JANUARY, 1929 PHYSICAL REVIEW VOLUME 33

THE TUBE-CORRECTION IN MEASUREMENTS OF THE VELOCITY OF SOUND IN GASES

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Abstract

The evidence concerning the validity of the Helmholtz-Kirchhoff equation

$$\Delta V/V_0=[\eta^{1/2}+(\kappa/c_v)^{1/2}(\gamma-1)/\gamma^{1/2}]/D(\pi\nu d)^{1/2}$$

for the change in velocity of sound in a tube, in terms of the viscosity, thermal conductivity of the gas, diameter of tube and frequency of the sound, including some tests by existing data not hitherto utilized for this purpose, is summarized and discussed in this paper. The indications are that the equation is correct, within the limits of error, at the higher frequencies and larger tube-diameters usually employed in present day measurements. Under such conditions, this method of correction appears to be the most reliable available. A convenient approximate expression is deduced for the variation of the correction with temperature, and the constants required for its application calculated for several gases. At low frequencies and for small tubes, as commonly employed in the older measurements, the adequacy of the Helmholtz-Kirchhoff equation is not established. Partly for this reason and partly because they may correct other errors, the methods of correction that depend upon the inverse diameter law are to be preferred under these conditions, and perhaps in all cases where enough precision of measurement is obtainable. On the other hand, the system of tube-calibration by measurements with a standard gas, especially as applied in much recent work at high temperatures, is in practice particularly subject to large errors, and is theoretically justified only if the Helmholtz-Kirchhoff equation is correct.

To account quantitatively for the reduction in the speed of propagation of sound, due to the effect of viscosity and conduction of heat at the surface of containing tubes, Kirchhoff,[1] amplifying the earlier work of Helmholtz,[2] deduced an equation which, for small decrements, may be written as follows:

$$(V_0-V)/V_0=\Delta V/V_0=[(\eta)^{1/2}+(\kappa/c_v)^{1/2}(\gamma-1)/(\gamma)^{1/2}]/D(\pi\nu d)^{1/2} \tag{1}$$

In this equation V_0 is the velocity in the free gas, V the measured velocity in the tube, η is the viscosity, κ the thermal conductivity, d the density and c_v the specific heat of the gas at constant volume, and γ is the ratio of its specific heats at constant pressure and constant volume. The diameter of the (cylindrical) tube is represented by D and the frequency of the sinusoidal oscillation by ν. It is assumed in the derivation that the layer of gas in contact with the tube adheres to it, and that the walls of the tube are rigid and remain at constant temperature, i.e., that they are of very great heat capacity or conductivity as compared with the gas.

Numerous experimental investigations of the validity of Eq. (1) have been made. Many conflicting results have been obtained and divergent conclusions drawn, with consequent confusion and distrust of the theory.

[1] Kirchhoff, Ann. d. Physik **134,** 177 (1868).
[2] Helmholtz, Crelles Journal **57,** 1 (1859).

It is the purpose of this paper to discuss the present status of the equation, introducing some new tests by existing data, and urging considerations not hitherto given sufficient weight. The possibility of its application at high temperatures, where it becomes of much importance in connection with the determination of specific heats of gases, is the particular object toward which this work is directed.

In nearly all of the earlier investigations[3] bearing upon Eq. (1), the dust figure method of Kundt was employed. It is obvious theoretically and found experimentally that the presence of dust in the tube further diminishes the velocity of sound in it. While the effect of the dust may be minimized by favorable choice of amount and fineness, it must always constitute a doubtful factor. Results by this method can be given little weight, and conclusions based on them can scarcely be carried over to the more modern methods.

Schulze,[4] however, employed the resonance method of Quincke. Working with very small tubes and at relatively low frequencies (the most severe conditions of test), he found the calculated correction too small and observed that the velocity was different in tubes of the same diameter but of different materials. The order of the variation of the correction in relation to the material of the tube can certainly be predicted from the thermal properties (heat capacity per cubic centimeter and conductivity for heat). Schulze's results, however, are not systematically related to these quantities, a fact that casts doubt on their validity and indicates the presence of some spurious effect. The more recent and more precise results of Dixon, Campbell and Parker[5] with larger tubes of lead, steel and silica glass showed no detectable dependence of the velocity upon the material of the tube.

Stevens,[6] also employing a resonance method, was able to obtain very consistent values of V_0 by a method of calculation depending upon combination of measured velocities in various pairs of tubes of differing diameters. He considered that his results substantiated the Helmholtz-Kirchhoff theory. In fact, however, his calculations prove only that the correction is very closely inversely proportional to D, which is an obvious necessity by any theory. To see to what extent his results are in agreement with Eq. (1), the corrections corresponding to his conditions have been calculated by it. The values corrected by the equation are shown in column 6 of Table I, together with the corrected values found by Stevens (last column). The agreement is by no means perfect. It is best, however, in the experiments of greatest accuracy (Nos. 1 and 2). Moreover, it will be observed that while the corrections calculated from Eq. (1) for the experiment at 20° are smaller than found by Stevens' method of combination, at 100° they are larger. These facts suggest that the method of combination (or

[3] Kundt, Ann. d. Physik **135,** 337, 537 (1868); Schneebelli, ibid, **136,** 296 (1869); Seebeck, ibid, **139,** 104 (1870); Kayser, ibid, **2,** 218 (1877); Low, ibid, **52,** 664 (1894); Müller, ibid, **11,** 331 (1903); Stürm, ibid, **14,** 822 (1904).

[4] Schulze, Ann. d. Physik **13,** 1065 (1904).

[5] Dixon, Campbell and Parker, Proc. Roy. Soc. London (A), **100,** 1 (1921).

[6] Stevens, Ann. d. Physik **7,** 285 (1902); Verh. deut. phys. Ges. **3,** 54 (1901).

extrapolation), corrects not only for the genuine effect of the tube upon the velocity of sound, but for certain minor apparent effects due to imperfections in the method or technique of measurement.

TABLE I. *Tube corrections to the velocity of sound in air from measurements of Stevens.*

No.	Material of tube	Diameter of tube mm	Temp. °C	Measured Velocity meters/sec.	V_0 calc. meters/sec.	V_0 comb. meters/sec.
1	Porcelain	40.4	20	341.19	342.73	343.27 (40–20)
2	Porcelain	29.5	20	340.47	342.57	343.15 (40–30)
3	Porcelain	20.2	20	339.11	342.18	—
4	Chamotte	46	20	340.80	342.15	343.25 (46–23)
5	Chamotte	23	20	338.36	341.04	—
6	Porcelain	40.4	99.6	385.51	387.66	386.90 (40–20)
7	Porcelain	29.5	99.6	384.95	387.89	387.03 (40–30)
8	Porcelain	20.2	99.6	384.12	388.42	—

Recent studies by Grüneisen and Merkel[7] and Cornish and Eastman[8] confirm the Helmholtz-Kirchhoff equation. Their work was done with hydrogen and with air in tubes ranging from 2.5 to 10 cm in diameter and at frequencies ranging from 5000 to 12000 cycles per second. The average of their results with hydrogen at 0° as computed by the inverse diameter law agrees within the limit of error with that calculated by Eq. (1). The latter equation applied to the results of Cornish and Eastman with air at 24° gave entirely consistent values of V_0 with two tubes of different diameters. The results of Grüneisen and Merkel with air at 0° are also in close agreement with the Helmholtz-Kirchhoff equation. Contrary to most of the earlier results, the correction is larger in the instance calculated by them from the equation than obtained by extrapolation.

Most of the experiments cited in the preceding were at temperatures not far removed from atmospheric. For the desired application to specific heat measurements, the variation of the correction at high temperatures must be known. Partly for the purpose of carrying out such tests of the equation as can be made at high temperatures, and partly with the view of supplying a convenient form of the equation for use in the elevated range, some consideration has been given to this question.

For convenience in discussion, the quantities in Eq. (1) that are properties of the gas may be gathered together into a single factor, C, the equation then being written

$$\Delta V/V_0 = C/D(\pi\nu)^{1/2} \tag{2}$$

in which
$$C = [(\eta)^{1/2} + (\kappa/c_v)^{1/2}(\gamma-1)/(\gamma)^{1/2}]/(d)^{1/2} \tag{3}$$

It is now desired to obtain C as a function of the measured quantities V and T (absolute temperature). The error allowable in the correction depends, of

[7] Grüneisen and Merkel, Ann. d. Physik **66**, 344 (1921).

[8] Cornish, and Eastman, J. Am. Chem. Soc. **50**, 627 (1928). (Eq. 22, p. 646 of this reference was incorrectly transcribed. Values in Table IX were calculated, however, from the correct equation.)

course, upon the accuracy desired in the results for the derived specific heats. If the latter is set at 1 percent, it will usually prove sufficient to know C within 10 percent. This limit enables the use of equations involving γ, d, V and T based on the behavior of ideal gases, but applicable with enough exactness in most of the real cases of interest. We may thus make use at once of the equations

$$d = pM/RT \tag{4}$$

and

$$\gamma = MV^2/RT \tag{5}$$

in which p is the pressure and M the molecular weight of the gas. For the remaining quantities of Eq. (3) (viscosity and thermal conductivity), use will be made of certain results of the kinetic theory.

It has been shown by Chapman[9] that in any gas whose molecules follow an inverse power law of force, the viscosity is expressible by an equation of the form

$$\eta = kT^n \tag{6}$$

where k and n are constants characteristic of the gas. The degree to which this behavior is followed by a number of representative gases is shown in Figure 1. In this figure, the logarithm of the measured viscosities[10] is plotted against the logarithm of the temperature. The linear character of the curves so obtained justifies the use of equations of the form of (6) for interpolation and extrapolation. From the curves, values of the constants have been calculated and are tabulated below.

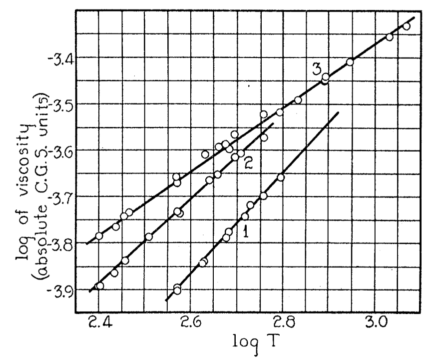

Fig. 1. Viscosity of gases. Curve 1, H_2O; curve 2, CO_2; curve 3, air.

TABLE II. *Constants of Equation (6) connecting viscosity (in absolute C.G.S. units) and temperature of gases.*

Gas	N_2	Air	H_2O	CO_2
k	2.28×10^{-6}	3.48×10^{-6}	2.04×10^{-7}	8.67×10^{-7}
n	0.765	0.696	1.085	0.905

The thermal conductivity is known from kinetic theory to be related to the viscosity, and to γ. Jeans,[11] combining the theory of Chapman with a suggestion of Eucken obtains the semi-theoretical result,

$$\kappa = \tfrac{1}{4}(9\gamma - 5)\eta c_v \tag{7}$$

and shows it to be well substantiated experimentally. An equation of a different form, wholly empirical and equally well verified experimentally

[9] Chapman, Phil. Trans. A, **216**, 279 (1916).

[10] From Landolt-Börnstein, Tabellen, which may be consulted for detailed references.

[11] Jeans, Dynamical Theory of Gases, Cambridge Univ. Press, p. 318 (1916).

has been proposed by Pollock.[12] This equation proves slightly less convenient than the one above in the present connection and for that reason has not been employed. The agreement as applied to individual cases, of the two very different equations may, however, be regarded as an indication of the correctness of the values obtained by them.

The combination of Eqs. 3, 4, 5, 6, and 7 leads finally to the expression, (writing a for M/R),

$$[C=(k/ap)^{1/2}T^{(n+1)/2}1+1.12(1.8-T/aV^2)^{1/2}(aV^2/T-1)] \qquad (8)$$

Eq. (8) is approximately valid at all temperatures and pressures at which the gas concerned does not deviate greatly from the ideal. For comparison, values calculated by it are given in Table III below, together with some calculated by Dixon, Campbell and Parker[5] and by Shilling.[13] These authors employed the Sutherland formula for the extrapolation of viscosity somewhat after the manner of Fürstenau.[14] The differences are larger in some instances than the desirable limit of error. It is believed that those calculated by Eq. (8) are to be preferred to the others.

TABLE III. *Values of constant C of Equation 2.*

Gas	Temp. °C	C (Eq. 8)	C, Dixon	C, Shilling
CO_2	600	0.998	0.97	1.017
CO_2	1000	1.31	—	1.398
N_2	1000	2.03	1.85	—
H_2O	1000	1.95	—	1.643

For the testing of Eq. (8) at high temperatures, only a few rather inaccurate data[15] by Stevens relating to air at temperatures between 850 and 1000°C are available. These results, obtained with tubes of 40 and 20 mm diameter, are plotted in Figure 2. The determinations with the smaller tube are represented here by circles and those with the larger by crosses. The latter are less consistent than the former, and allow much latitude in the placement of a curve to fit them. The curve drawn by Stevens (Ref. 6a, p. 306) can scarcely be right since it deviates less at the higher temperatures from the measurements with the small tube than it does at lower. To make the test desired here, therefore, the procedure was as follows. The best curve (Line 1, Fig. 2) for the smaller tube was assumed to be correct. Employing Eq. (8) the speeds that should have been found in the larger tube, if the equation is correct, were calculated. These are given by Line 2 of Figure 2. This line falls somewhat outside the region included by the four measured points,

[12] Pollock, J. Roy Soc., New South Wales, **49,** 249 (1915); Phil. Mag. **31,** (1916).

[13] Shilling, Phil. Mag. **3,** 273 (1927).

[14] Fürstenau, Ann. d. Physik **27,** 735 (1908).

[15] The first experiments of Stevens (Ref. 6, a) at high temperatures which are the ones used here, were made under very difficult conditions. The experiments were later repeated (Ref. 6, b) with better facilities and greatly improved accuracy, but the detailed results were not published.

indicating that the theoretical correction is too small. The theoretical curve, however, does not differ from the line best fitting the experimental points much more than the poorer points deviate from it. If it be assumed that minor defects of method (such as the failure of exactly integral ratios between the quarter and half wave-lengths, mentioned by Stevens), were not of equal influence in the two sets, the discrepancy may be further reduced. While the disagreement appears, therefore, greater than the error, and perhaps points to partial failure of the equation at low frequencies, the intimation persists that this is not the case in view of the good results by the more accurate methods at low temperatures, and the reversal in sign of the discrepancy in Stevens' own work at 100°. It at least emphasizes the necessity of further study in this field. It should be noted at this point that Stevens' own method of treating his results is considered entirely justifiable and right, provided that the improved accuracy in his final work (Ref. 6, b) permitted definite placement of his curves. From the general high quality of the other portions of his work, this may be assumed to have been the case.

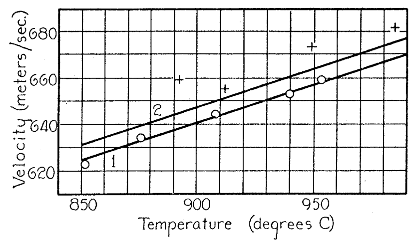

Fig. 2. Velocity of sound in air, Steven's measurements. Curve 1, (circles) measured, 2 cm tube. Curve 2, calculated, 4 cm tube. Crosses are measured values for 4 cm tube.

Review of the evidence adduced in the preceding shows that in the measurements of greatest accuracy, the Helmholtz-Kirchhoff equation is very closely substantiated; certainly within the limit of error. These measurements involved moderately high frequencies and large tubes. If the experiments at low frequencies and with very small tubes (excluding, of course, those by the dust-figure method) are given much weight, it is possible to claim that the theory is not exactly correct and fails under conditions that exaggerate its imperfections. Even in these cases, indications were found that errors of method, rather than of the theory, are responsible for the apparent discrepancies. It is believed that more accurate and complete measurements, which will be required before the question is finally settled, will show close correspondence with the theory. Any future measurements should include the field of high temperatures where the present evidence is indecisive.

Of the several methods which have been employed for making the tube-correction, that depending upon graphical or algebraic application of the inverse diameter law is to be preferred, provided the measurements are of enough precision to give the required accuracy of extrapolation. The reason for this preference lies not only in the fact that it is independent of any detailed theory, but also in that it corrects partially for any errors of method that vary with the diameter of the tube. This method assumes, of course, that measurements with two or more tubes are available. When this is not the case, or if enough precision is not attainable for accurate extrapolation, the Helmholtz-Kirchhoff equation should be applied. The question of precision of measurements is important because the error in the calculated result by the two-tube method is necessarily greater than the experimental uncertainty of measurement in either of the tubes alone. While it would appear to be always possible to reduce this error to any desired limit by a sufficient number of measurements, a practical consideration arises that makes this difficult, at least with some methods. Thus it was found in the measurements already cited[8] that the results in the smaller tubes were less reproducible than in the larger. It seemed in this case that more reliable values could be obtained by applying the Helmholtz-Kirchhoff equation directly to the measurements of greatest accuracy (those in the large tubes). The same appeared also to be true (cf Ref. 8, p. 648) of the work of Grüneisen and Merkel.[7]

The method of correction adopted by Dixon, Campbell and Parker[5] and by Shilling,[13] consisting in the "calibration" of a tube by comparison of the velocity measured in it with a standard accepted value for the free gas, employing their theoretical constant C of Eq. (2) to determine a "tube constant," is open to rather serious objection. In the first place, it requires that both the standard of comparison and the calibrating measurements be of an accuracy and reliability not attained in many existing measurements. All of the error in the large velocities, which, in view of the difference commonly found in results of different observers of the same quantity is not to be estimated from the apparent precision of any one set of measurements, is thrown into the small correction term, making possible very large percentage errors in it. As these errors are again magnified in calculation of specific heats, the question of the attainable accuracy is extremely serious. Secondly, if the Helmholtz-Kirchhoff equation is not correct and the properties of the tube have to be considered, which is urged by Partington and Shilling as one of the reasons for its use, this method becomes theoretically unjustified. It is obvious, for example, that if the thermal conductivity and specific heat of the tube walls cannot be considered infinite as compared with the gas, that the Helmholtz-Kirchhoff expression involving the conductivity in the gas will no longer hold. The calibration made with one gas could, therefore, not be used with another. Moreover, the properties of the tube change with temperature, and this, together with the variation of the function covering the properties of the gas, prevents the use of a calibration made at one temperature at any other. The method of correction employed, therefore, by these authors in their high temperature specific heat work tacitly presupposes the validity of the Helmholtz-Kirchhoff assumptions.

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October 11, 1928.