REVIEWS OF MODERN PHYSICS VOLUME 27, NUMBER 1 JANUARY, 1955

Absorption and Velocity of Sound in Vapors

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I. INTRODUCTION

The admirable review by Markham, Beyer, and Lindsay,[1,*] entitled *Absorption of Sounds in Fluids*, gives experimental results mainly on liquids. Since dispersion is scarcely established in liquids, these authors perhaps rightly surmised that there was not much to be gained by including velocity measurements in their survey.

It is the object of the present author to supplement the first review by describing techniques used in studying the propagation of ultrasonics (mainly) and sound in gases and vapors, the results attained and to say something of the light which they throw on other processes and applications in which vapors may be involved. Since the prewar data are fairly completely documented elsewhere this survey will only cover the past fifteen years. Moreover, as the theory of relaxation is well covered in the earlier Review, it is hoped that it will be unnecessary to reproduce it here in full.

Analysis of Results

Apart from intrinsic interest in the results, or for the purposes outlined in the final section of this report, workers in this subject have been interested in the equation of state of a vapor, to determine virial coefficients, for instance, or thermodynamical relationships connected therewith, particularly at low temperatures or near the critical state; or else they have been looking for single or multiple relaxations of the molecule, connected with a lag in the transfer of translation into other forms of energy, vibrational or rotational. Fortunately, in many vapors, it is the former type which occurs and that monotonically, so that the theory proposed by Henry,[2] Kneser,[3] and others can be applied.

Elaborate and alternative forms of the single relaxation hypothesis are to be found in the paper[1] already cited. It will be sufficient for our purposes to state the results to be expected from this hypothesis; thus: If p is the pressure on the vapor, ρ the density, ω the pulsatance ($\omega=2\pi f$) and τ the relaxation time, C_p and C_v the usual specific heats, C_v' the complex specific heat appropriate to this case is defined by

$$C_v'=C_1+C_\omega(1+i\omega\tau)^{-1}, \tag{1}$$

wherein C_1 is the part associated with translation, C_ω that associated with vibrations (or rotations). The velocity of sound is given by

$$V^2=\frac{p}{\rho}\left\{1+(C_p-C_v)\frac{C_v+C_1\omega^2\tau^2}{C_v^2+C_1^2\omega^2\tau^2}\right\}, \tag{2}$$

and the ratio of specific heats peculiar to sound propagation

$$\gamma=1+R\cdot\frac{C_v+C_1\omega^2\tau^2}{C_v^2+C_1^2\omega^2\tau^2}. \tag{3}$$

When V_0 is the low-frequency velocity, V_∞ the high-frequency velocity and the mid-frequency value $\{V_0^2+\frac{1}{2}(V_\infty^2-V_0^2)\}$ occurs at a frequency f_m, the relation between V and f is

$$\frac{V^2-V_0^2}{V_\infty^2-V_0^2}=\frac{(f/f_m)^2}{1+(f/f_m)^2}, \tag{4}$$

also

$$f_m=\frac{1}{2\pi\tau}\cdot\frac{C_v}{C_1}. \tag{5}$$

If μ the (amplitude) absorption per wavelength is plotted against $\log f$, a symmetrical curve is obtained, of which the maximum μ_m is given approximately by

$$\mu_m=\frac{\pi}{2}\cdot\frac{R(C_v-C_1)}{C_1(R+C_1)}=\pi\left(\frac{V_\infty}{V_0}-1\right). \tag{6}$$

If α/f^2, α being the absorption per unit length, is plotted against $\log f$, the curve has the shape of the velocity dispersion reversed reaching the classical value (by interpolation of the viscosity coefficient) at high frequencies and lying $2\mu_m/V_0f_m$ higher at zero frequency.

As Herzfeld[4] has shown this quantity can also be expressed as

$$\frac{\alpha}{f^2}=\frac{2\pi^2}{V_0}\frac{C_p-C_v}{C_p\cdot C_v}\cdot C_\omega\tau. \tag{7}$$

If V_0 is not determined, it may be deduced from an assumed equation of state.

II. INTERFEROMETERS

Theory

The standard apparatus for ultrasonic work in gases remains the Pierce[5] variable path interferometer, in which the load on a quartz or other transducer due to a gas column of varied length is made to influence the anode current in the electronic tube coupled to the transducer. Writing the particle velocity in the (plane)

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[*] References will be found in Sec. XI, Bibliography, at the end of the paper.

progressive and retrogressive waves in the column (extending along x from 0 to l) as

$$\dot{\xi}_1 = Be^{-\alpha x}e^{i(\omega t-\beta x)},$$

and

$$\dot{\xi}_2 = Ce^{\alpha x}e^{i(\omega t+\beta x)}$$
$$(\beta = 2\pi/\lambda), \tag{8}$$

with $\dot{\xi}_0$ as that at the quartz, we may deduce the pressure amplitude by multiplying by the characteristic impedance (ρV) of the gas. Following Hubbard[6] we can divide it into two parts, one dependent on and one independent of frequency, thus,

$$p_0 = \rho V(\dot{\xi}P + \omega\xi Q). \tag{9}$$

The factors are given by conditions at the source face i.e.

$$P = \frac{\sinh 2\alpha l}{\cosh 2\alpha l - \cos 2\beta l}, \tag{10}$$

$$Q = \frac{\sin 2\beta l}{\cosh 2\alpha l - \cos 2\beta l}. \tag{10b}$$

At a resonance, where βl is zero we find

$$p_{\text{max}} = \rho V \dot{\xi}_0 \frac{\sinh 2\alpha l}{\cosh 2\alpha l - 1}. \tag{11a}$$

The minimum value occurs for a further increase of length of $\lambda/4$, to l', and is

$$p_{\text{min}} = \rho V \dot{\xi}_0 \frac{\sinh 2\alpha l'}{\cosh 2\alpha l' - 1}. \tag{11b}$$

The difference of these values may be read off from the driving circuit to give us the value of α.

Hardy[7] has pointed out that if the reflector is used in a region so far from the source that $\lambda/4$ is a small fraction of l the difference between the two values of pressure amplitude given in Eq. (11) allows simplication to

$$\Delta p = \frac{2\rho V \dot{\xi}_0}{\sinh 2\alpha l}. \tag{12}$$

(A discarded term involves $\alpha^2\lambda^2$ as coefficient. The latter quantity is negligible in practical ultrasonics.)

The reaction on the driving circuit causes a proportionate change in grid voltage as the path is lengthened. This again results in a proportionate change in mean anode current, I, the quantity that is measured. When l is large, we can, in fact, consider the resistance of the source to be constant. Thus if ΔI_a, ΔI_b are the differences between the respective values of these quantities at resonance and antiresonance, respectively, for two distances l_a and l_b,

$$\frac{\Delta I_a}{\Delta I_b} = \frac{\Delta p_a}{\Delta p_b} = \frac{\sinh 2\alpha l_b}{\sinh 2\alpha l_a},$$

or

$$\log_e \frac{\Delta I_a}{\Delta I_b} = 2\alpha(l_b - l_a). \tag{13}$$

This suggests a simple way of deriving α from a series of resonant and antiresonant peaks in the anode current as the reflector is moved. Correction may of course still be needed for diffraction effects.

Following this idea, many investigators have sought to determine α from a straight line plot of ΔI against l but the method is not to be adopted without consideration of the conditions under which the operation of the interferometer satisfies the underlying assumptions of these equations (*vide infra*).

Before enunciating these, let us apply Eq. (8) to a fixed column interferometer of resonant length in which the standing wave ratio $p_{\text{max}}/p_{\text{min}}$ is determined by a suitable detector, in place of observations on the coupling circuit as l is changed.

Adding the particle velocities given by Eq. (8) with the condition that at the reflector $x = l$, $\dot{\xi} = 0$, we have

$$\dot{\xi} = Ce^{(\alpha+i\beta)l}\left[e^{(\alpha+i\beta)(x-l)} - e^{-(\alpha+i\beta)(x-l)}\right]e^{i\omega t}. \tag{14}$$

Omitting the time factor and writing $A = Ce^{\alpha l}$ we obtain, for the velocity amplitude at the location x,

$$\langle \dot{\xi}^2 \rangle_{\text{Av}} = 2A^2[\cosh\{2\alpha(x-l)\} - \cos\{2\beta(x-l)\}]. \tag{15}$$

In a vapor α is usually small compared to β so that the maxima and minima in Eq. (15), as the location x of the detector is varied, are $2A\cosh\{\alpha(x-l)\}$ and $2A\sinh\{\alpha(x-l)\}$; whence α and β can be determined.

Conditions under which α can be determined from the Locus of Peaks

Hardy[7] himself has stated the conditions under which Eq. (13) is valid to be (a) $2\mu n > 2.5$, where μ is the absorption per wavelength and n the number of wavelengths elapsed between the source and the commencement of measurement as l increases, and (b) $\Delta I/I < 0.03$. These conditions have been verified for a capillary tube interferometer by Lawley.[12] When either of these conditions is unfulfilled the graph of $\log \Delta I$ against l is not a straight line.

Another condition, difficult to fulfil at low frequencies, is that the sound waves in the tube shall be plane. If the tube is wide enough, relative to the source diameter, for a diffraction pattern to be set up in front of the latter, one must consider how the wave form may thereby be changed. Near the source, considered as a disk of radius a, we have the Fresnel region of optics, in which the intensity fluctuates cyclically along the axis; further out at a distance greater than about $2a/\lambda$, the Fraunhofer region is found in which the central beam is fringed by "wings," the first minimum lying on a cone of solid angle $(0.61)^2\pi\lambda^2/a^2$.

It is evident that such diffraction, since it is always more or less present, will spoil the effects of molecular absorption such as may be taking place in the medium. In a truly plane progressive wave such as occurs in a pipe for wavelengths large compared to the diameter, the amplitude will be given by $\xi_0 e^{-\alpha x}$, but with diffraction, we must make the propagation constant complex. Born[8] has attempted to introduce such a damping factor into the equations of diffraction.

He shows that it is still possible to derive α from two axial measurements of pressure amplitude p_a and p_b provided the stations are outside the Fresnel regime. For example, at x and $x+\delta x$ the ratio

$$\frac{p_a}{p_b}=e^{\alpha x}\frac{\sin\frac{\beta}{2}\{\surd(a^2+x^2)-x\}}{\sin\frac{\beta}{2}\{\surd(a^2+\langle x+\delta x\rangle^2)-\langle x+\delta x\rangle)\}}, \tag{16}$$

whence

$$\alpha x=\log\frac{p_a}{p_b}\cdot\frac{\sin q/(x+\delta x)}{\sin q/x} \tag{17}$$

if x is large compared to a and q is written for $\pi a^2/2\lambda$.

As far as the author knows, however, this formula has not been applied by any experimenter. When diffraction would take part of the central orb outside the reflector, a loss correction for this cause based on simple geometry, and under the assumption that all the energy lies within the angle previously cited, is usually applied.

Even when diffraction loss is negligible another difficulty may be experienced in the form of satellite peaks alongside the main ones as the column length is varied. These may persist even after adjustment to parallelism of source and reflector. The origin of these was first suggested by Jatkar,[9] a further theory was given by Krasnooshkin,[10] and an experimental confirmation by Bell.[11] The latter has shown that radial vibrations may be set up in the interferometer tube, especially if the supposed piston-like motion of the source should fail.

A characteristic property of these waves is the dispersion of their velocity propagation. Thus

$$\lambda_s^2=\lambda^2/\{1-\lambda^2/\lambda_0^2\}. \tag{18}$$

Here λ is the wavelength for plane waves and λ_0 is a function of the tube diameter d, and the mode:

$$\lambda_0=\pi d/b_{MN}. \tag{19}$$

Here b_{MN} is the Mth root of the first derivative of the Bessel function of the first kind of order N. For complex modes b_{MN} is large and λ_0 is small. When $\lambda\equiv\lambda_0$, λ_s is infinite (at this wavelength the phase velocity is infinite and energy can no longer be propagated in the mode). λ_0 is known as the cut-off wavelength for the particular mode.

In most experimental cases investigated $\lambda\ll\lambda_0$. Then Eq. (18) approximates to

$$\frac{\lambda_s-\lambda}{\lambda}=\frac{\lambda^2}{2\lambda_0^2}. \tag{20}$$

If satellites are radial mode resonances their wavelengths must follow this law.

By finding the positions of satellites in a hydrogen filled interferometer (its tube 1-in. in diameter and a source of 250 kc/s X-cut quartz crystal), Bell[11] was able to measure the satellite wavelengths and identify them as cross modes in these formulas.

When these cross modes are present the observed absorption will be in excess of the true absorption of the gas by an amount due to the interference between different modes. The latter will be especially important when the former is small, as in monatomic gases.

Pierce Types

These follow broadly the design of their originator. The main requirements are the provision of a good screw, means of adjusting the source and reflector parallel, a container for the gas capable of withstanding the pressure to be applied, and of being maintained at the requisite temperature.

Double Crystal Types

Two crystals which are exactly matched as to frequency face each other across an intervening column of gas. The length l is varied by moving one of the crystals. A voltage of fixed amplitude is applied to one. Then the voltage developed at the other is measured and is found to pass through maxima and minima, as the separation changes, proportional to $\sinh\alpha l$ and $\cosh\alpha l$, whence again α and β.

Capillary Tube Types

These have been used (particularly by Lawley[12]) partly in an attempt to overcome some of the difficulties mentioned above as to deviation from plane waves and partly to test the validity of the formula of Kirchhoff[13] which applies in this case. The velocity of propagation is (slightly) reduced below the free-space value, V:

$$V_t=V\left[1-\frac{1}{r}\cdot\left(\frac{\nu}{2\omega}\right)^{\frac{1}{2}}\right]. \tag{21}$$

The absorption coefficient in the tube of radius r is

$$\alpha_t=\frac{1}{rV}\left(\frac{\omega\nu}{2}\right)^{\frac{1}{2}}. \tag{22}$$

On the other hand, in unrestricted space for plane waves

$$\alpha=\frac{\omega^2}{2\rho V^3}\left(\frac{4}{3}\nu+\frac{\gamma-1}{\gamma}\frac{\nu'}{C_v}\right), \tag{23}$$

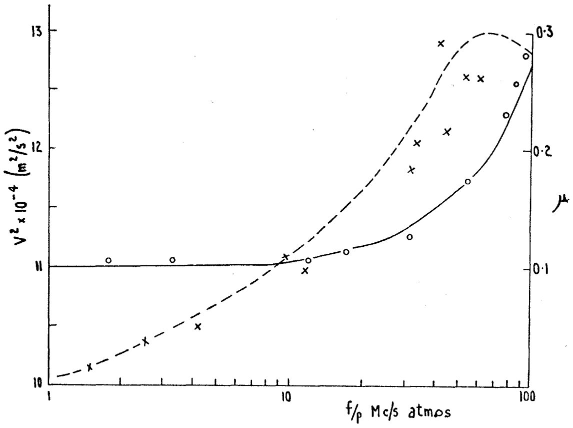

FIG. 1. Square of sound velocity (continuous line) and absorption per wavelength (broken line) plotted against parameter frequency/pressure in oxygen (*Thaler*).

where ν is the kinematic viscosity of the fluid, and ν' is the thermal diffusivity.

Lawley,[12] Weston and Campbell[14] have verified the validity of this formula, using gases of known viscosity in tubes down to 1 mm diameter. The sources were nickel needles maintained in magnetostriction oscillation and the reflectors brass pistons moved along the tube.

With such frequencies and slightly wider tubes there should be two sources of attenuation, given by Eqs. (22) and (23). Lawley has shown that the two effects are additive.

Hot-Wire Types

The hot-wire interferometer as usually practiced is an example of a fixed-path instrument to which Eq. (15) applies. It has been used by the author and a colleague on vapors.[15] Where a nickel or platinum wire of about 0.001 in. in diameter is set parallel to the wave front it may have its change of resistance directly proportioned to the velocity amplitude in a sound wave. From a plot of maximal and minimal readings in the vapor as the hot wire is moved between fixed reflector and source, set at a separation to produce standing waves, α and β may be obtained.

III. OTHER METHODS

It is possible, in theory, to make absorption measurements in progressive (either spherical or plane) waves if reflection from the walls and the end of the container is prevented by layers of absorbent material. At one time the radiation pressure on a vane, set at various distances from the source, was much used for this purpose. Now it is felt that its presence is liable to return energy to the source and/or disturb the wave front. Thus it is less used than formerly.

The Q of resonators filled with the gas have been measured mostly at sonic frequencies (by Tucker,[16] Oberst,[17] and others) with a view to deriving the velocity of sound and absorption in the gas.

Reverberation times in chambers filled with vapor have also been determined at sonic frequencies (Knudsen[18]) to get the absorption coefficient in the gas, after allowing for that due to the walls.

Pulse methods are hardly used in vapors except at low pressures because the usually small impedance of the gas and long ringing time of the quartz requires very long columns and short excitation times.

The method of passing a beam of light athwart a glass-sided column containing the fluid conveying plane progressive waves, was frequently used at one time in liquids especially for velocity. But this method had received little attention by those interested in gases, presumably because it requires high intensity at the source to obtain a sufficient change of density in the sound fronts to diffract the light. Bömmel[19] however was able to apply the method.

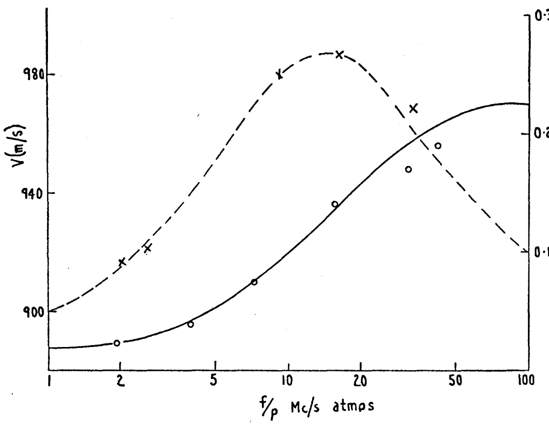

FIG. 2. Sound velocity and absorption per wavelength plotted against frequency/pressure in hydrogen (*Stewart*).

IV. RESULTS AT VARYING PRESSURE

When the rise in velocity and peak in absorption per wavelength, characteristic of a fluid having a single relaxation and occurring at the relaxation pulsatance, were first observed in carbon dioxide, it became apparent from the work of Richards and Reid,[20] and Railston and Richardson[21] at varying pressure in this gas that it was possible to bring all results onto a single curve, if they were plotted against the parameter frequency/pressure.

It has indeed become common practice to assume that this parameter will be relevant to the results in any vapor and accordingly to make a series of measurements at one or two frequencies over a range of pressure going down (usually) below atmospheric. Examples of the use of this procedure will be found in Figs. 1–4.

Air

From the work of Schmidtmüller,[22] gases of the atmosphere show no dispersion at audio-frequencies or low ultrasonic frequencies. However, recent results of Thaler[23] show dry, CO_2-free oxygen to have a relaxation at $f/p=60$ Mc/s atmos (Fig. 1). In nitrogen (Zmuda[24]) this effect occurs at 80 Mc/s atmos. Hydrogen and deuterium (Stewart and Stewart[26] and Rhodes[27]) exhibit a similar effect at about 15 Mc/s atmos (Fig. 2).

These are ascribed to a relaxation in the passage of translational into rotational energy. The specific heat of vibrations in these gases would come into the picture only at low sonic—almost infrasonic—frequencies.

Rare Gases

These show no dispersion which can be ascribed to relaxation and their absorption is classical, i.e., that given by Eq. (23).

When the pressure on a gas is greatly reduced, say to a few cm Hg the attenuation of a sound wave becomes very high. This in turn makes measurements of velocity in an interferometer very difficult and rather uncertain, for reaction on the source fails after a few peaks and one is wily-nily working very close to the source. Abbey and Barlow,[28] using a loud-speaker fed from a 1000 cps tone and a microphone in a tube, measured velocity to a few mm Hg in the gases of air, carbon dioxide, and methane. A tube correction based on Eq. (21) must be applied and, unfortunately, has the greatest effect at low pressures. Without it, there was no significant drift of V with f, but after correction V^* increased in all cases as the pressure was reduced below 10 cm Hg. (The term V^* indicates velocity reduced to 0°C where Charles' law is assumed.) Similar experiments have been made by Maulard[29] and Caro and Martin.[30] Though the former supported Abbey and Barlow, Caro and Martin with a somewhat more refined apparatus were unable to confirm this result (in air). They applied a tube correction 10 percent in excess of the Kirchhoff value (on the basis of the estimates of previous workers). They found the corrected velocity to agree with the accepted value for normal pressure. Zartman[31] recorded velocity and absorption in air, nitrogen, hydrogen, and carbon dioxide to 4.5 mm Hg and frequencies $\frac{1}{2}$ to 2 Mc/sec.

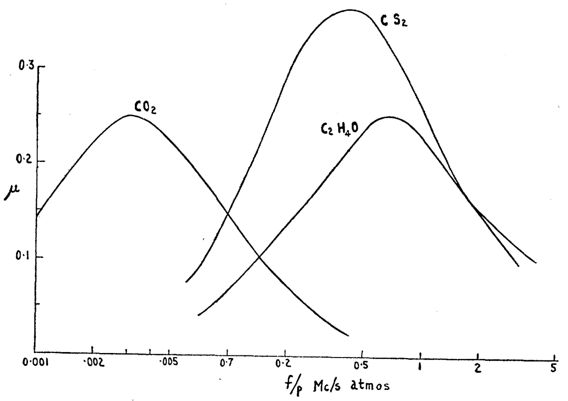

FIG. 3. Absorption per wavelength plotted against frequency/pressure in carbon dioxide, carbon disulfide, and ethylene oxide (*Angona*).

For a sufficiently high value of the product of sound frequency and kinematic viscosity ν, dispersion is possible even in a monatomic gas, where relaxations are not observed. The measured velocity is found to rise with a "Reynolds number of vibrations," a nondimensional parameter defined as $V_0^2/\omega\nu$. Results in helium have been obtained by Greenspan[32] at 1 Mc/s and pressures to 0.1 mm Hg (to vary ν) when the sound frequency is only about twice the molecular collision rate. Boyer[33] reported increases in velocity in argon, nitrogen, oxygen, and air at very low pressures where the wavelength approached the mean free path.

Parker, Adams, and Staveseth[34] measured absorption in argon, nitrogen, and oxygen from 1 to 10 mm Hg pressure. They used pulses from sources of about 60 kc/s to give a range of f/p of 5 to 50 Mc/s atmos. In all three α/f^2 was proportional to $1/p$ but the factor was greater than the classical in the air gases.

Triatomic Molecules

The notable dispersion of velocity in *carbon dioxide* at 20 kc/s at atmospheric pressure was already noted by Pierce.[5] Since then it has been confirmed as a function of f/p by many workers. This is also true of *nitrous oxide.* In *carbon disulfide* vapor the change in velocity is not so marked. In both this and in *ethylene oxide,*[35] plots of μ against $\log f/p$ give bell-shaped curves corresponding to single relaxation frequencies (for vibration) of 465 kc/s. (Fig. 3). COS has a relaxation at 300 kc/s; SO_2 at 1 Mc/s (Fricke[36] and Petralia[37]).

Polyatomic Molecules (Organic Vapors)

Ammonia

Steil[38] found a small dispersion of velocity in this gas from 429 to 431 m/s. This has been confirmed by Ozdogan[40] in the region $\log f/p$ 2 to 3.8.

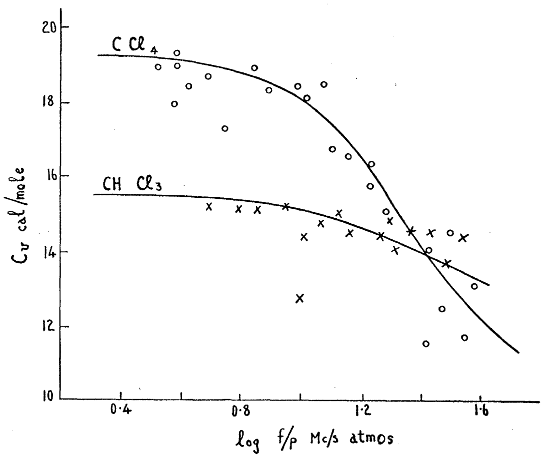

FIG. 4. Specific heats of vibration plotted against frequency/pressure in carbon tetrachloride and chloroform (*Fogg, Hanks, and Lambert*).

Ethyl Ether

Slight dispersion (V^*, 317 to 325 m/s) is evident, α/f^2 is about 20 times classical, and the maximum absorption is at $f/p=1$. (Matta and Richardson,[15] Nomoto,[41] and McConvrey *et al*[42]).

Propylene

Telfair[43] found no dispersion in this vapor at 12 Mc/s.

Ethylene Oxide

Angona's[35] μ values are shown in Fig. 3.

Dichlorethylene

This occurs in two forms, i.e., *cis* and *trans*. In both V and α have been measured by Sette, Busala, and Hubbard.[44] There is dispersion at $f/p=2.27$ and 10.5 Mc/atmos. In both C_v/R falls from 7.5 at 1 Mc/s to 3.5 at 100 Mc/s.

Ethylene Chloride and Ethylidene Chloride

Rao[45] has found that these vapors have slight dispersion at f/p 100 and 60, respectively.

Ethyl Alcohol

There is no dispersion to 1.8 Mc/s ($V^*=262$ m/s) (Railston[46]).

Ethyl Iodide

Here a slight dispersion (V^* 151 to 154 m/s) is evident (Railston[46]).

Ethyl Formate

Pusat[47] has measured velocities in this vapor and reports a relaxation of 2×10^{-8} sec.

Methyl Alcohol

No dispersion is evident. (Railston[46]).

Acetaldehyde

A number of workers, including Alexander and Lambert[48] and Matta and Richardson,[15] have reported a marked dispersion in this vapor (V^* 243 to 252 m/s). Furthermore the maximum μ at $f/p=0.3$ Mc/s atmos.

Benzene

Recently this vapor has been thoroughly tested by Lambert and Rowlinson[49] and Cheng.[50] Its velocity, reduced to 0°C, rises from 181.0 to 197.0 m/s with a maximum of absorption, $\mu=3$, at $f/p=9$ Mc/s. Cheng determined α by peak width at 30°C. He tried two relaxations at 4.4 and at 13 Mc/s atmos, but the fit of the experiments to a single one at 9 Mc/s atmos looks equally good. The other measurements were near 100°C.

In benzene α is 600 times classical at 100 kc/s and 23 times at 700 kc/s (Railston[46]).

Methane

This vapor was shown by Quigley[51] to have a velocity decreasing linearly with temperature below 0°C, at atmospheric pressure. Eucken and Aybar,[52] and also Telfair and Pielemeier[53] found, at temperatures near 100°C, a dispersion region about 300 kc/s corresponding to a relaxation of about 8×10^{-7} sec.

Pentane and Iso-Pentane

Here there is a gradual rise in V as the pressure is increased to 100 kg/cm^2 (Kling, Nicolini, and Tinsot[54]).

Carbon Tetrachloride and Chloroform

In this instance CCl_4 at 80°C showed <1 m/s and $CHCl_3<2$ m/s dispersion at atmospheric pressure, according to Railston[39] (to 700 kc/s). Jatkar[55] found similar results in CCl_4 at 97°C and $CHCl_3$ at 134°C. Fogg, Hanks, and Lambert[56] found, however, at 100°C (varying the pressure), a change in velocity in CCl_4 in the neighborhood of 2 Mc/s atmos. Hence they calculate the specific heats of vibration and compare these with values derived from spectroscopic data (Fig. 4). At 30°C Hubbard, Busala, and Sette[57] find these relaxations at 23.3 (CCl_4) and 27.3 ($CHCl_3$).

Halogen-Methane Derivatives

The velocities in a number of less common halogen-substituted methanes have been examined by the last two triumvirates. In CH_3Cl a rise, near 1 Mc/s, occurs at 100°C and at 30°C. In *methylene chloride* (CH_2Cl_2) the Oxford group find a single step at 2.5 Mc/s atmos but the Washington group claim a second rise at 105 Mc/s atmos. *Methyl chloride, bromide, and iodide* have single relaxations from 0.2 Mc/s atmos upwards; likewise, *methyl fluoride* CH_3F at 0.05, *fluoroform* CHF_3 at 0.30, *methylene fluoride* CH_2F_2 at 2, *carbon tetrafluoride* CF_4 at 0.3 Mc/s, all at or near 100°C. Byers[58] has values of μ in CF_4 at 22°C which agree with his velocity results to give a maximum at 0.48 Mc/s atmos. *Sulfur hexafluoride*, according to O'Connor,[59] has a relaxation which, at a temperature of 36°C, is located at 5.89×10^{-7} sec as determined from velocity measurements at pressures from atmospheric downwards. When 0.066 mole fraction of helium was added this time was reduced to 5.46×10^{-7} sec.

The *freons* can be regarded as substituted methanes, containing both chlorine and fluorine, which have low velocities combined with high absorptions and so have some technical importance (*vide infra*). Miyahara and the author are experimenting on these. Freon-12 (CCl_2F_2) has dispersion in the neighborhood of 1 Mc/s atmos where its absorption coefficient is as high as 0.04 ($\mu=0.2$).

The velocities in certain organic vapors will be found listed in the papers of Jatkar.[55] These have not been included here, because the range of frequency was insufficient to determine whether dispersion existed and the pressure remained atmospheric.

V. RESULTS AT VARIOUS TEMPERATURES

When temperature is varied, even on one of the more perfect gases, it is difficult to correlate the results with any chosen parameter. Mostly the attempt has been made with carbon dioxide. The only results which cover a sufficient range of frequency are those of Penman[60] and Warner.[61] However, these are in disagreement, as to the range of $V:T$, with the later ones of Overbeck and Kendall[62] who suspect that the earlier samples of gas were not free from impurity. At about 100 kc/s, the dispersive region, the velocity curve passes through the same drop with rising temperature as with rising pressure.

It is natural to attempt to plot against the parameter f/T, T being the absolute temperature, but the result is not very happy. Using Penman's and Warner's results, one can only say that the frequency corresponding to the middle of the downcast increases with the temperature in linear fashion.

Little work has been done at high temperatures in the neighborhood of 1000°C. Only that of Sherratt and Griffiths[63] on carbon monoxide can be cited and they used only two frequencies in the kilocycle gamut. The major difficulty is that the source, magnetostrictive in their case, must be kept cool so that it is almost impossible to avoid temperature gradients in the working section; further attempts should be made.

Most of the work at very low temperatures has been done by van Itterbeek and his colleagues. With Mariens[64] he made measurements in carbon dioxide, with van Paemal[65] in oxygen and deuterium, with van Doninck[66] in mixtures of hydrogen, nitrogen, oxygen, carbon monoxide, and helium, in carbon monoxide and deuterium,[67] and with Lauwers[68] in ammonia at various pressures. Most of these results are on velocity and they have been used to estimate the second virial coefficients in the equation of state at low frequency. (See Sec. VIII). A linear relationship between V and ρ is also found by Schneider and Thiessen[69] in helium.

VI. MIXTURES OF VAPORS

Although it was known in a qualitative fashion that the humidity of the atmosphere affected the attenuation of sound therein, it was Knudsen who precisely investigated the phenomenon at sonic frequencies in his reverberation chamber. Pielemeier[70] and Mokhtar and Richardson[71] pursued the effect to ultrasonic frequencies. Other adulterants, e.g., organic vapors in oxygen, increase the attenuation even when at low concentrations and usually, if the main gas shows a maximum of absorption, this is pushed to higher frequencies by the addition.

Possibly because there is no fundamental explanation of the effect, mixtures have been studied less frequently of late, although van Itterbeek and van Doninck[58] have studied mixtures of diatomic gases at low temperatures. Angona[35] worked with mixtures of the three vapors which he had studied separately. Sette and Hubbard,[72] studying the effect of impurities on the dispersion curve of carbon dioxide, found differences between light and heavy water vapor. (See also Pielemeier and Byers,[73] Knötzel,[74] and Petralia[75]).

It should be noted that in none of these cases is a chemical reaction concerned. However, Richards and Reid[76] have studied the dissociation of nitrogen tetroxide in the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ by ultrasonic methods. This was done in the hope of being able to sort out the relaxing effect we have been discussing from a purely chemical one. Both these lead to the same ultrasonic effects, *viz.*, increase of velocity and absorption. These writers, contrary to Teeter,[77] think that it should be possible, at least in gases for which the heat of dissociation is large, to disentangle the two effects. This would be particularly true if readings in the dispersion range were made at various pressures and temperature.

VII. RESULTS NEAR THE CRITICAL STATE

After the construction and testing of the pioneer high-pressure interferometer of Hodge and Hubbard,[78] Herget,[79] and Noury[80] measured carbon dioxide and ethylene velocities at one frequency (266 kc/sec) to the critical pressure (76 and 52 atmos, respectively) and

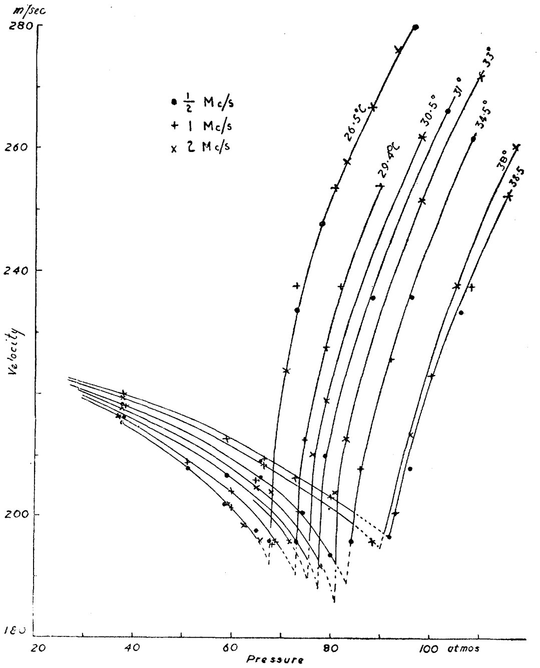

FIG. 5. Sound velocity plotted against pressure for various temperatures in carbon-dioxide (*Parbrook and Richardson*).

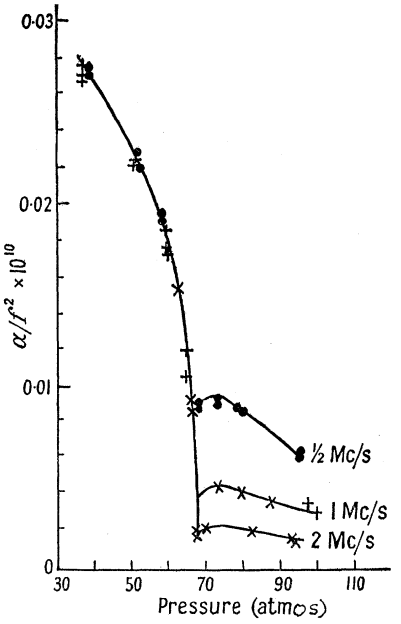

FIG. 6. Absorption divided by square of frequency against pressure at critical temperature in carbon dioxide (*Parbrook and Richardson*).

found the sharp minimum characteristic of this point. In the last few years both V and α have been determined by Schneider,[81] Anderson and Delsasso,[82] Parbrook and Richardson,[83] and Teilsch and Tanseberger.[84] In these gases the last authors used three frequencies and extended the range of pressure into the liquid phase. At pressures above that corresponding to $f/p=0.1$ there is no dispersion of the velocity, but the minimum just referred to is displaced with temperature (Fig. 5).

By selecting published values of the product pv (v being the specific volume) which represents the square of the isothermal velocity and dividing into the square of the measured (adiabatic) velocity, it is possible to exhibit deviations from the perfect gas law. At low pressures this quotient is the ratio of specific heats for these gases. (See Table I).

Schneider[81] first noted a very high value of the absorption at and near the critical point, which he ascribed to a relaxation. However, if one tries parameters of α and f, it proves to be α/f^2 which is relevant to the vapor phase, as usual, whereas α/f brings the author's results into coincidence on the liquid side of transition (Fig. 6). This strongly suggests, by its form, a scattering mechanism such as one observes in the passage of light through a suspension of globular entities of size comparable to the wavelength of the radiation.

TABLE I. Values of ratio of specific heats.

Gas	Temp.	Pressure (atmos.) 1	30	40	50	60	70	80
CO_2	38°C	1.29	1.30	1.32	1.33	1.35	1.45	1.66
CO_2	31.°C	1.29	1.31	1.32	1.35	1.40	1.68	2.78
CO_2	26.5°C	1.29	1.32	1.34	1.37	1.50	2.68	5.45
C_2H_4	18.7°C	1.25	1.30	1.31	1.35	1.43	2.15	3.30

Schneider[85] has studied other two-phase systems. Sulfur hexafluoride ($t_c=45.6$°C, $p_c=36$ atmos) at 600 kc/s shows very well the sharp inflections—in opposite senses—as the temperature rises along an isobar (Fig. 7). With Chynoweth[86] he measured both V and α in zenon.

It may be noted that other critical transitions are found in helium at temperatures of a few degrees absolute. For example, when the gas turns to liquid HeI and again in the transition HeI to HeII (liquid), Atkins and Chase,[87] van Itterbeek,[88] Lacam,[89] and Noury[90] find a continuous rise of velocity in argon (at 950 kc/s) and nitrogen along isothermals. In methane, however, Lacam[77] notes a dispersion at high pressures—he goes to 900 atmos—which is the opposite to that at low pressures; the velocities at 3 and 5 Mc/s lie below those for 900 kc/s both at 25°C and 50°C. These French investigators are working well above the critical point, so that the inflections noted above are not to be anticipated.

VIII. DERIVATION OF THERMODYNAMIC RELATIONS

Now that quite detailed and precise measurements of the velocity of sound in vapors are available the question arises whether they can be used to derive some of the thermodynamic relationships which are now required by physical chemists and chemical engineers. For these it is necessary to have values over a detailed field of pressure and temperature, such as those of Fig. 5, at frequencies where dispersion is not evidenced. In part, this detail must be precise enough to enable one to measure gradients of the curves with accuracy.

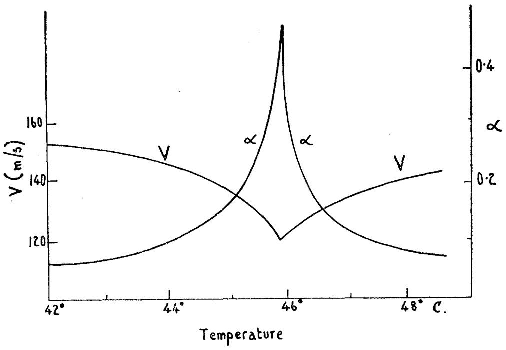

FIG. 7. Sound velocity and absorption coefficient at critical pressure plotted against temperature in sulfur hexafluoride (*Schneider*).

To give examples, the velocity of sound may be expressed, when v is the specific volume, as

$$V^2=-v^2\left(\frac{\partial p}{\partial v}\right)_T+v^2\left(\frac{\partial p}{\partial T}\right)_v^2\cdot\frac{T}{C_v},\tag{24}$$

(Hardy, Telfair, and Pielemeier[91]). When the slope along an isothermal goes to zero, as at the critical point, we are left with the second term. From this $(\partial p/\partial T)_v$ can be calculated, given C_v from other experiments.

The velocity of sound may also be expressed in terms of entropy S, as $V^2 = -v^2(\partial p/\partial v)_S$, which has the advantage of having entropy as independent variable. Or, in terms of pressure and temperature,

$$V^2 = \frac{-\left(\frac{\partial G}{\partial p}\right)^2 \cdot \left(\frac{\partial^2 G}{\partial T^2}\right)}{\frac{\partial^2 G}{\partial p^2} \cdot \frac{\partial^2 G}{\partial T^2} - \left(\frac{\partial^2 G}{\partial p \cdot \partial T}\right)^2}. \qquad (25)$$

The independent variables herein are pressure and temperature and this is convenient for deriving tables of Gibbs' function G.

These examples are given to show the possibilities of applying acoustic measurements to the compiling of thermodynamic tables.

The velocity of sound can also be expressed by using the molecular weight M_0 thus

$$V^2 = -\gamma\left(\frac{\partial p}{\partial v}\right)_T \cdot \frac{v^2}{M_0}. \qquad (26)$$

To determine the second virial coefficient B of a gas near its condensation point from plots of velocity as a function of pressure at various temperatures, van Itterbeek and Keesom[92] used the equation of state of Kamerlingh Onnes, *viz*, $pv = RT(1 + B/v)$.

Equation (26) then becomes

$$V = V^*\left(1 + \frac{Sp}{RT}\right), \qquad (27)$$

$$X = B + \frac{T}{h} \cdot \frac{dB}{dT} + \frac{T^2}{2h(h+1)} \cdot \frac{d^2B}{dT^2} \quad \text{with} \quad h = C_v/R.$$

Plots of V against p are usually straight lines and, for different temperatures, these can be extrapolated to zero pressure to give V^*. This can be checked against its value based on the ideal γ (for $p=0$). The slopes of these lines enable X to be determined for different temperatures, against which it is plotted. Van Itterbeek and Paemel,[57] for their measurements in oxygen at low temperatures, tried an expansion for B in the form

$$B = a + bT^{-3} + cT^{-4} + dT^{-5} + eT^{-6}. \qquad (28)$$

To find the coefficients $a \cdots e$, several test values of B can be computed from Berthelot's equation

$$B = \frac{9}{128} \frac{RT_c}{p_c}\left(1 - \frac{6T_c^2}{T^2}\right), \qquad (29)$$

(the suffixes refer to the critical point) and combined with values of X from the experiments. Figure 8 shows the results for oxygen; X and B are plotted against T^{-1}.

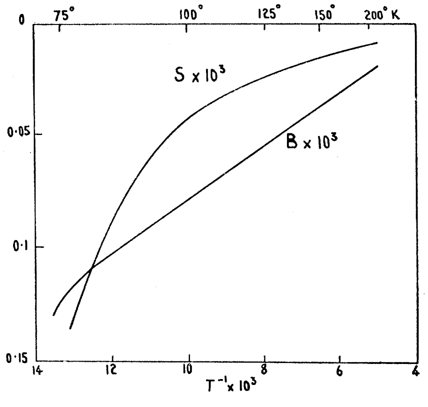

FIG. 8. Virial coefficients in oxygen: B and X *versus* reciprocal of absolute temperature (*van Itterbeek et al.*). S on block stands for X.

A number of the workers already quoted, e.g., van Itterbeek *et al.*[64–66] and Lambert *et al.*[48,56] used this method of computing.

IX. SHOCK WAVES IN VAPORS

The shock waves initiated when a gas impinges on an obstacle at a speed U near or above the velocity of sound are intense sound waves. It is no longer possible to consider the density as constant, therefore, Bernoulli's equation must be modified accordingly and the ratio of the specific heats, γ, enters into the equations connecting pressure, temperature, and density as well as the Mach number, $\mathrm{M} = U/V$.

At low velocities, forces on a body of chord c are a function uniquely determined by the Reynolds number $\mathrm{Re} = Uc\rho/\eta$, η being the viscosity and ρ the density of the ambient fluid. To suit experimental convenience we can alter the values of velocity, etc. provided we keep the Reynolds number the same. There is, however, no point in changing from one gas to another without changing the pressure since all gases have about the same value of η. At speeds where the compressibility of the air has to be taken into account the Mach number of the flow enters as a second similarity parameter. It is obvious here that the substitution of air by a vapor having a low value of V will result in the same Mach number for lower power. The power expended in a wind tunnel of cross section A can be written $k\rho AU^3$, where k is the power factor of the tunnel and depends on the tunnel design. To keep the tunnel area/model size the same, A/c^2 must be constant. It can easily be shown that if this is done, for constant Re and M, the power varies as $\eta V^3/\gamma p$.

The suggestion has been made by Smelt[93] and others that one of the chloro-fluorine derivatives of methane (known in the refrigerating industry as freons or arctons) or one of the hexafluorides should form the substitute vapor. In them the velocities are less than half that in air and they are inert and nontoxic withal. In fact, high-speed tunnels of this type using freon-12

(CCl_2F_2) are in operation in the United States and in England. Certain questions arise, however, as to the exact correspondence of fields of flow even when the Reynolds number and Mach number are correct. The principal questions are:

(1) Does the change in γ significantly alter the flow field and, if it does, can a correction be made for this?
(2) Is the equation of state of the same form?
(3) Will the vapor condense due to the lowering of temperature in an expansion.

With regard to the variation of flow field with γ, von Doenhoff, Braslow, and Schwartzberg[94] have shown that, at a particular speed, variation of γ can be compensated by a change in the relative thickness of the model. This is true even though a change in γ from 1.4 in air to 1.13 in freon, involves an almost negligibly small change in the thickness of the chord ratio. The speed range over which freon is an adequate substitute for air is, however, limited and is, in fact, from low speeds to about 1.2 times the speed of sound.

If the relaxation time differs from that of air the whole flow pattern may be altered. The work of Miyahara and the author referred to in Sec. VI is pertinent. If the relaxation time in freon 12, 1.5×10^{-7} sec, is confirmed it means that a shock taking place at a local $M=2$ ($U=300$ m/sec) at a distance of 1/20 mm in front of the nose would be completely relaxed in this distance, whereas the shock front in air would be scarcely affected in the corresponding passage. One would think this must affect the local pressure on the model.

In this connection a method other than acoustical for measuring relaxation times was suggested by Kantrowitz.[95,96] It consists in measuring with a Pitot tube the total pressure head in a jet of gas debouching from a reservoir. One would expect this to equal the pressure inside the reservoir, provided there are no losses in turbulence, etc. But, if the gas is stopped more suddenly at the nose of the Pitot tube than the time required for the energy adjustments we have been discussing, the pressure registered by the Pitot manometer will be different for the compression will take place as though vibrational.

Proximity of conditions in the working fluid to the critical state affect both questions (2) and (3). Assuming, say, van der Waals' equation, it would be possible to make some modifications of the thermodynamic expressions for the pressures and temperatures in terms of the constants a and b of that equation, but a general formula of correction would be difficult to obtain. It has been estimated that the temperature at the surface of a model, where the velocity is highest, is γ^{-1} times the stream temperature. This sets a limit to the temperature at which a tunnel containing a vapor can be operated to avoid condensation. Also, as Fig. 5 shows, there is a disadvantage in power consumption if one works near the critical state. In such an instance V and η are rapidly changing.

This eliminates carbon tetrafluoride (one which has been suggested), but we are making sound measurements on the hexafluorides of sulfur, selenium, and tellurium which look promising.

It is difficult to say precisely what the high absorption coefficient in these vapors (as compared to air) signifies in this application. It must, one would think, have an effect on the devolution of the shock wave front.

It should be possible to measure changes in wave front thickness due to such relaxations by a schlieren method. This has been attempted by Hubbard, Kankovsky, and Thaler[97] with intense ultrasonic waves in carbon dioxide, while Hornig *et al.*[98–100] have been taking shadow photographs of the density in pulsed shock fronts progressing along a tube filled with nitrogen or oxygen in an attempt to correlate these densities with some assumed relaxations in heat capacity. Present day optical techniques do not seem sufficiently developed to base precise conclusions on the photographs.

X. ACKNOWLEDGMENT

The author is indebted to Assistant Professor Y. Miyahara for assistance in checking the numerical data and references.

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