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TECHNICAL MEMORANDUM
NO. 29

COMPUTATION OF THE VELOCITY OF SOUND IN GASES

BY

PRESTON W. SMITH, JR.

NOVEMBER 5, 1952

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Technical Memorandum 29

Computation of the Velocity of Sound in Gases

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Preston W. Smith, Jr.

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Abstract

A method is summarized for the precise computation of the velocity of sound in a real gas and of its variations with experimental conditions. Specifically, two problems are discussed: (a) the inclusion of the effects of departures of the equation of state from the perfect gas law, and (b) the computation of specific heats from spectroscopic data. The method is applied to air and data for the computation of the velocity in air, under pressures between 720 and 820 mm. Hg. and temperatures between 0° C and 30° C, are presented. These results are summarized in the form of correction factors for the reduction to standard conditions of velocities measured at various frequencies and in this range of pressure and temperature.

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Computation of the Velocity of Sound in Gases

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I

INTRODUCTION

The recognized factors which can influence the phase velocity for propagation of sound in gases under various experimental conditions are numerous to a point of annoyance. However, when the gas is uniform and unbounded and the temperature, pressure, and frequency are not extreme, the situation is considerably simplified.

The classical expression for the phase velocity of an acoustic signal of small amplitude in an unbounded gas is the well-known expression,[1*]

$$c = (\gamma P_0/\rho_0)^{\frac{1}{2}} , \qquad (1)$$

where γ is the ratio of specific heats, P_0 is the equilibrium pressure, and ρ_0 is the equilibrium density of the gas. The assumptions implicit in this equation are that the gas is "ideal" (i.e., the equation of state is the perfect gas law) and that the sound disturbance is an isentropic (reversible adiabatic) process. It is usually assumed that γ is independent of the experimental conditions; it follows that the velocity should vary only as the square-root of the absolute temperature.

In this memorandum, we shall consider the problem of the theoretical calculation of the velocity of sound with a precision which invalidates some of the preceding assumptions. First, a method will be outlined for the incorporation of the effects of the "imperfection" of the gas (i.e., the departure of its experimentally determined equation of state from the perfect gas law). Secondly, the means for the computation of the specific heat from spectroscopic data will be presented. No consideration will be given to the effects upon the velocity

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*All numbered references appear at the end of the report.

of the radiation and conduction of heat or the viscosity, since these phenomena are of importance only at the extremes of the frequency scale. A review of these effects can be found in a recent paper by Markham, et al.[2] The results of computations for air will be presented.

From the results of theoretical calculations of this nature, measurements of the velocity of sound made under different experimental conditions can be corrected for these known effects and accurately compared at a common reference condition.

II

THEORY

The distribution of pressure in a sound field in an unbounded medium can be shown to be the solution of the wave equation,[3]

$$\nabla^2 p + (\omega^2/V^2)p = 0, \qquad (2)$$

where, in lieu of a specified equation of state for the medium, the symbol V^2 stands for the differential quotient,

$$V^2 = (\partial p/\partial \rho). \qquad (3)$$

In these equations, p is the instantaneous variational pressure, ρ is the instantaneous density of the medium, and ω is the angular frequency.* For generality, V must be considered to be a complex number (*the complex velocity of sound*). However, the situations to be considered in this memorandum are limiting or asymptotic cases in which V is real; in that case, it is readily recognized as the phase velocity or, more commonly, *the* velocity of sound.

---

*The assumptions implicit in the mathematical derivation are:

a. the pressure is a scalar point function of the space coordinates,
b. there are no sources or sinks of mass in the region,
c. the external, or "body," forces on the medium are constant,
d. the pressure and density disturbances are very small, and
e. the time derivative of V^2 is zero.

1. Velocity of Sound in Imperfect Gases

The differential quotient for the square of the complex velocity [Eq. (3)] can be evaluated in terms of fundamental thermodynamic variables from the equation of state for the gas. If the perfect gas law is assumed, one reverts to Eq. (1).

The method we will use for evaluating V was apparently first developed by van Itterbeek and Keesom[4] for determination of the real gas equation of state from sound velocity measurements; subsequently, both Richards[5] and Hardy[6] employed similar expressions in the consideration of the inverse problem -- that with which we are concerned -- of prediction of the variations of sound velocity from equation-of-state data.

The treatment proceeds from the fundamental definition, [Eq. (3)], and by means of standard thermodynamic relationships valid for pure substances* arrives at the expression

$$V^2 = \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{MT}{\rho^2 C_v}\left(\frac{\partial p}{\partial T}\right)_\rho^2 \qquad (4)$$

where P is the total pressure,
T is the absolute temperature,
C_v is the specific heat at constant volume, and
M is the molecular weight of the medium.

However, further manipulation is necessary since the specific heat of a real gas is not constant; its derivative, known from thermodynamics, must be integrated to obtain the value of C_v at the temperature and pressure of interest. The equation then reduces to

$$V^2 = \frac{RT}{M} f \left[1 + \frac{g/f}{\frac{C_{v0}}{R} + \Delta} \right], \qquad (5)$$

---

* The term "pure substance" is used here in its thermodynamic sense. Keenan in Thermodynamics (Wiley, 1941) defines it as: "A system which is homogeneous in composition and homogeneous and invariable in chemical aggregation..." (p. 18). The restriction is necessary in order to eliminate the complexities of phase changes and chemical reactions.

where R is the universal gas constant,

M is the molecular weight of the gas,

C_{vo}/R is the ratio of the specific heat at constant volume to the universal gas constant in the limit as the pressure approaches zero, and

f, g, and Δ are dimensionless functions of the equilibrium values of P and T.* **

The defining equations for f, g, and Δ (from which they can be evaluated if an equation of state relating P, ρ, and T is known) are:

$$f = \frac{1}{RT}\left(\frac{\partial P}{\partial \rho}\right)_T$$

$$g = \frac{1}{\rho^2 R^2}\left(\frac{\partial P}{\partial T}\right)_\rho^2 \qquad (6)$$

$$\Delta = \frac{C_v - C_{vo}}{R} = -\frac{T}{R}\int_0^\rho \left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \frac{d\rho}{\rho^2} .$$

The quantities f and g differ only slightly from unity, and Δ from zero, by an amount determined by the imperfection of the gas; for a perfect gas [Eq. (5)] reduces to [Eq. (1)], i.e., $V^2 = (\gamma P_o/\rho_o)$.

The significance of the individual factors of Eq. (5) can be shown to be as follows:

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*In his paper, Hardy (ref. 6, above) used a function, h, related to our Δ by the equations $(C_v/R) = h(C_{vo}/R) = (C_{vo}/R) + \Delta$. The difference lies primarily in the fact that, whereas Δ can be evaluated from the equation of state alone, h involves also the value of C_{vo}. However, C_{vo} varies with temperature independently of Δ; therefore, the present notation is simpler and preferable.

**The factors f, g, Δ, and C_{vo}/R in this equation are all dimensionless; any consistent set of units can be used in the computations leading to their evaluation. The units of the resultant figure for the velocity of sound depend wholly on the factor, RT/M. If it is desired that the velocity have the units, (cm/sec), it is appropriate to express T in degrees Kelvin, M in grams per mole, and R in ergs per mole · degree.

(a) (RTf/M) is the real gas isothermal bulk modulus of elasticity: $-v(\partial P/\partial v)_T$, where v is the specific volume.

(b) (g/f) is the difference of the specific heats divided by the gas constant: $(C_p - C_v)/R$, where C_p is the specific heat at constant pressure.

(c) Δ is the increment in the ratio, C_v/R, from zero concentration of the gas to the experimental concentration. Therefore, the quantity, $(C_{vo}/R) + \Delta$, is the actual value of C_v/R as defined by the expression: $(\partial U/\partial T)_v/R$, where U is the internal energy of the medium.

(d) The whole factor in square brackets in Eq. (5) is therefore the real γ, i.e., the ratio of the specific heats evaluated at the particular temperature and concentration for which f, g, C_{vo}/R, and Δ are computed.

Of course, any equation of state which is an accurate analytic representation of the P, ρ, T interdependence can be used to compute these functions, f, g, and Δ; the Beattie-Bridgman equation[7] is one of the best available for this purpose for substances in vaporous phase. That equation expresses P as a power series in ρ, the coefficients being functions of T; it involves five constants determined for each gas by a process of fitting the various derivatives of the pressure to a best match with data measured by various experimenters. In its general form, the equation can be written

$$P = (RT)\rho + (RTB_o - A_o - \frac{RD}{T^2})\rho^2 + (A_o a - RTB_o b - \frac{RdB_o}{T^2})\rho^3 + (\frac{RdB_o b}{T^2})\rho^4 \qquad (7)$$

where, in the units usually employed,

P is the absolute pressure in atmospheres,

R is the universal gas constant (atmosphere liter/mole degree).

T is the absolute temperature (degrees Kelvin),
ρ is the molar density (moles/liter), and
A_o is a constant with units of (atmosphere liter^2/mole^2),
B_o, a, b, are constants with units of (liter/mole), and
d is a constant with units of (degree^3 liter/mole).

This equation is sometimes conveniently abbreviated in the virial form

$$P = \alpha\rho + \beta\rho^2 + \gamma\rho^3 + \delta\rho^4 \qquad (8)$$

where the four coefficients (α, β, γ, δ) are functions of temperature and independent of density.

Expressions for the functions needed in Eq. (5) for the velocity are readily evaluated from these equations as power series in ρ. In the general case,

$$f = 1 + \frac{2\beta}{\alpha}\rho + \frac{3\gamma}{\alpha}\rho^2 + \frac{4\delta}{\alpha}\rho^3 ,$$

$$g^{\frac{1}{2}} = 1 + (B_o + \frac{2d}{T^3})\rho + (-B_o b + \frac{2dB_o}{T^3})\rho^2 + (-\frac{2dB_o b}{T^3})\rho^3 , \qquad (9)$$

$$\Delta = \frac{6d}{T^3}\rho\left[1 + \frac{B_o}{2}\rho - \frac{B_o b}{3}\rho^2\right].$$

The following approximate formulas, retaining only the first non-"ideal" terms, can be verified from the expressions given above.

$$\rho = \frac{P}{RT}\ [1 + (-B_o + \frac{A_o}{RT} + \frac{d}{T^3})\frac{P}{RT}] \qquad (8a)$$

$$f = 1 - 2(-B_o + \frac{A_o}{RT} + \frac{d}{T^3})\rho$$

$$g/f = 1 + (\frac{2A_o}{RT} + \frac{6d}{T^3})\rho \qquad (9a)$$

$$\Delta = \frac{6d}{T^3}\rho$$

In some check calculations for oxygen at room temperature and atmospheric pressure, the results of the approximate formulas differed but slightly from the results of the more accurate expressions. The errors were: less than +1 part per million in ρ, +4 parts per thousand in $(1-f)$, -1 part per thousand in $(g-1)$, and -1 part per thousand in Δ.

2. Evaluation of the Specific Heat

In order to compute the velocity of sound from Eq. (5) it is also necessary to obtain an accurate value for the specific heat at infinite dilution, C_{vo}. It has frequently been pointed out that theoretical computations by the methods of statistical thermodynamics, with data obtained by spectroscopic analysis of molecular spectra, are more accurate than direct measurements. However, one must first consider the possible differences between the specific heat effective at a given sound frequency and that which would obtain in a quasi-static process.

Variation with Frequency

The definition of the specific heat can be written as

$$C_v = (\partial U/\partial T)_v \tag{10}$$

where U is the internal energy of the medium, T is the absolute temperature, and the subscript v signifies a constant volume process. This process must be envisioned as a periodic variation at the frequency of the sound wave. Now the internal energy consists of both translational energy and energy associated with the various "excited" (rotational and vibrational) states of the molecules. In an equilibrium condition a certain small fraction of the molecules exists in each excited state, the proportions being dependent on temperature. The periodic variational temperature resulting from a sound wave will, therefore, cause a periodic variation of the proportions of the excited molecules; i.e., a periodic variation in the internal energy associated with the excited states. This energy is in addition to the translational energy and is therefore seen to modify the effective specific heat. However, the adjustment in the proportions of molecules in the various states is not instantaneous; it can be shown that there is a "time constant" associated with the response mechanism which introduces a phase difference between the temperature variations and the resultant energy variation. Therefore the effective specific heat, C_v, and the velocity, V, will each be complex. In two cases, C_v and V will be real: first, when the sound frequency is very low and the gas can be considered to be moving through equilibrium states only; secondly, when the sound frequency is so very high that there is no time for an adjustment in the proportions of molecules in the various states. Between these two limiting cases, the effective specific heat will have decreased by an amount equal to the contribution of the energy in the excited states to the quasi-static specific heat; the velocity will have increased correspondingly.[8]

In the general case it is found that the transition for all the states in any one "degree of freedom" occurs at a single characteristic frequency, although these frequencies may be (and usually are) different for different degrees of freedom.[8] The picture that develops is the following. The quasi-static specific heat (that effective at zero frequency) includes terms attributable to each of the translational, vibrational, rotational, and electronic degrees of freedom of the molecules. As the frequency increases, these terms successively drop out from the effective specific heat. Thus the velocity should increase in a sequence of steps. A careful analysis shows that the velocity makes a smooth transition between these steps, but at frequencies far from the transition region the value of the velocity is essentially that of the "step." (See Fig. (1).) We shall be concerned here with the computation of the values of these steps. Therefore we wish to evaluate the contribution of each of the degrees of freedom to the specific heat. More specifically, only the limiting values, as the pressure approaches zero, must be known (see Eq. (5)); therefore, the gas can be considered an ideal gas in this section. The determination of the transition frequencies for the various degrees of freedom is an entirely distinct problem which is not considered in this memorandum. It is, at present, approached most readily by the experimental measurement of the dependence of the velocity and attenuation of sound upon frequency.[8]

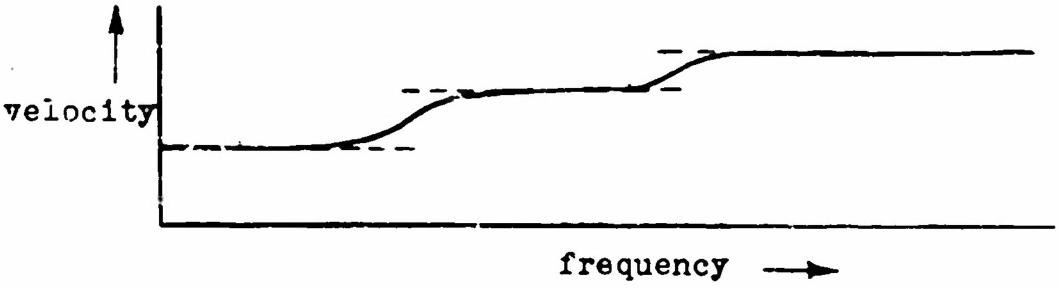

Fig. 1. Variation of Velocity with Frequency.

Computation from Spectroscopic Data

There are a number of papers and books which discuss, in varying degrees of completeness and complexity, the computation of specific heats of gases from spectroscopic data; however, it is appropriate to summarize here the basic theory and the methods used in this memorandum. Since this report is primarily concerned with the gaseous mixture, air, attention will be centered on its component gases which are mostly diatomic. The many complications of detail which obtain for polyatomic gases and at extremes of temperature are thereby avoided.[9]

The fundamental theoretical expression for the specific heat at constant volume of a pure gas is[10]

$$C_v/R = T^{-2}\, \partial^2\, \ell n\, f(T)/\partial(1/T)^2, \tag{11}$$ [*]

where f(T) is the partition function. The partition function for a gas depends on the temperature and the energy levels of the various states of the molecules. Its analytic expression is[9]

$$f(T) = AT^{3/2} \sum_i p_i\, \varepsilon^{-E_i/T}, \tag{12}$$

where A is a constant independent of temperature, p_i is the relative statistical weight of the i^{th} state, and E_i is the energy (in units of degrees)[**] of the i^{th} state. The statistical weight is the number of distinct configurations of the molecule which have the same energy, E_i, and therefore need not be distinguished in the sum for the partition function. It is readily verified from Eqs. (11) and (12) that neither the constant multiplier A nor a change in the datum for energy (the same change for all states) will affect the value of the specific heat.

If the equation (12) is substituted into Eq. (11), the results can be written:

$$C_v/R = (C_v^{trans}/R) + (C_v^{int}/R), \tag{13}$$

where
$$C_v^{trans}/R = T^{-2}\, \partial^2\, \ell n(T^{3/2})/\partial(1/T)^2 = 3/2,$$

$$C_v^{int}/R = T^{-2}\, \partial^2\, f^{int}/\partial(1/T)^2,$$

$$f^{int} = \sum_i p_i\, \varepsilon^{-E_i/T}.$$

---

[*] The subscript "o", indicating evaluation at zero concentration, has been omitted from C_v throughout this section.

[**] The energy, in degrees, of a particular state can be obtained from the corresponding wave number (in cm^{-1}) by multiplication by the constant, hc/k where h is Planck's constant, c is the speed of light, and k is Boltzmann's constant. The two units are entirely equivalent.

The first term, equal to 3/2, is the contribution of the translational energy to the specific heat. The second term measures the contribution of the "internal" degrees of freedom or, in the terminology used earlier, of the excited states of the molecule. The evaluation of this term is the major concern of this section. It is seen that the internal partition function, f^{int}, is formally determined by the energy levels, E_i, and their corresponding weights, p_i. These energy levels (in units of the wave number, cm^{-1}) can be directly measured spectroscopically from the absorption and emission spectra of the gas. It is essential to the systematic computation of the specific heat, however, that one employ the theoretical forms for the differences between successive energy levels as determined by quantum mechanics with values of the necessary constants determined by a best match with the experimental spectroscopic data.

In the usual convention, the total energy of a molecule in a given state is expanded in the form

$$E = E_e(e) + E_v(e,v) + E_r(e,v,j) \quad , \qquad (14)$$

where $E_e(e)$ is the energy level of the e^{th} electronic state of a molecule, in the hypothetical case where there is no vibration or rotation, $E_v(e,v)$ is the additional energy which the molecule would have if it were in the v^{th} vibrational level of the e^{th} electronic state, without rotation, and $E_r(e,v,j)$ is the energy possessed by a molecule in the j^{th} rotational level in excess of the total energy without rotation. Furthermore, the statistical weight, p_i, can be factored into the product of a weight for the rotational level, $p_r(j)$, and a weight for the electronic state, $p_e(e)$.

The internal partition function can now be written

$$f^{int} = \sum_{e=0} p_e(e)\varepsilon^{-\frac{E_e(e)}{T}} \sum_{v=0} \varepsilon^{-\frac{E_v(e,v)}{T}} \sum_{j=0} p_r(j)\varepsilon^{-\frac{E_r(e,v,j)}{T}} \quad . \qquad (15)$$

In many cases, in gases, the couplings between the rotational, vibrational, and electronic states are sufficiently small that their effects on the partition function can be neglected. Mathematically, this statement means that if the values of the sums $\sum_{j=0}$ and $\sum_{v=0}$ are relatively independent of the other quantum numbers,* their dependence on those numbers can be neglected. This is particularly true when the value of E_v (or E_e) increases greatly with the quantum number so that the multiplicative factor, $\varepsilon^{-E_v/T}$ (or $\varepsilon^{-E_e/T}$) decreases sharply.

When couplings between degrees of freedom are negligible, their individual contributions to the specific heat can be shown [from Eqs. (13) and (15)] to be independent and additive. Thus we can write

$$C_v^{int}/R = (C_v^{el}/R) + (C_v^{vib}/R) + (C_v^{rot}/R) \quad , \qquad (16)$$

when the individual terms are to be evaluated by means of Eq. (11) from the partition functions for the individual degrees of freedom:

$$\begin{aligned} f^{el} &= p_e(0) + \sum_{e=1} p_e(e)\, \varepsilon^{-\frac{E_e(e)-E_e(0)}{T}} \\ f^{vib} &= 1 + \sum_{v=1} \varepsilon^{-\frac{E_v(v)-E_v(0)}{T}} \qquad\qquad (17) \\ f^{rot} &= \sum_{j=0} p_r(j)\, \varepsilon^{-\frac{E_r(j)}{T}} \quad . \end{aligned}$$

---

*The identifying index for the electronic state, e, is not properly called a quantum number; that term is being misused here in order to simplify the discussion. A further complication of nomenclature arises in the case of polyatomic molecules; the sum over v must then be replaced by a double sum since two numbers are necessary to identify a single vibrational state: a modal index and the quantum number identifying the level within the mode.

Methods of computation.

There are two particularly useful methods for evaluating the contributions to the specific heat from these series. The value of $(C_v{}^{vib}/R)$ can be reduced to the closed form[11]

$$C_v{}^{vib}/R = x^2/\sinh^2 x \quad ,$$

where (18)

$$x = [E_v(1)-E_v(0)]/2T \ .$$

This expression is derived under the fairly accurate assumption that the successive vibrational energy levels are evenly spaced (the "harmonic vibrator" assumption). However, the expression is also a valid approximation, without the harmonic assumption, if the temperature is low enough that only the lowest two vibrational levels are significantly populated (i.e., if ε^{-4x} is negligible). Therefore, Eq. (18) is very accurate at room temperature but is somewhat in error at high temperatures.*

The most accurate method for evaluating any of the contributions to (C_v/R) is computation directly from the series (Eqs. (17)) by means of Eq. (11). The labor is readily adapted to machine calculation. It can be verified that, if the partition function has the form

$$f = \sum p_i \varepsilon^{-E_i/T} \quad ,$$

the contribution to the specific heat is[12]

$$C_v/R = \frac{f\,f'' - (f')^2}{f^2} \quad , \qquad (19)$$

where

$$f' = \sum p_i (E_i/T)\,\varepsilon^{-E_i/T}$$

---

*This equation is also valid for the contributions of each of the vibrational modes of a polyatomic molecule, if the modes can be considered "harmonic vibrators."

$$f'' = \sum p_i \, (E_i/T)^2 \; e^{-E_i/T} \quad .$$

This method of calculation must be used to evaluate the contribution of the rotational degrees of freedom and can be used for each of the internal degrees of freedom.

Formulas for the energy levels and statistical weights

There remains only the problem of determining the values of the energy levels and the statistical weights for the various degrees of freedom. As discussed earlier, we shall use the theoretical formulas determined by quantum mechanics.

The electronic contribution to the specific heat is vanishing small, in the gases of interest, at all reasonable temperatures because of the large values of the differences in energy levels, $(E_e(e)-E_e(0))$. [See Eq. (17).] In oxygen, in which the effect is larger than in most gases, the first electronic state, $^1\Delta$, above the ground state, $^3\Sigma$, contributes less than 1 part in 10^4 for temperatures less than 800°K.[13]

The spacing of the energy levels of the vibrational degree of freedom can be written approximately as

$$E_v(v) - E_v(0) = (\omega_e - x_e\omega_e)v - (x_e\omega_e)\, v^2 \quad , \qquad (20)$$

where ω_e is a wave number (reduced to degrees), and x_e is a small, positive constant included to compensate for the anharmonicity of the seccessive energy levels.[14] The values of ω_e and x_e are tabulated in references on molecular spectra.

The rotational energy levels, for a nonrigid molecule in the $v^{\underline{th}}$ vibrational level, are given by the equation[15]

$$E_r(v,j) = B_v \, j(j+1) + D_v \, j^2(j+1)^2 \quad , \qquad (21)$$

where

$$B_v = B_e - \alpha(v + \tfrac{1}{2})$$

$$D_v = D_e + \beta(v + \tfrac{1}{2}) \quad .$$

Here, the small factor D_v corrects for the effect of the non-rigidity of the molecule in rotation, this effect is sometimes called "centrifugal stretching." The small factors α and β correct for the coupling between the vibrational motion and the rotation. Were this formula to be used in calculation, the partition function for the vibration-rotation levels could not be separated into products as in Eq. (15) nor could the contributions of vibration and rotation to the specific heat be separated as in Eq. (16). However, since the coupling is small, its effect on the specific heat is quite negligible at all but extremely high temperatures. It is therefore sufficient to use Eq. (21) with v = 0. The quantities usually tabulated are the constants $B_o = B_e - (\alpha/2)$ and α. The various constants are related to one another by the equations[15]

$$D_e = -4\, B_e^3/\omega_e^2$$

$$\beta/D_e = (\omega_e/24\, B_e)(\alpha/B_e)^2 + 5\,(\alpha/B_e) - 8\, x_e \quad . \qquad (22)$$

By these equations, all constants can be determined from the tabulated values and the energy levels computed.

It is still necessary to determine the statistical weights, $p_r(j)$, for the rotational levels. For the gases of major interest in this report, these weights can be written[16]

$$p_r(j) = g_j(2j + 1) \quad , \qquad (23)$$

where the value of g_j is different for odd values of j from that for even j's. The ratio ($g_{j\ odd}/g_{j\ even}$) is a constant for the gas. All the equations necessary for the computation of the rotational contribution to the specific heat have now been summarized.* **

---

*Strictly speaking Eqs. (21) and (23) apply only to singlet electronic states such as the ground state of $N_2(^1\Sigma)$. In the ground state of O_2, the triplet $^3\Sigma$, the energy levels and statistical weights vary slightly between the three states. Fortunately, this distinction is not significant except at very low temperatures; at room temperatures and higher, the ground states of O_2 can be considered to be a single degenerate state of weight, 3.

**It is frequently assumed that, at room temperature, the rotational

Specific Heat of Mixtures of Pure Gases

The preceding comments have been concerned with the calculation from spectroscopic data of the specific heat of a pure gas at zero concentration, C_{vo}/R. Since a gas at zero concentration can be considered to be an ideal gas, the specific heat of a mixture can be computed by the usual formula,

$$(C_{vo}/R)_{tot} = \sum x_i \, (C_{vo}/R)_i \quad , \tag{24}$$

where x_i is the mole fraction (part by volume) of the i^{th} component.[17]

---

states of the molecule are so fully excited that the rotational degrees of freedom are behaving entirely classically and that the contribution of each to the specific heat, C_v/R, is therefore equal to 1/2. This is strictly true only for the theoretical case of a rigid rotator. The calculations performed for this report indicate that the effect of centrifugal stretching increases the value of C_v^{rot}/R for oxygen by two parts per thousand at room temperature. The effect increases with increasing temperature.

III

COMPUTATIONS AND RESULTS FOR AIR

1. Computations for Imperfections of Air

The equation for the square of the velocity of sound in an imperfect gas was derived in a previous section. [See Eq. (5), p. 4.] The effect of the imperfection of the gas is contained in three functions: f, g, and Δ which must be evaluated from the equation of state. Expressions for the three functions have been derived [Eq. (9), p. 6] in terms of the temperature, the density, and the five constants A_o, a, B_o, b, and d which appear in the Beattie-Bridgman equation of state.

The process of computation of these functions requires some comments. First it is to be noted that the independent variables in Eq. (9), as in the equation of state [Eq. (7)], are the molar density and the absolute temperature. Since the measurable quantities are pressure and temperature, it is necessary first to compute the molar density, ρ, [by a process of successive approximation, using Eq. (7)] for selected values of P and T. The unit of pressure is the normal atmosphere so that conversion is necessary when the measurement is made in millimeters of mercury. Finally the values of the universal gas constant, R, and the ice point, T_o(°K) used by Beattie and Bridgman in the computation of the constants A_o, a, B_o, b, and d are R = 0.08206 atmosphere liter/mole degree and T_o = 273.13 degrees Kelvin, respectively; these figures must, of course, be employed in all further calculations with these five constants, namely, in the determination of the values of f, g, and Δ. However, in Eq. (5) for the square of the velocity of sound, the absolute temperature appears explicitly; here the best contemporary value for the ice point should be used. The value T_o = 273.16 degrees Kelvin has been used in this report.[18] The values of the desired functions, f, g, and Δ, and the ratio g/f, can now be calculated from Eq. (9) for any particular gas or vapor for which the five constants, A_o, a, B_o, b, d, have been determined. Mixtures of these gases can also be treated by a method developed by Beattie.[19]

Table I presents the result of such calculations of the functions f, g/f, and Δ, for air in the region: 0 to 30°C, 720 to 820 mm. Hg; the values[20] used for the constants of the Beattie-Bridgman equation were

$A_o = 1.3012 \qquad B_o = 0.04611 \qquad d = 4.34 \times 10^4$

$a = 0.01931 \qquad b = -0.01101$

The results contained in Table I, with the knowledge of the specific heat, C_{vo}/R, are sufficient to compute the ratio of velocities of sound at different conditions of temperature and pressure. However, in order to compute an absolute value for sound velocity from these theoretical considerations, it is necessary as well [see Eq. (5)] to know the value of the molecular weight, M. M is not determinable from the equation of state alone;* indeed, it never appears therein when the volume unit is molar (e. g.,liter/mole). It can, however, be determined simply from molar density, ρ (mole/liter), and the density proper, ρ' (grams/liter), if both are known at the same experimental conditions, for, by definition, $\rho' = \rho M$. Furthermore, the value of the molar density is readily computed from the equation of state [Eq. (7)]. Therefore the problem reduces to determining the density in grams/liter.

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*I can find no satisfactory answer in the literature to the problem of how, from experimental data in which the unit of volume was presumably in cgs units (cm^3, liter, or specific volume units of cm^3/gm, liter/gm, or equivalents), the constants for Eq. (7) could have been determined in molar units without simultaneously determining the value either of the molecular weight, M, or of the individual gas constant which is the ratio, R/M. Indeed, in their first paper, J. Am. Chem. Soc. 49, 1665 (1927), Beattie and Bridgman present results for ethyl ether and carbon dioxide which give both the values of the five constants and the value of the ratio, R/M; none of the other papers do so.

Table I. The Functions f, g/f, and Δ, Representing the Imperfections

temperature:	0°C	5	10	15	20	25	30°C	
pressure:								
720 mm. Hg.	0.998 818	0.998 935	0.999 044	0.999 146	0.999 242	0.999 331	0.999 415	
740	785	905	018	123	221	313	399	
760	752	876	0.998 991	099	200	295	383	
780	720	847	965	076	179	276	367	f
800	687	817	939	052	158	258	351	
820	655	788	913	029	138	240	335	
720 mm Hg.	1.005 457	1.005 243	1.005 042	1.004 852	1.004 673	1.004 504	1.004 343	
740	608	388	182	987	803	629	464	
760	760	534	322	1.005 121	933	754	585	g/f
780	912	680	462	256	1.005 062	879	706	
800	1.006 064	826	602	391	192	1.005 004	826	
820	216	971	741	525	322	129	947	
720 mm. Hg.	0.000 541	0.000 503	0.000 468	0.000 437	0.000 408	0.000 381	0.000 356	
740	556	517	481	449	419	392	366	
760	571	531	495	461	430	402	376	Δ
780	586	545	508	473	442	413	386	
800	601	559	521	485	453	423	396	
820	616	573	534	498	465	434	406	

Unfortunately, no single value for the density of air can be stated for the simple reason that the word "air" comprehends a whole class of vaporous mixtures of sensibly different compositions. One can even eliminate the well-known variations in the proportions of water vapor and carbon dioxide and in the relative proportions of O_2 and N_2 at different altitudes; there remains a fluctuation of density, of approximately ±0.0004 gram/liter, more or less dependent on the barometric pressure at the time the sample was obtained for measurement.[21] This variation is ascribed to changes in the relative proportions of oxygen and nitrogen brought about by mass movements of gas within the atmosphere — an atmospheric "stirring" in times of changing weather conditions. (This amount of variation in density causes a corresponding variation in the velocity of sound of about ±0.05 m/s.) Perhaps as satisfactory an answer as possible is that the density of dry air with 0.03 per cent CO_2, at sea level, should average (over months) about 1.2930×10^{-3} grams/cm^3 under standard conditions of temperature and pressure.[22, 23] Assuming this value to be exact, the molecular weight of air, computed by the method described above, is $M = 28.9627$ grams.

It must be mentioned, however, that these slight variations in composition of "air" and in the molecular weight of the mixture should not significantly affect the values of the functions f, g/f, and Δ used to correct measurements to standard conditions of temperature and pressure.

2. Computations for Specific Heat of Air

A summary was given in the last chapter of the methods and formulas used to compute the specific heats of pure gases and mixtures. We shall present here the values of the experimental constants and the results of the computation.

For the purposes of this section, air is considered to be a mixture of four gases mixed in the following proportions by volume:

N_2, 78.09%; O_2, 20.95%; A, 0.93%; CO_2, 0.03%.

Although some variation in the values of the proportions of these gases appears in the literature, these figures are among the most recent.[24]

Two constants are necessary to evaluate the exponents, E/T, from the spectroscopic data given in $(cm)^{-1}$ units; the values used are:

absolute temperature of the ice point:

$T_o = 273.16^\circ K$;

energy level conversion factor (cm^{-1} to deg):

$\frac{hc}{k} = 1.438337$ deg·cm.

The data used for the individual gases follow:

Argon is taken as a monatomic gas with energy of translation only; $C_v/R = 1.5000$.

Carbon dioxide is taken as a linear polyatomic molecule with fully excited rotational states and only slightly excited higher vibrational levels. Precisely, account is taken of the energy of the first vibrational levels above the ground state in each of four modes for which the energy levels are taken as:

$E_v(\ell,v)-E_v(0,0) = 9.54, 9.54, 18.9, 33.6$ degrees,

respectively. Equation (18) is then used to evaluate the contribution of each mode to the specific heat.[25] The result need not be too accurate since the mole fraction of CO_2 in air is so small.

Oxygen is treated as a diatomic molecule in a degenerate electronic state ($^3\Sigma$). The contribution of the next highest electronic state ($^1\Delta$) to the specific heat is neglected. The small coupling between vibrational and rotational states is ignored and the vibrational component of the specific heat was computed at 5-degree intervals from 0°C to 30°C by the use of Eq. (18). These data were checked by direct computation from the series expansion for the partition function at temperatures of 0°C and 20°C; no significant difference was detected. The rotational specific heat, C_v^{rot}/R, was computed at 0°C, 10°C, and 20°C from the appropriate series by Giauque's method [Eq. (19)]. The values of the spectroscopic constants used for these computations are:[26]

<u>vibrational</u> <u>contribution</u>: (in $^3\Sigma$ electronic state)

$\omega_e = 1584.91$ cm^{-1} , $\omega_e x_e = 11.645$ cm^{-1}

<u>rotational</u> <u>contribution</u>: (in $^3\Sigma$ electronic state)

$B_o - B_e - \frac{\alpha}{2} = 1.438$ cm^{-1} $p_r = (2j+1)$, j odd

$\alpha = 0.016$ cm^{-1} $= 0$, j even

Computations for <u>Nitrogen</u> were made in a manner similar to that for oxygen. The vibrational specific heat, C_v^{vib}/R, was computed at intervals of 5°C from 0°C to 30°C, using Eq. (18). The rotational specific heat, C_v^{rot}/R, was computed at 0°C and 20°C from the series expansion for the partition function by Giauque's method. The values of the parameters used in these computations are:[27]

<u>vibrational</u> <u>contribution</u>: (in $^1\Sigma$ electronic state)

$\omega_e = 2359.60$ cm^{-1} $\omega_e x_e = 14.445$ cm^{-1}

<u>rotational</u> <u>contribution</u>: (in $^1\Sigma$ electronic state)

$B_o = B_e - \frac{\alpha}{2} = 1.992$ cm^{-1} $p_r = 2(2j+1)$, j odd

$\alpha = 0.018$ cm^{-1} $= (2j+1)$, j even

In Table II, the computed values of specific heats are presented for each gas and for the mixture, air. The specific heats for air are also given, omitting the vibrational contributions of various combinations of the component gases; these would be the <u>effective</u> specific heats at various high frequencies.[28] The few values for specific heats given by Hardy[29] show no significant difference from these results.

3. Computed Velocities for Air

The results of the computations of the previous two sections can now be combined and theoretical values computed [by Eq. (5), p. 4)] for the velocity of sound in air and its variations with temperature, pressure and frequency.

The velocity of sound in air, at the reference conditions generally accepted as standard, is thereby computed to be 331.45 m/s. These reference conditions are: temperature, 0°C; pressure, 760 mm Hg; proportion of CO_2 by volume, 0.03%; humidity, zero; frequency, sufficiently low that the specific heat should assume its quasi-static value.

The computed variations of the velocity of sound with temperature, pressure, and frequency are presented in the accompanying figures (Fig. 2) in the form of the fractional correction which should be applied to experimental measurements to reduce them to reference conditions. The correction factor given is the amount by which the ratio of the velocity at reference conditions to the velocity at stated conditions exceeds unity. The curves are lines of constant correction factor (and therefore of constant velocity); they are plotted as functions of temperature and pressure. Four charts are given representing different frequency regions. The four charts in Fig. (2) represent data computed with effective specific heats for air which omit various contributions from the internal degrees of freedom of the component gases. Thus in Fig. (2a) ("Low Frequencies"), no contribution is omitted; in Fig. (2b) ("Intermediate Frequencies I"), the contribution of the vibrational degrees of freedom of O_2 is omitted; in Fig. (2c) ("Intermediate Frequencies II"), the contributions of the vibrational degrees of freedom of O_2 and N_2 are omitted; in Fig. (2d) ("High Frequencies") all vibration contributions are omitted and the effective specific heat includes only translational and rotational terms.

Table II. Specific Heats, C_v/R_* of Air and Its Component Gases

temperature:		$0^\circ C$	5	10	15	20	25	$30^\circ C$
gas:								
A (all components)		1.50	1.50	1.50	1.50	1.50	1.50	1.50
CO_2:	translation and rotation	2.50	2.50	2.50	2.50	2.50	2.50	2.50
	vibration	0.83	0.86	0.88	0.91	0.94	0.97	0.99
O_2:	translation	1.500	1.500	1.500	1.500	1.500	1.500	1.500
	rotation	1.00180	1.00184	1.00187	1.00190	1.00193	1.00196	1.00200
	vibration	0.01816	0.02031	0.02260	0.02505	0.02764	0.03039	0.03329
N_2:	translation	1.500	1.500	1.500	1.500	1.500	1.500	1.500
	rotation	1.00108	1.00110	1.00112	1.00114	1.00116	1.00118	1.00120
	vibration	0.00070	0.00085	0.00101	0.00120	0.00141	0.00166	0.00193
TOTALS FOR AIR (N_2: 78.09%; O_2: 20.95%; A: 0.93%; CO_2: 0.03%)								
with all components		2.49652	2.49712	2.49776	2.49845	2.49919	2.49998	2.50083
omitting O_2 vibration		2.49272	2.49287	2.49303	2.49320	2.49339	2.49361	2.49386
omitting O_2 and N_2 vibrations		2.49217	2.49221	2.49224	2.49226	2.49229	2.49232	2.49235
omitting all vibrations		2.49192	2.49195	2.49197	2.49199	2.49201	2.49203	2.49206

The frequency regions in which the charts are valid are those far from the transition frequencies where the velocity is changing most rapidly.* [See Fig. (1), p. 9.] Unfortunately the transition frequencies are not definitely determined for all gases. Knötzel[30] has indicated that the transition frequency attributable to the vibrational degree of freedom of O_2 is not above about 40-60 c/s in dry pure oxygen or dry air, however he was unable to fix its position definitely. Measurements of the ratio of specific heats of O_2 made by Koehler[31] at a frequency of about 3 c/s tend to indicate that that frequency is still somewhat above the transition; unfortunately, the experimental probable error is too great to allow much dependence upon this deduction. Other measurements have not given significant results for dry air.** There is no information about the transition frequency attributable to the vibrational degree of freedom of N_2. Some of the transition frequencies for the three vibrational modes of CO_2 have been located. The deformation mode is most important of these and its transition frequency (in dry, pure CO_2) is about 17 kc/s.[32]

The charts in Fig. (2) have been computed on the assumption that the transition frequency for the vibrational degree of freedom of N_2 lies at some unknown point, "X", above that for O_2. Under this assumption, Fig. (2a) is applicable below the transition frequency for O_2, which is not higher than 40-60 c/s; Fig. (2b)

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*The numerical value of the term, "far from," depends on the desired accuracy. It can be shown from the standard equations for the phase velocity in the transition region [V.O. Knudsen, J. Acoust. Soc. Am. 6, 199 (1935)], that 88 per cent of the total change in velocity takes place in a frequency band of two octaves on either side of the transition frequency. Such a factor of four in frequency is therefore usually quite adequate.

**Of course, this transition frequency has been determined in moist air and moist oxygen, in which cases it is much higher. [See V. O. Knudsen, J. Acoust. Soc. Am. 6, 199 (1935)]. However, neither the data on the effect of imperfection of the gas nor the specific heats apply directly to moist air.

is applicable between this point and "X"; Fig. (2c) is applicable between "X" and the transition frequency of CO_2 at 17 kc/s; finally Fig. (2d) is applicable in the frequency region above 17 kc/s. The upper limit of applicability of Fig. (2d) is determined by transition frequencies attributable to the rotational degrees of freedom of the component gases. Where dispersion of this type has been detected, the transition frequency (at atmospheric pressure) has been high in the megacycle region.[33]

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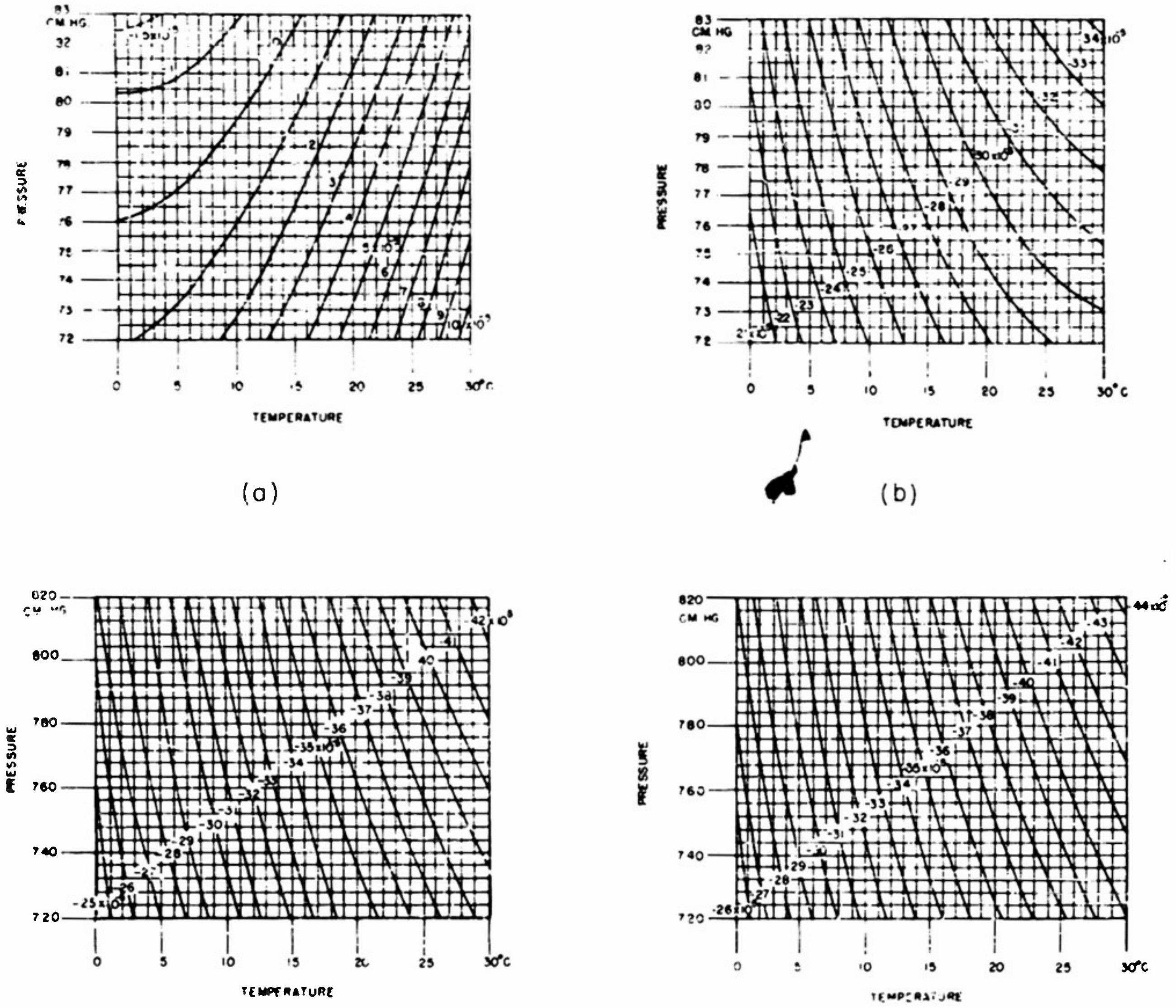
8. The discussion of the mechanism at intermediate frequencies is intentionally avoided, although it is of paramount interest to the question of attenuation of the sound wave. For such a discussion the reader is referred to the papers: V. O. Knudsen, J. Acoust. Soc. Am. 6, 199 (1935); J. J. Markham, R. T. Beyer, and R. B. Lindsay, Rev. Mod. Phys. 23, 353 (1951).



(a) (b)

(c) (d)

FIG. 2 CORRECTION FACTOR FOR THE VELOCITY IN AIR, AS A FUNCTION OF TEMPERATURE AND PRESSURE. THE CORRECTION FACTOR IS THE FRACTIONAL CORRECTION THAT MUST BE APPLIED TO EXPERIMENTAL MEASUREMENTS TO REDUCE THEM TO STANDARD CONDITIONS. THE FOUR CHARTS APPLY TO DIFFERENT FREQUENCY REGIONS.

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