The propagation of sound in relaxing gases in tubes at low frequencies

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The frequency dependence of the velocity and attenuation of sound waves in a gas which undergoes vibrational relaxation have been investigated theoretically. At low audible frequencies the attenuations due to viscosity, thermal conduction and relaxation in the gas, add linearly, while the velocity is the relaxation velocity diminished by the Helmholtz–Kirchhoff factor. The relations have been confirmed experimentally, and the free gas velocities of sound at zero frequency, one atmosphere pressure and 30 °C, found for carbon dioxide, air and oxygen, are $270{\cdot}57 \pm 0{\cdot}04\ \mathrm{m\,sec^{-1}}$, $349{\cdot}18 \pm 0{\cdot}02\ \mathrm{m\,sec^{-1}}$ and $331{\cdot}33 \pm 0{\cdot}03\ \mathrm{m\,sec^{-1}}$, respectively. The corresponding specific heats are $C_p/R = 4{\cdot}537 \pm 0{\cdot}008$ for carbon dioxide and $C_p/R = 3{\cdot}547 \pm 0{\cdot}003$ for oxygen.

Introduction

Accurate measurements of the velocity of sound in a gas combined with an accurate equation of state can yield precise values for the specific heats of the gas. For gases other than air, a container such as a cylindrical tube must be used. The speed then found is less than that in the free gas and is given by the Helmholtz–Kirchhoff equation. The limits within which the approximation given by Rayleigh (1894) applies have been investigated by Weston (1953) and it appears that almost all the work carried out to date at low frequencies falls within these limits. A considerable amount of work has been done in the ultrasonic region on gases in which vibrational relaxation occurs, and the practice has been to neglect the possibility that the velocity may at these frequencies be modified by the viscous and thermal interaction with the walls of the container, and to subtract from the measured attenuation the theoretical values of the small contributions from the bulk viscous (Stokes's) absorption and the tube absorption to obtain the relaxation absorption.

Recently some very accurate low-frequency determinations of the velocity of sound in non-relaxing gases have been made (Harlow 1954). When the work was extended to include relaxing gases (Wintle 1959*a*, *b*) it was clear that the absorptions due to the relaxation effect and to the presence of the tube were of the same order of magnitude, and that since the Helmholtz–Kirchhoff absorption and the relaxation absorption both depend on the transport properties of the gas, an interaction might well take place.

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Theory

The sound pressures involved in the present work are about 2×10^{-6} atmospheres, and the non-linear terms in the hydrodynamical differential equations are therefore omitted. The classical equations governing the propagation in a tube are given to the required degree of approximation by Rayleigh (1894, sect. 348). They are:

continuity $$\operatorname{div} \mathbf{V} = -\frac{\partial s}{\partial t}, \tag{1}$$

state $$p = p_0(s + T/T_0), \tag{2}$$

motion $$\frac{\partial u}{\partial t} + \frac{1}{\rho_0}\frac{\partial p}{\partial x} = -\nabla^2 u - \frac{1}{3}\frac{\eta}{\rho_0}\frac{\partial^2 s}{\partial x\,\partial t}, \tag{3}$$

where $\mathbf{V}$ = particle velocity, s = condensation, u = x-component of $\mathbf{V}$, p = pressure, η = viscosity, ρ = density, t = time, T = temperature, and the subscript 0 indicates the ambient value.

The thermal equation will be modified as follows. It will be assumed that the energy stored in the vibrational degrees of freedom is exchanged only with the translational and rotational degrees of freedom, so that if there were no other form of heat exchange, we would have

$$C_v^\infty \frac{\partial T}{\partial t} = -C_i \frac{\partial \theta}{\partial t},$$

where C_v^∞ is the translational and rotational specific heat, C_i is the vibrational specific heat, and T, θ are the corresponding temperature amplitudes. If we specify that $T = 0$ on the bounding wall, then this equation holds up to the boundary. This condition is in fact employed in the later working. The full equation, including the effects of compression and of thermal conduction, becomes

$$\frac{\partial T}{\partial t} = (\gamma_\infty - 1)\,T_0 \frac{\partial s}{\partial t} + (\gamma_\infty - 1)\,T_0 \nabla^2 T - b\frac{\partial \theta}{\partial t}, \tag{4}$$

where $b = C_i/C_v^\infty$ and $\gamma_\infty = C_p^\infty/C_v^\infty$. Following Henry's (1932) method the relaxation will be specified by the equation.

$$\frac{\partial \theta}{\partial t} = \frac{1}{\tau}(T - \theta), \tag{5}$$

where τ is the relaxation time.

It follows from the diagram given by Weston (1953, fig. 1) that most low-frequency experimental systems lie in the 'wide tube' region, and that terms beyond the leading ones in the expansions for the velocity of sound c and the amplitude attentuation α are negligible. From equations (1) to (5) above one can eliminate T and then follow the calculation given by Rayleigh (1894). The propagation coefficient q is given by

$$q^2 = \pm\left(\frac{iw}{c_\infty}\right)\frac{(1 + iw\tau + b)}{(1 + iw\tau + b/\gamma_\infty)}\left(1 + \frac{(1-i)}{r(2w)^{\frac{1}{2}}}(\mu^{\frac{1}{2}} + \nu^{\frac{1}{2}}G)\right),$$

where $q = \alpha + iw/c$,

$$G = \left(\frac{1+iw\tau}{\gamma_\infty + iw\tau\gamma_\infty + b}\right)^{\frac{1}{2}} \left(\frac{1+iw\tau}{1+iw\tau+b}\right)(\gamma_\infty - 1),$$

c_∞ = high-frequency limit of the velocity of sound in the free gas,

$\mu = \eta/\rho_0$,

$\nu = k/\rho_0 C_v$ is the thermal diffusivity, and

w = angular frequency.

So long as $\arg G$ is small, the effect of the imaginary part of $(\mu^{\frac{1}{2}} + \nu^{\frac{1}{2}}G)$ on q is negligible. This is true for the cases of subsequent interest, for which the values of b are $< 0{\cdot}01$ and $0{\cdot}4$, and the values of $w\tau$ in the present experiments are $< 0{\cdot}35$ and $< 0{\cdot}04$ for oxygen and carbon dioxide, respectively. After simplification, we obtain

$$c = c(w\tau)\left(1 - \frac{\alpha_{HK}c}{w}\right),$$

$$c(w\tau) = c_0\left(\frac{1+b}{1+b/\gamma_\infty}\right)^{\frac{1}{2}} \left(\frac{(1+b/\gamma_\infty)^2 + (w\tau)^2}{(1+b)^2 + (w\tau)^2}\right),$$

$$\alpha = \alpha_{HK} + \alpha_r,$$

$$\alpha_{HK} = \frac{1}{rc}\left(\frac{w}{2}\right)^{\frac{1}{2}} (\mu^{\frac{1}{2}} + (\nu/\gamma)^{\frac{1}{2}}(\gamma - 1)) = gf^{\frac{1}{2}},$$

$$\alpha_r = \left(\frac{b(1-1/\gamma_\infty)}{c\tau}\right)\left(\frac{(w\tau)^2}{(1+b)(1+b/\gamma_\infty) + (w\tau)^2}\right),$$

where f is the frequency of oscillation.

At low frequencies we may neglect $(w\tau)^2$ in the denominator of the last equation and so obtain

$$\alpha_r = H\tau f^2,$$

where

$$H = \frac{4b(1-1/\gamma_\infty)\pi^2}{c(1+b)(1+b/\gamma_\infty)}.$$

So far, no attention has been paid to the effect either of viscosity in the body of the gas, or of the direct radiation of heat from the gas to the walls of the container. The former Stokes's absorption is given (see Rayleigh 1894) by

$$\alpha_c = \frac{8\pi^2\mu f^2}{3\rho_0 c_0^3},$$

while the latter, according to Bhatia (1957), is such that

$$\alpha_{\text{radiation}}/\alpha_{HK} \simeq f^{-\frac{1}{2}},$$

when f is expressed in cycles per second. There is no indication that either of these gives rise to a measurable effect in the present apparatus (Harlow 1954).

At the low frequencies used, $c(w\tau)$ is practically constant, so the above equations reduce to:

$$1/c = 1/c_0 + g/2\pi f^{\frac{1}{2}},$$

$$\alpha = gf^{\frac{1}{2}} + H\tau f^2.$$

Plots of $1/c$ against $1/f^{\frac{1}{2}}$ and of $\alpha/f^{\frac{1}{2}}$ against $f^{\frac{3}{2}}$ should both give straight lines yielding values of c_0 and g, and of g and $H\tau$ respectively.

Apparatus

The apparatus used was an acoustic interferometer 175 cm long with an internal diameter of 3·78 cm, enclosed in a thermostat. Plane waves were excited at constant amplitude from an electromagnetic loudspeaker with a flat diaphragm at one end of the sound tube, and reflected from a flush-fitting steel plate at the other end. A detailed description is given by Harlow (1954) and the later modifications described by Wintle (1959*a*). The results were obtained in the form of the current $\mathscr{I}$ required to operate the loudspeaker at constant amplitude at various frequencies in the neighbourhood of a natural resonance frequency of the tube. The quantity $\mathscr{I}/f$ is of the nature of a transfer impedance and changes rapidly from a maximum to a minimum in passing through a natural resonance frequency of the acoustic system. It can be plotted on a circle diagram. From the diagram the true resonance frequency and the corresponding attenuation can be determined. The velocity in the tube c which is obtained from the resonance frequency f_n is given by

$$\frac{4\pi f_n l}{c} = 2n\pi - \alpha\frac{lc}{\pi}\frac{\partial\alpha}{\partial f},$$

where l is the length of the tube, and n is an integer. (This relation will be derived in a further publication.)

The velocities found are individually correct to about 0·01 % and the attenuations to 10 % when relaxing gases are used. The variation of the attenuation with frequency is such that the last term in the above equation corrects the velocity by about 0·5 cm sec^{-1} in the present work, and can be neglected.

If the loudspeaker employed is of the electromagnetic type, the difference between extreme values of $\mathscr{I}/f$ in the neighbourhood of a resonance frequency is given by

$$\Delta(\mathscr{I}/f) = A\rho_0 c\,\frac{\operatorname{sh} 2\alpha l}{\operatorname{ch} 2\alpha l - 1}\,\frac{2\pi a_0}{BL},$$

so that $f/\alpha\Delta\mathscr{I} \simeq BLl/2\pi a_0 A\rho_0 c$, where A is the cross-sectional area of the sound tube, a_0 the amplitude of oscillation of the loudspeaker diaphragm, L the length of the coil winding, and B the field in the magnet gap. The amplitude a_0 is determined by the disappearance of a set of interference fringes in the manner described by D. H. Smith (1945). Using the first disappearance of fringes formed by mercury green light, the amplitude a_0 is about 1000 Å and the quantity $f/\alpha\Delta\mathscr{I}$ was found to be constant to about 10 %, the limit being set by the uncertainty in the measured values of α. This provides a valuable check that the effects found at different frequencies are not due to defects in the apparatus.

Preparation of the gases

Carbon dioxide

The gas was prepared in a Kipp's apparatus. The crude gas was washed with distilled water and saturated sodium hydrogen carbonate solution and passed through a solid carbon dioxide trap and over phosphorus pentoxide. It was then condensed in a liquid-air trap and the system pumped down to a pressure of 1 μ Hg for 15 min. The gas was then sublimed into the evacuated sound tube and the pressure brought up to 1 atm.

The conditions of preparation were such that the likely impurities, methane, ethane, carbon monoxide, sulphur dioxide, hydrogen chloride and water were removed in the carbon dioxide trap or pumped off the solid. Each sample prepared was discarded after a fortnight.

Air

Air taken from the laboratory was passed through a saturated potassium hydroxide solution, up a calcium chloride tower and then over phosphorous pentoxide before entering the sound tube.

Oxygen

The gas was prepared from 'Analar' grade potassium permanganate by heating. A similar preparation by Hoge (1950) showed that the impurity to be expected is about 2 parts in 10^7.

Results

Determinations of velocity and attenuation were made on each gas at frequencies between 80 cyc $\sec^{-1}$ and 1500 cyc $\sec^{-1}$. The measured values of velocity were reduced to the standard values of 1 atm pressure and 30 °C by assuming that over the experimental range of temperatures (less than two degrees) the velocity is proportional to the square root of the absolute temperature. The pressure correction, due to the imperfection of the gas, amounts to only 0·2 cm $\sec^{-1}$ (cm Hg)$^{-1}$ for CO_2 and is less for air and oxygen. The attenuations were reduced to the standard conditions by assuming that α is proportional to $p^{-\frac{1}{2}}$. This is a good approximation since the relaxation absorption is proportional to p^{-1} in the region of interest. The results of the velocity determinations are plotted in figures 1 and 2, and the results of the attenuation determinations in figures 3

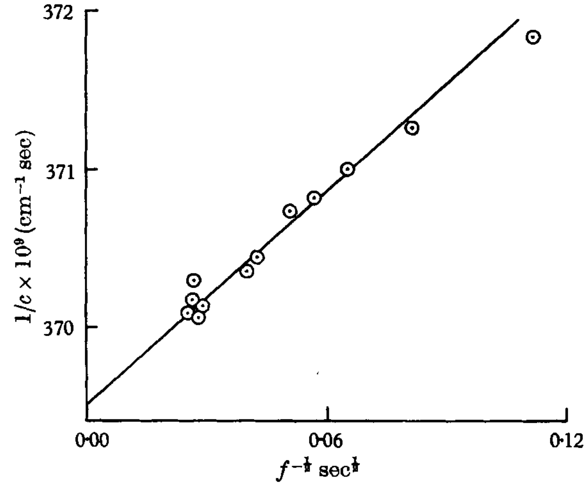

FIGURE 1. The reciprocal of the sound velocity in carbon dioxide as a function of frequency.

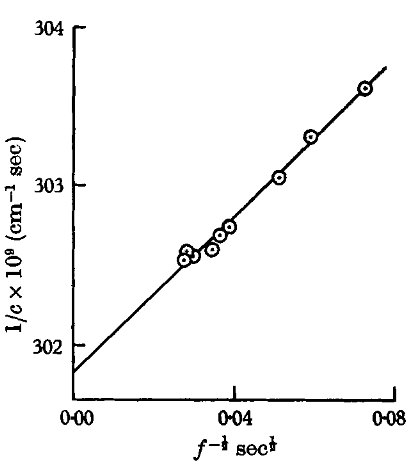

FIGURE 2. The reciprocal of the sound velocity in oxygen as a function of frequency.

and 4, and the details summarized in table 1. The velocities in air were found by the direct application of the Helmholtz–Kirchhoff relation to the measured values of tube velocity and attenuation.

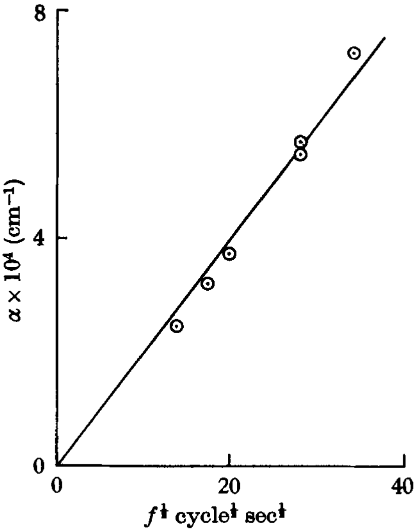

FIGURE 3. The attenuation in air as a function of frequency.

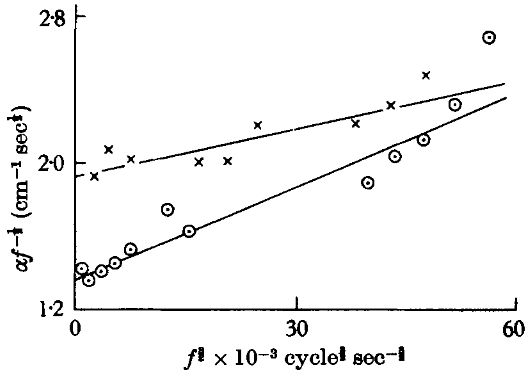

FIGURE 4. The total attenuation in carbon dioxide and oxygen as a function of frequency. ⊙, CO_2; ×, O_2.

Gas	CO_2	O_2	Air
No. of determinations	41	18	6
No. of frequencies	12	9	5
c_0 (m sec^{-1})	$270{\cdot}57 \pm 0{\cdot}03$	$331{\cdot}33 \pm 0{\cdot}04$	$349{\cdot}18 \pm 0{\cdot}02$
g (deduced from velocity) (cm^{-1} sec$^{\frac{1}{2}}$)	$1{\cdot}42 \times 10^{-5}$	$1{\cdot}54 \times 10^{-5}$	—
Correlation coeff.	0·96	0·99	—
g (deduced from absorption) (cm^{-1} sec$^{\frac{1}{2}}$)	$1{\cdot}36 \times 10^{-5}$	$1{\cdot}93 \times 10^{-5}$	$1{\cdot}90 \times 10^{-5}$
$H\tau$ (cm^{-1} sec^2)	$1{\cdot}70 \times 10^{-10}$	$0{\cdot}87 \times 10^{-10}$	—
Correlation coeff.	0·92	0·80	—
g (theoretical) (cm^{-1} sec$^{\frac{1}{2}}$)	$1{\cdot}20 \times 10^{-5}$	$1{\cdot}58 \times 10^{-5}$	$1{\cdot}60 \times 10^{-5}$
H (expected) (cm^{-1} sec)	$9{\cdot}3 \times 10^{-5}$	$2{\cdot}1 \times 10^{-6}$	—
τ (sec)	$1{\cdot}8 \times 10^{-6}$	4×10^{-5}	—

TABLE 1

The expected values of g were determined by calculating the viscosity and thermal conductivity from the data given by Keyes (1952), and using four-figure approximations for the density and ratio of specific heats.

The uncertainty in the velocity quoted is obtained for carbon dioxide and oxygen as the sum of the uncertainty due to the intercept of the graph plus the standard deviation obtained by correcting the individual velocity measurements by the Helmholtz–Kirchhoff formula, assuming these values to have a Gaussian distribution. Only the second term is considered for air.

The expected values for H are obtained from the formula above, assuming that for carbon dioxide $C_v^0 = 5R/2$, $C_v = 3{\cdot}515R$, and for oxygen that C_i is given by a single Einstein function with $\theta = 2260$ °K.

The specific heats

The velocity of sound in a free body of gas is given by

$$c_0^2 = \gamma(\partial p/\partial \rho)_T,$$

where γ is the ratio of the principal specific heats.

Gas	CO$_2$	O$_2$
	Beattie–Bridgman equations	
$\left(\frac{\partial p}{\partial \rho}\right)_T \frac{M}{RT}$	0·990 359	0·998 767
$\frac{C_p - C_v}{R}$	1·021 89	1·005 234
$\frac{(C_v - C_v^0)}{R}$	$5{\cdot}713 \times 10^{-3}$	$1{\cdot}653 \times 10^{-4}$
	Virial equations	
$\left(\frac{\partial p}{\partial \rho}\right)_T \frac{M}{RT}$	0·900 506	0·998 859
$\frac{C_p - C_v}{R}$	1·023	1·005 020
	Uncertainties	
$\frac{(C_p - C_v)}{R}$	0·001	0·0001
$\left(\frac{\partial p}{\partial \rho}\right)_T \frac{M}{RT}$	0·0001	0·0001

TABLE 2

Gas ...	...	CO$_2$	O$_2$
30 °C, 1 atm	γ	1·2907 ± 0·0004	1·3954 ± 0·0003
	C_v/R	3·515 ± 0·006	2·542 ± 0·002
	C_p/R	4·537 ± 0·008	3·547 ± 0·003
30 °C, zero pressure	γ^0	1·2849 ± 0·0004	1·3934 ± 0·0003
	C_v^0/R	3·509 ± 0·006	2·542 ± 0·002
	C_p^0/R	4·509 ± 0·008	3·542 ± 0·003

TABLE 3

The most accurate closed equation of state for carbon dioxide is that of Beattie and Bridgman (see Beattie & Stockmayer 1940). A virial expansion for oxygen has been given by Meyers (1948) and for carbon dioxide, using new data, by Michels & Michels (1937). The relevant thermodynamic functions are given in table 2. By adopting the numerical values given by the Beattie–Bridgman equation, together with the values $R = 8{\cdot}31436$ joule deg^{-1} mole^{-1} (Birge 1941), $M = 44{\cdot}011$ for CO$_2$ (Wichers 1954) and $M = 32{\cdot}00$ for O$_2$, the experimental values of the velocity of sound have been used to find the specific heats and specific heat ratios given in table 3.

Discussion

Most recent work on the velocity of sound in carbon dioxide has been carried out at ultrasonic frequencies, and the extrapolation to zero frequency does not have the precision required for the present purpose. The most accurate low-frequency determinations are listed in table 4. A correction suggested by Woolley (1953) has been applied to the work of Katz, Leverton & Woods (1949).

	Date	Frequency (cycle sec^{-1})	velocity ($m\ sec^{-1}$)
	Carbon dioxide		
Abbey & Barlow	1948	1000	271·2 ± 0·2
Katz, Leverton & Woods	1949	Low	270·67 ± 0·05
Koehler	1950	Low	270·87 ± 0·05
This work	1959	100–1500	270·57 ± 0·04
	Oxygen		
Abbey & Barlow	1948	1000	331·8 ± 0·2
Knötzel & Knötzel	1948	Audible	331·30 ± 0·08
Koehler	1950	Low	331·70 ± 0·13
This work	1959	200–1300	331·33 ± 0·04

TABLE 4. Velocity of sound determinations at 30 °C and 1 atm pressure.

	Date	Method	C_p^0/R
	Carbon dioxide		
Kistiakowsky & Rice	1939	Expansion	4·501 ± 0·008
Lapshina & Khomyakov	1951	Flow comparison	4·487 ± 0·009
Masi & Petkof	1952	Constant flow	4·495 ± 0·007
Woolley	1954	Spectroscopic	4·493
This work	1959	Velocity of sound	4·510 ± 0·008
	Oxygen		
Wacker, Cheney & Scott	1947	Constant flow	3·536 ± 0·005
Woolley	1948	Spectroscopic	3·536 ± 0·003
Masi & Petkof	1952	Constant flow	3·537 ± 0·005
This work	1959	Velocity of sound	3·542 ± 0·003

TABLE 5. Specific heat determinations at 30 °C

The best determinations in oxygen at low frequencies are also given in table 4. The values quoted by Knötzel & Knötzel (1948) were based on a value for the velocity of sound in air of 342·94 m sec^{-1} at 19 °C and 1 atm pressure. The value quoted in the table has been corrected in the light of more recent determinations. Recent specific heat determinations for both gases are compared in table 5.

With the exception of the work by Katz *et al.*, Koehler and the present authors, no account has been taken in the velocity investigations of the impedance effect pointed out by P. W. Smith (1952). He showed that the apparent wavelength measured in a tube is not independent of the transfer impedance between the acoustic and detecting systems. The analysis was carried out specifically for a two pole network, but there seems no bar to extending the argument to a system in which the exciting and detecting elements are separate. The frequency change brought about by allowing for the detector impedance is about 1 part in 500 in the present instance, so that the uncorrected velocity results from similar systems are suspect to about the same extent.

From the data given by Sette & Hubbard (1953), the apparent concentration of water vapour in the samples of carbon dioxide and oxygen was about 0·05 and 0·4 % respectively. However, the drying agents should have reduced the water-vapour content to about 1 part in 10^8. It is possible that the diffusion of excited molecules from the body of the gas to the walls of the tube, which takes place in a time of the order of 10^{-4} sec, plays a considerable part in the relaxation characteristics. Support for this assumption is given by the lack of relaxation effects in the results of Harlow (1954) and Lee (1957) on air.

Conclusion

The velocities of sound and specific heats found by the authors are in excellent agreement with other determinations. The velocities quoted by Koehler (1950) appear in both cases to be somewhat high.

It is seen from figures 1 and 2 that the form of the Helmholtz–Kirchhoff relation is obeyed by relaxing gases at low frequencies. The theoretical prediction that at these frequencies the tube and relaxation absorptions add linearly is confirmed from figure 4. The experimental Helmholtz–Kirchhoff coefficients are about 15 % in excess of the theoretical values, in agreement with the majority of work in this field (for a bibliography, see Lee 1957).

The measurement of the specific heats of gases by the velocity-of-sound method cannot be further improved until a more detailed knowledge of the equation of state is available.

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