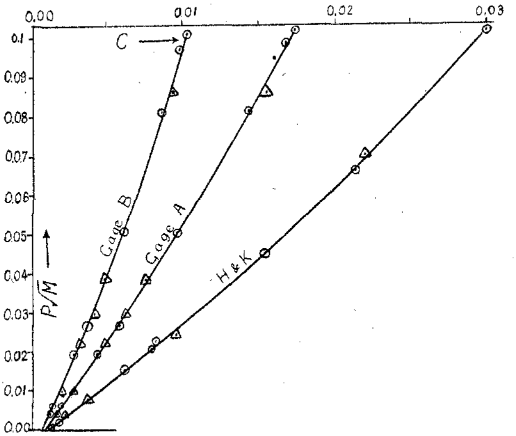

Fig. 3

Although the gages here described were constructed primarily for use in the upper range, they can also be used in the lower range, but are not quite so sensitive as those of Haber and Kerschbaum. Fig. 3 shows the curves for air and hydrogen in Cartesian coördinates, together with one of Haber and Kerschbaum's. The freedom from harmonic vibrations secured by bifilar construction is particularly valuable here, as undesired modes of vibration, once set up, persist for a long time; the gage cannot be read until they have died out. It will be noticed that the relation between C and $p\sqrt{M}$ is not strictly linear, even in this range.

The fact that the quartz-fiber manometer reads in terms of $p\sqrt{M}$ rather than p alone of course limits its applicability to those cases in which the gas to be measured has a known molecular weight, or is a mixture in known proportions of gases of known molecular weights. On the other hand, if M is unknown it can be determined by comparing the quartz-gage readings with those of some other form of delicate manometer, such as Carver's, which reads p directly. Evidently, this would furnish a method for identifying an unknown gas, analyzing a mixture of known gases of different molecular weights, and investigating the possibility of dissociation, at very low pressures. The method could be extended to higher pressures, in the first two cases, by reversing the principle of the McLeod gage; that is, by *expanding* the unknown gas in a sufficiently large ratio to bring it within the optimum range of the quartz-fiber gage.

Summary

A form of bifilar quartz-fiber manometer is described, from which troublesome harmonic vibrations are eliminated.

A method is described by which the instrument may be read up to pressures of 0.1 to 1 mm., depending on the gas used. The method involves calibration over the whole range with a permanent gas and a McLeod gage and, in addition, either a single measurement with the gas used and a McLeod gage at relatively high pressure, or a knowledge of the viscosity of the gas. So extended, the range of the instrument overlaps that of the McLeod gage, even with easily condensable vapors.

It is suggested that the gage may be used to determine molecular weights of gases at very low pressures.

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ERRORS IN THE DETERMINATION OF HYDROGEN SULFIDE

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Considerable interest is attached to a knowledge of the quantity of hydrogen sulfide present in natural waters. Such data are of value to the chemist, biologist and the public health officer. Hydrogen sulfide in natural waters is thought to be derived from both organic and inorganic sources and the quantity of it present in any water is likely to undergo rapid and rather great changes. Hydrogen sulfide in solution is rapidly oxidized and careful tests on solutions of the gas in distilled water show that 50% of the hydrogen sulfide may be lost in this way while a solution is kept overnight in a closed container at room temperature. Con-