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Dispersion of the Velocity and Anomalous Absorption of Sound in Hydrogen

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The velocity and absorption of sound in hydrogen were measured at frequencies of 3.855 Mc and 6.254 Mc and pressures of 1.00, 0.83, 0.67, and 0.50 atmos., with all observations made at 25°C. Dispersion of the velocity from 1321.9 m/sec. to 1382.0 m/sec. and anomalous absorption which were observed are interpreted as caused by molecular absorption induced by loss of the rotational degrees of freedom. Calculations place the inflection point of the dispersion curve at 10.95 Mc and the peak of the absorption curve at 10.0 Mc from velocity data, and at 16.1 and 14.8 Mc from absorption data. The relaxation times for pressures of 1 atmos. from the two sets of data are 1.9 and 1.7×10^{-8} sec. The f/p law is not strictly obeyed.

INTRODUCTION

THE so-called molecular dispersion and absorption of sound in gases was first inferred by Herzfeld and Rice[1] from considerations advanced by Rice regarding the velocity of chemical reactions in gases. As first postulated by these authors: "A slow rate of exchange between external and internal degrees of freedom keeps the internal degrees from taking up the whole amount of heat, and therefore acts as if the effective specific heat were decreased, and the velocity of sound increased with increasing frequency." The well-known results of G. W. Pierce[2] on CO_2 were already at hand to serve as a partial test of the theory. Bourgin[3] followed with another approach to the problem, and Kneser[4] derived useful equations and gave new experimental results, using the Pierce piezoelectric oscillator.

With the exception of the results presented in the present paper, and the indications obtained by Stewart, any dispersion in the velocity may be explained in terms of a lag of equilibrium between the translational and vibrational states of the molecule activated by the sound wave. Evidence of dispersion due to such a lag between translational and rotational states has hitherto not been found, though looked for, especially in hydrogen.

Richards and Reid[5] reported a dispersion in hydrogen in the 400-kc region, but Wallmann[6] later showed that there was no dispersion between 385 kc and 1.48 Mc. Roy and Rose,[7] from theoretical considerations, predicted that any dispersion in hydrogen should come above 1.5 Mc, and found experimentally that it did not occur up to 1.465 Mc. Van Itterbeck and his co-workers,[8] who have made extensive studies of hydrogen at 300 kc and 600 kc, found at times a small increase in the velocity over the classical value. However, they were never able to reproduce the effect, and finally determined that it did not exist at their frequencies. Their work on velocity is significant because it illustrates the wide variation in different samples of hydrogen and indicates the great care that must be taken to secure pure gas. They did find an anomalous absorption which they ascribed to molecular absorption because of the loss of the rotational degrees of freedom. This absorption they studied as a function of temperature and pressure and determined a relaxation time.

The present study was instigated by Stewart's[9] measurements in this laboratory on impure hydrogen, which indicated a dispersion in the frequency region between four and eight megacycles. The purpose of the present work was to

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[1] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

[2] G. W. Pierce, Proc. Am. Acad. Sci. **60**, 271 (1925).

[3] D. G. Bourgin, Nature **122**, 133 (1928); Phys. Rev. **42**, 721 (1932).

[4] H. O. Kneser, Ann. d. Physik [5] **11**, 761 (1931).

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[8] A. Van Itterbeck and P. Mariens, Physica **4**, 609 (1937); A. Van Itterbeck and L. Thys, Physica **5**, 889 (1938); A. Van Itterbeck and R. Vermaelen, Physica **9**, 345 (1942).

[9] J. L. Stewart, Dissertation, Johns Hopkins University (1943); Rev. Sci. Inst. **17**, 59 (1946).

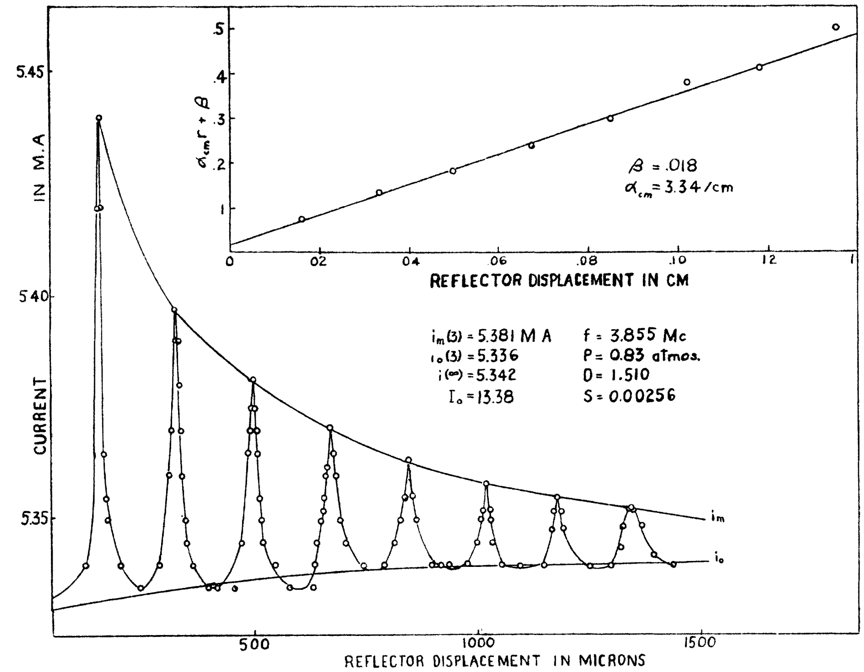

FIG. 1. Graph of peak structure and ($\alpha_{cm}r+\beta$) *vs.* r for $\alpha=3$/cm and $\beta=0.02$.

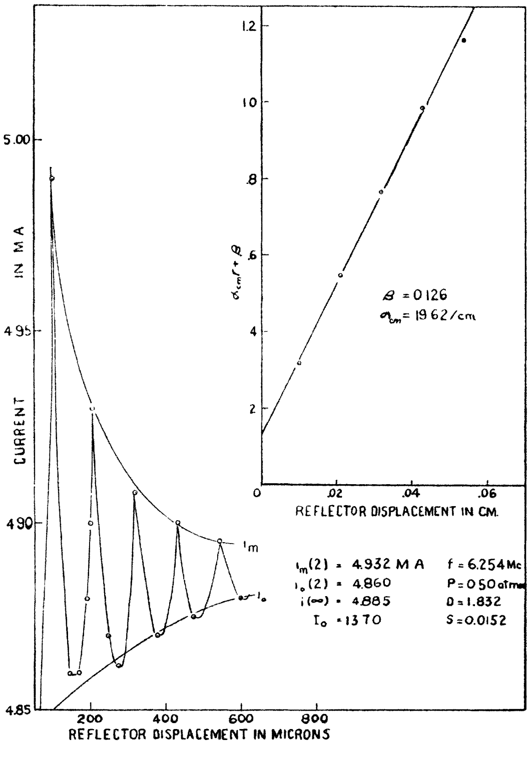

FIG. 2. Graph of peak structure and ($\alpha_{cm}r+\beta$) *vs.* r for $\alpha=20$/cm and $\beta=0.13$.

determine whether such a dispersion and the associated increased absorption did occur in pure hydrogen at frequencies above four megacycles. A preliminary report of the results has been made.[10]

THEORY

The acoustic interferometer circuit, of the type used in this work, was developed and first analyzed by Hubbard[11] for the measurement of ultrasonic absorption and reflection coefficients. Alleman[12] modified the treatment to include dissipative losses in emission as well as reflection at the source. The present paper employs a new treatment developed by Hubbard[13] for the case in which the absorption coefficient is large.

With the interferometer crystal in the resonant circuit, the current in the thermocouple-cross in the circuit is a function of the amplitude of vibration of the crystal, which, in turn, is a function of the reflector displacement, as shown in Fig. 1 and Fig. 2. These figures illustrate the

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[10] E. S. Stewart, J. L. Stewart, J. C. Hubbard, Phys. Rev. **68**, 231 (1945).

[11] J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932).

[12] R. S. Alleman, Phys. Rev. **55**, 87 (1939).

[13] J. C. Hubbard (to be published).

resonance of the fluid column and the associated damping of the vibration of the crystal. Since this damping results in current peaks, the determination of the positions of these peaks gives a simple method of measuring the velocity of sound.

The calculation of absorption and reflection coefficients for hydrogen from these data is more difficult. According to the theory[11,12] a certain function, ϕ, of the current in the thermocouple cross has the property that the reciprocal of its values for successive peaks, $1/\phi_m$, is a linear function of tanh $(\chi_m/2)$, where $\chi_m/2=\alpha r_m+\beta$. Here α is the amplitude coefficient of absorption per cm for particle velocity, r the distance of reflector from source, and $e^{-\beta}=\gamma$, the amplitude coefficient of reflection between gas and solid (source or reflector). Absorption coefficients measured hitherto by this method have been small enough to allow the approximation, $\tanh(\chi/2)\doteq(\chi/2)$. From the slope of the $\chi/2$ *vs.* m curve and the half-width of a peak, the absorption and reflection are evaluated. In the present work the value of α was so great that the above approximation is not valid. Moreover, approximations made in the previous work using peak width data are no longer valid, necessitating a restudy of the whole procedure of evaluating α and β from the data.

As a result of this the following method for calculating the absorption and reflection coefficients has been developed.[13] We define $\sigma_0=i_0/I_0$ and $\sigma_m=i_m/I_0$ in which (Fig. 1) i_0 is the current at the minima of the reaction curve, i_m is the value at the maxima, and I_0 is the value of the current when the interferometer and crystal are replaced by their equivalent capacity.

From Alleman's[12] paper we have

$$P=\sinh\chi/(\cosh\chi-\cos\delta), \tag{1}$$

where

$$\chi=2(\alpha r+\beta),\quad \delta=\frac{r-n\lambda/2}{\lambda/2}\cdot 2\pi.$$

TABLE I. Velocity of sound in pure hydrogen at 25°C.

f(Mc)	p(atmos.)	$\bar{V}$(m/sec.)	S.D. (m/sec.)	S.D. (%)	Number of determinations
3.855	1.00	1321.9	1.08	0.082	6
	0.83	1329.8	2.59	0.15	7
	0.67	1340.7	4.03	0.30	6
	0.50	1349.9	4.08	0.31	6
6.254	1.00	1365.0	3.28	0.24	6
	0.83	1366.0	3.82	0.28	4
	0.67	1373.4	5.91	0.43	5
	0.50	1382.0	3.59	0.26	8

Hubbard[11] showed that, S and D being constants,

$$\sigma=(1+SP)/(1+SP+D). \tag{2}$$

For reaction peaks $r=n\cdot\lambda/2$, so $\delta=0$ and

$$\begin{aligned}P=P_m(n)&=\sinh\chi/(\cosh\chi-1)\\&=1/[\tanh(\alpha r+\beta)].\end{aligned} \tag{3}$$

Similarly for troughs $r=(n-\frac{1}{2})\cdot\lambda/2$, $\delta=\pi$, and

$$\begin{aligned}P=P_0(n-\tfrac{1}{2})&=\sinh\chi/(\cosh\chi+1)\\&=\tanh(\alpha r+\beta).\end{aligned} \tag{4}$$

If curves are drawn through the experimental points $i_0(n-\frac{1}{2})$ a hypothetical value of $P_0(n)$ can be found at $r=n\cdot\lambda/2$ by interpolating for $i_0(n)$. Then from (3) and (4)

$$P_m(n)=1/P_0(n). \tag{5}$$

Using (2) we obtain the equations

$$SP_m(n)=\frac{\sigma_m(n)}{1-\sigma_m(n)}D-1, \tag{6}$$

$$SP_0(n)=\frac{\sigma_0(n)}{1-\sigma_0(n)}D-1. \tag{7}$$

For the case of high absorption, i_0 and i_m rapidly approach the same limiting value $i_0(\infty)=i_m(\infty)=i(\infty)$ and from (6) or (7)

$$S=\frac{\sigma(\infty)}{1-\sigma(\infty)}D-1. \tag{8}$$

D can be separated from S by squaring (8) and equating to the product of (6) and (7), and S is then calculated from (8). After S and D have been found $P_m(n)$ can be determined for each value of n.

According to (3)

$$\tanh^{-1}(1/P_m)=\alpha_{cm}r+\beta. \tag{9}$$

Therefore, if $\tanh^{-1}(1/P_m)$ is plotted against r, the intercept is β and the slope is α_{cm}. This is shown in Fig. 1 and Fig. 2 for two different α's. α_λ, the exponential amplitude absorption coefficient per wave-length, is $\alpha_{cm}\cdot\lambda$. The exponential intensity absorption coefficients are $\mu_{cm}=2\alpha_{cm}$ and $\mu_\lambda=2\alpha_\lambda$. The exponential intensity reflection coefficient $\beta^*=2\beta$.

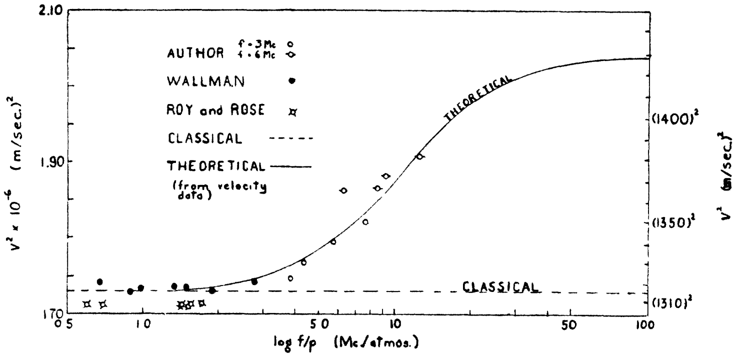

FIG. 3. V^2 against log (f/p) for hydrogen at 25°C.

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this work consists of three parts: the interferometer, the electrical circuits, and the gas-handling system.

The interferometer is that described by Stewart.[9] It is a variable-path, constant-pressure interferometer designed for high frequency work, with the piston surface kept parallel to the crystal to an accuracy of two light fringes. The path is varied by a micrometer screw whose motion is communicated to the piston through a bellows. The micrometer screw was driven by a small, reversible Telechron motor.

A conventional oscillator-amplifier combination was used to drive the interferometer crystal in the usual resonant circuit, and a thermocouple-galvanometer combination was used to detect and measure the r-f current.

The interferometer was part of a vacuum system that was evacuated before the gas was admitted and contained a trap to which refrigerants could be applied.

Since it has been shown that the velocity in hydrogen depends a great deal on the purity of the gas, every attempt was made to obtain and maintain a high degree of purity. The gas used was said to have a purity of 99.9 percent. In spite of all the precautions taken while transferring the gas from the tank to the vacuum system, some impurities not removed by a liquid nitrogen trap contaminated the gas as evidenced by low values for the velocity. Finally liquid hydrogen, applied after the trap had been cooled with liquid nitrogen, was used. Both the gas and liquid hydrogen were supplied by the CY Laboratory, Johns Hopkins University.

Before making the velocity and absorption measurements, the resonance circuit was tuned to the natural frequency of the crystal so the crevasse came below the peak of the resonance curve. With the oscillator driving the crystal in its crevasse, the piston was moved away from the crystal, and galvanometer deflections were recorded as a function of micrometer readings (Fig. 1 and Fig. 2). The galvanometer and thermocouple combination had been calibrated with direct current, making it possible to convert galvanometer readings into currents through the thermocouple. With full power (approximately 1.5 volts across the crystal) the deflection of the first peak at one atmosphere pressure was about three centimeters. Because of the large absorption, at reflector distances of a few wave-lengths the deflections fell off to one or two millimeters. It was necessary to read these deflections to one-tenth of a millimeter.

The frequency of the crevasse was measured by beating the oscillator against a calibrated precision signal generator concurrently checked by a 10-kc, crystal-controlled multivibrator. The temperature of the gas was measured by a calibrated thermometer with tenth-degree graduations.

Velocities, which were measured at 25°C, were calculated by

$$V = f\lambda. \tag{10}$$

As it was suspected that these measurements were made in a region of molecular absorption, the velocities were not reduced to 0°C by the classical temperature correction because it does not hold in such regions. Measurements were made at frequencies of 3.855 and 6.254 Mc.

The absorption and reflection coefficients were

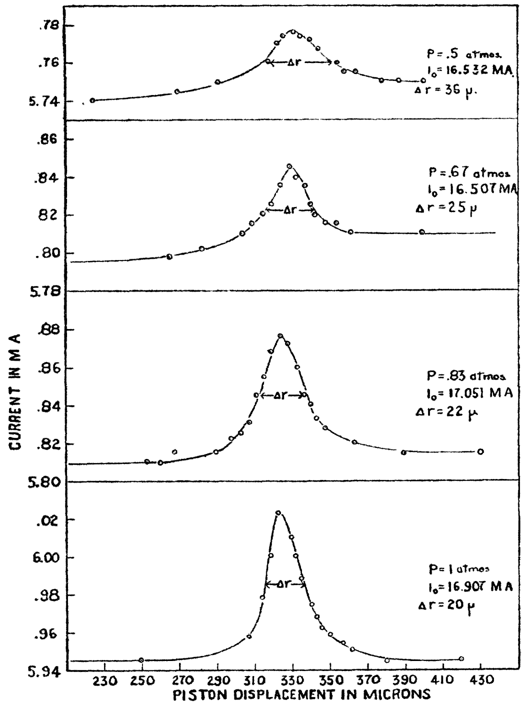

FIG. 4. Structure of the second peak at four pressures, $f=3.855$ Mc, illustrating the increased displacement from the crystal, the increased width at half-height, and the decreased current.

calculated according to the method outlined in the section on theory. To obtain the best values of $\sigma_0(n)$, $\sigma_m(n)$, and $\sigma(\infty)$ smooth curves were drawn through the maxima and minima of the current-displacement graphs (Fig. 1 and Fig. 2), and values of $i_0(n)$ and $i_m(n)$ were taken from these curves at half-wave-length intervals. The value of $i(\infty)$ was also estimated from these curves.

DISCUSSION OF RESULTS

Velocity Measurements

Table I gives the mean values obtained for the velocity of sound in hydrogen at frequencies of 3.855 and 6.254 Mc and pressures of 1.00, 0.83, 0.67, and 0.50 atmos. at 25°C. Figure 3 shows these data graphically as the conventional plot of V^2 against log (f/p) and in addition gives the classical value,* the theoretical dispersion curve, and the experimental values of Wallmann[6] and Roy and Rose[7] reduced to 25°C by the classical temperature correction

$$V_{25}=V_t\left(\frac{273.2+25}{273.2+t}\right)^{\frac{1}{2}}. \tag{11}$$

This applied since their measurements were not made in a dispersion region.

There is a definite change in velocity with both frequency and pressure. To determine whether such changes were significant an analysis based on Fisher's[14] discussion of the significance of means was made. This involved the calculation of the standard deviation (S.D.) of the mean velocity for each frequency and pressure, the calculation of the "t" function for the differences of the means, and finally the determination from Fisher's tables of the probability (P) of this occurring by chance. An example is the following: For the difference of the means at $p=1$ atmos., $f=3.855$ and 6.254 Mc, it was found that "t"$=11.25$ and $P=10^{-9}$. Consequently the change in velocity cannot be caused by chance but is physically significant; that is, a dispersion does exist. Likewise it was found that the differences in the velocities at 1 and 0.5 atmos., $f=3.855$ Mc, and at 1 and 0.5 atmos., $f=6.254$ Mc, were significant. It should be noted that V_{25} for 3.855 Mc and 1 atmos. is 0.6 percent higher than the classical value of 1315.8 m/sec.

From Fig. 3 it is seen that V^2 against $\log f/p$ does not give the conventional dispersion curve in that the dependence on f is not the same as the dependence on $1/p$. It was thought that this discrepancy might be caused by differences in the magnitude of the acoustical reaction when the effect of halving the pressure is compared with doubling the frequency. However this was disproved by measurements made on the same filling of gas ($p=1$ atmos., $f=3.855$ Mc) at two different powers (deflections of first peak 0.135 and 0.017 ma). The difference in velocities in

TABLE II. Velocity of sound in dry, CO_2-free air at 0°C.

f(Mc)	p(atmos.)	$\bar{V}$(m/sec.)	S.D. (m/sec.)	S.D. (%)	Number of determinations
3.855	1.00	331.7	0.22	0.07	3
	0.50	332.4	0.25	0.08	2
6.254	1.00	333.2	0.35	0.10	3

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* This was calculated using $\gamma=1.404$, $p=76$ cm, $\rho=8.23\times10^{-5}$ g/cm³, and $t=25$°C.

[14] R. A. Fisher, *Statistical Methods for Research Workers*, (Oliver and Boyd Ltd., Edinburgh, 1944), ninth edition, pp. 122–128, 169.

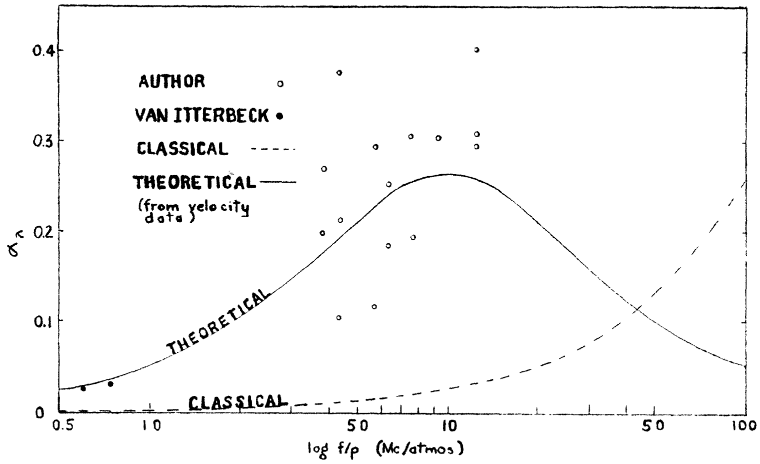

FIG. 5. The molecular and classical absorption coefficients (amplitude per wavelength) against log (f/p) for hydrogen at 25°C.

these two cases was only 0.47 percent and the greater velocity was obtained for the lower acoustic reaction, the opposite of the observed effect.

TABLE III. Exponential reflection and absorption coefficients of hydrogen at 25°C.

f(Mc)	p(atmos.)	β	α_{cm} (exp)	α_λ (exp)	α_λ (class)	α_λ (mol)
3.855	1.00	0.31	6.09	0.209	0.010	0.199
		0.07	8.49	0.281		0.271
	0.83	0.02	3.40	0.117	0.011	0.106
		0.04	6.43	0.222		0.211
		0.20	11.19	0.386		0.375
	0.67	0.02	3.83	0.133	0.015	0.118
		0.51	8.90	0.309		0.294
	0.50	0.22	6.17	0.216	0.020	0.196
6.254	1.00	0.05	9.22	0.201	0.016	0.185
		0.17	12.35	0.269		0.253
	0.83	0.07	14.86	0.324	0.019	0.304
	0.67	0.03	14.84	0.327	0.024	0.303
	0.50	0.21	15.44	0.342	0.032	0.308
		0.16	14.80	0.328		0.296
		0.25	19.62	0.434		0.402

Next an attempt was made to determine the causes of the errors in the means for a given f and p. Two sources of error are involved in each mean—the measurement of length in the individual samples and the possible variations in the amounts of impurities in the different fillings of gas. Each $\lambda/2$ was an average over several peaks, the number depending on the pressure of the gas and decreasing with decreasing pressure. The standard deviations of $\bar{\lambda}/2$ for the different runs were calculated. In each case the S.D. of the mean V was less than the S.D. of the mean of the $\bar{\lambda}/2$'s used to calculate the velocity. For example:

f/p(Mc/atmos.)	$\bar{V}$(m/sec.)	S.D.$(\bar{V})$%	S.D.$(\bar{\lambda}/2)_{\text{Av}}$%
3.855	1321.9	0.08	0.28
12.508	1382.0	0.26	0.67

Consequently any error due to differences in the gas measured must be less than the error due to measurement of length. The reason for the increase in the standard deviation as pressure decreased lies in the measurement of $\lambda/2$ as shown in Fig. 4. As the peaks became broader with decreasing pressure, the center of the peak was less accurately determined. Also the magnitude of the deflections decreased, decreasing the number of peaks that could be measured.

Measurements were also made on dry, CO_2-free air (Table II). With the same power as for hydrogen, at atmospheric pressure, *one hundred* peaks were measured in air with the same accuracy as that of *ten* measured in hydrogen. In addition the air peaks were sharper making the determination of the peak position more precise. The difference between the acoustical reactions of air and hydrogen is due to two effects. First, the lesser mass of hydrogen makes the initial reaction (deflection of the first peak) less than for air. Second, the greater absorption of hydrogen causes the amplitude to fall off much more quickly. The small changes in the velocity in air with pressure and frequency which were observed are on the border of significance but because of the small number of measurements this is considered insufficient evidence for the existence of dispersion in air. However, it is interesting to see that the variations with f and

TABLE IV. f_w and τ, from velocity measurements.

f(Mc)	p(atmos.)	f_w(Mc)	τ(sec.)	τ_{at}(atmos.-sec.)
3.855	1.00	16.1	1.65×10^{-8}	1.7×10^{-8}
	0.83	12.0	2.21	1.8
	0.67	11.0	2.41	1.6
	0.50	12.1	2.19	1.1
6.254	1.00	7.3	3.64	3.6
	0.83	8.7	3.05	2.5
	0.67	9.5	2.79	1.8
	0.50	10.9	2.44	1.2

$1/p$ are similar to those in hydrogen but have only one-tenth the magnitude.

Absorption Coefficients

Table III gives the experimental values of the amplitude absorption coefficient α_{cm} and $\alpha_\lambda = \alpha_{cm}\cdot\lambda$, the classical absorption per wavelength, and the molecular absorption per wavelength, which is the experimental absorption minus the classical. This last quantity is plotted in Fig. 5 together with the theoretical molecular absorption, the classical absorption, and experimental values from Van Itterbeck and Vermaelen.[15] The experimental values vary considerably and give only the order of magnitude. However they establish that there is a variation with f/p although they are not accurate enough to establish whether the variation with f differs from that with $1/p$.

There are two sources of error. First, there was considerable inaccuracy in the current measurements. The deflections of the last few peaks were only two or three millimeters and the oscillator-amplifier combination sometimes lacked stability. The measurements at 6.254 Mc, where the oscillator was more stable, are more consistent than those at 3.855 Mc. Second, the values of α and β also depend on the particular peak (n) used to calculate D and S.

The classical amplitude absorption coefficient was evaluated from

$$\alpha_\lambda(\text{class}) = \frac{2\pi^2 f}{\rho V^2}\left[\frac{4}{3}\eta' + \frac{\gamma-1}{C_p}K\right], \tag{12}$$

using $V = 1316$ m/sec., $\rho = 8.23\times10^{-5}$ g/cm^3, $\eta' = 1.146\eta$, $\eta = 8.935\times10^{-5}$ poises, $\gamma = 1.404$, $C_p = 3.424$ cal./g°, $K = 4.275\times10^{-4}$ cal./cm° sec., $p = 1$ atmos., and $t = 25$°C.

Both the classical and the experimental velocity were used in determining the classical absorption coefficient. The difference was much less than the experimental accuracy of the absorption measurements. The classical absorption was plotted in Fig. 5 to show its magnitude relative to that of the molecular absorption.

Reflection Coefficients

The extremely great absorption of hydrogen makes necessary the development of a more sensitive and more stable detector in order to use the method of calculation employed in this paper. This is evidenced by the results in Table III. The value of β, the exponential amplitude reflection coefficient, due to heat conduction was calculated from Herzfeld's[16] formula to be 0.03 at 4 Mc and 25°C.

The present results are very satisfactory in the sense that the measured values of β are without exception positive and in many cases are of the same order of magnitude as the result predicted. It should be noted however that the mean value of β is several times the predicted value. The large values of β accompanied by large α may be caused by poor alignment of the crystal. Further work should show whether this is the case or whether an extension of the Herzfeld theory must be made for high frequencies.

Application of Relaxation Theory

As in the case of CO_2 and other examples of dispersion the present results may be interpreted as caused by molecular absorption. According to the theory, dispersion in the velocity of sound occurs at frequencies where the periodicity of the change in energy in the sound wave is comparable to the time required to establish equi-

TABLE V. f_m and τ, from absorption measurements.

f(Mc)	p(atmos.)	α_λ(mole)	f_m(Mc)	τ(sec.)	τ_{at}(atmos.-sec.)
3.855	1.00	0.199	8.5	2.7×10^{-8}	2.7×10^{-8}
	0.83	0.106	20.7	1.2	1.0
	0.83	0.211	8.8	2.7	2.3
	0.67	0.118	24.4	1.0	0.7
	0.50	0.196	17.3	1.4	0.7
6.254	1.00	0.185	15.3	1.6	1.6
	1.00	0.253	8.4	2.9	2.9

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[15] A. Van Itterbeck and R. Vermaelen, reference 8, p. 351.

[16] K. F. Herzfeld, Phys. Rev. **53**, 899 (1938).

librium between the inner and outer degrees of freedom. At frequencies below this region energy flows into and out of the inner degrees, the molecule has all of its classical degrees of freedom, and the velocity of sound is classical. At frequencies above the dispersion region energy has not time to enter the inner degrees, the molecule exhibits only its outer degrees of freedom, and the velocity of sound is correspondingly increased. In the dispersion region the energy partially enters the inner degrees and then emerges out of phase with the wave, resulting in dissipation of energy. Thus in the dispersion region the velocity is between the two limiting velocities and a high absorption, called the molecular absorption, is present.

It is characteristic of this process that the increase in absorption commences at lower frequencies than the increase in velocity. This was observed for hydrogen. (Compare Fig. 3 and Fig. 5.) Also the f/p law should be obeyed by velocities in the case of molecular absorption, but in the present work this is only roughly true. As was shown in the discussion of velocity results, the scattering of the points is believed to be due to other causes than impurities in the gas.

Since at 300°K hydrogen is in the lowest vibrational state, the increase in velocity must be caused by the loss of its rotational degrees of freedom. Such a loss would increase the ratio of specific heats from 1.40 to 1.67 (approximately) and hydrogen would behave like a monatomic gas with only translational degrees of freedom. This would correspond to a velocity change from $V_0=1316$ m/sec. to $V_\infty=1435$ m/sec. at 25°C.

The dispersion formula may be written

$$f_w^2=f^2(V_\infty^2-V^2)/(V^2-V_0^2), \qquad (13)$$

where f_w is the inflection point of the V^2 against $\log f/p$ curve, V_0 is the velocity of sound for all degrees of freedom, V_∞ is the velocity for the translational degrees of freedom only, and V is the velocity at any frequency f. Table IV gives the values of f_w which were calculated for each experimental point. Using the average, $f_w=10.95$ Mc$\pm$8 percent, the complete theoretical dispersion curve was calculated according to (13). This is given in Fig. 3 together with the experimental results and shows that V_∞ should be reached in the 40–50 Mc region.

According to Kneser[17] the amplitude absorption coefficient per wave-length for molecular absorption is given by

$$\alpha_\lambda=\frac{\pi(Q^2-1)n}{1+Q^2n^2}; \quad \begin{matrix} Q=V_\infty/V_0 \\ n=f/f_w. \end{matrix} \qquad (14)$$

This has a maximum value

$$\alpha_\lambda(\max)=\pi/2(Q-1/Q) \qquad (15)$$

at the frequency

$$f_m=f_w/Q. \qquad (16)$$

For each experimental value of α_λ, f_m was found using a combination of (14) and (16),

$$f_m=\frac{f}{2\alpha_\lambda}\{\pi(Q-1/Q)\pm[\pi^2(Q-1/Q)^2-4\alpha_\lambda^2]^{\frac{1}{2}}\}. \qquad (17)$$

It can be seen from Fig. 5 and Table III that there were values of α_λ larger than $\alpha_\lambda(\max)=0.264$, calculated from (15). These substituted in (17) gave imaginary values for f_m and therefore are not included in Table V. These large α_λ's, as was mentioned in the discussion of reflection coefficients, are probably caused by malaligment of the crystal.

From the absorption data $f_m=14.8$ Mc$\pm$13 percent and $f_w=16.1$ Mc. f_m from the velocity data is 10.0 Mc. Since the velocity measurements are more accurate than the absorption measurements, the latter value for f_m was used in (14) to obtain the theoretical absorption curve shown in Fig. 5.

The relaxation time for equilibrium to be established between the translational and rotational degrees of freedom is given by

$$\tau=\frac{1}{2\pi f_w}\frac{C}{C_a}=\frac{1}{2\pi f_m}\frac{V_0}{V_\infty}\frac{C}{C_a}, \qquad (18)$$

in which C is the total specific heat per mole and C_a is that caused by translation. Since Van Itterbeck[8] has shown that τ is inversely proportional to pressure the quantity

$$\tau_{at}=\tau\cdot p \qquad (19)$$

was also calculated (Tables IV and V). The

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[17] H. O. Kneser, Ann. d. Physik [5] 16, 337 (1933).

average value for τ_{at} from the velocity measurements is 1.9×10^{-8} atmos.-sec. and from the absorption data is 1.7×10^{-8} atmos.-sec. Van Itterbeck gives 2.0×10^{-8} atmos.-sec. at 15°C and 1 atmos. from absorption measurements made at 600 kc.

The failure of these data to fit the $\int$ curve is now interpreted as caused by two assumptions in the Kneser theory of vibrational dispersion which are not applicable to the case of rotational dispersion. Since the relaxation times for adjustment between the unequally spaced rotational levels obviously are unequal, the curve should be a step curve, to which the $\int$ curve is a first approximation. The deviations from the f/p law are believed to be caused by the failure of the assumption that the number of favorable collisions is proportional to the pressure and are presumably caused by the effect of three-body collisions. A more rigorous interpretation of this dispersion, in the light of the above discussion, will be the topic of a subsequent paper.

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Theory of Long Period Magnetic Relaxation

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A discussion is given of the long period changes in magnetization in a mild steel specimen subjected to alternating stresses while in a weak magnetic field. The magnetization changes appear to occur with two time constants, of the order of three months and five years. A formal treatment of the phenomena is given along the lines of the time-dependent barrier potential used by Snoek in discussing other magnetic relaxation processes. The increase in the potential barrier is pictured as caused by the mechanical relaxation of local strains.

INTRODUCTION

DURING the war there was built up by physicists attached to the Naval Ordnance Laboratory, Washington, D. C., and to the Director of Scientific Research, British Admiralty, a body of experimental data relating to long period variations of magnetization of mild steel subject to alternating mechanical stresses while in a weak magnetic field. There has been little fundamental research, however, into the mechanisms involved. The existence of such time effects have been known for a very long time—see for example Ewing's book[1] or any manual on the compensation of ships' compasses. In view of the possible importance of the effects to our general understanding of ferromagnetism, it is desirable to summarize the main conclusions derived from the data and to indicate a phenomenological representation similar to that employed by Snoek[2] in discussing other magnetic relaxation processes.

The basic facts derived from observation at ordinary temperatures are given below. The applied fields involved are of the order of 0.5 gauss.

(*a*) After a period of the order of five years in a constant applied field the magnetization of a mild steel specimen subjected to alternating stresses ***approximates*** a state represented by infinite effective permeability, as was pointed out first by Dr. D. W. Ver Planck.

(*b*) When the applied field is changed suddenly, a considerable fraction of the magnetization changes practically instantaneously—this fraction is determined by the ordinary permeability and by the demagnetization coefficient.

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[1] J. A. Ewing, *Magnetic Induction in Iron* (The Electrician Publishing Company, London, 1892).

[2] J. L. Snoek, Physica **5**, 663 (1938).