magnetization, and, therefore, in resistivity, it was necessary to separate this effect from the change in restivity due to domain orientation. The separation was made by the method used by Englert,[19] by extrapolating the ρ *vs.* H curve, as illustrated in Fig. 12 for 83 percent nickel. The points for transverse magnetization lie on a straight line permitting easy extrapolation to the demagnetizing field corresponding to saturation; for the specimen of tape used this was small, $(N/4\pi)B_s=0.047\times 9800=450$. The same slope of ρ *vs.* H curve was used to extrapolate the longitudinal measurements to $H=0$.

The slope of the ρ *vs.* H line for nickel was nearly the same as that reported by Englert. The slopes for the other specimens are recorded in Fig. 13, as percent change in ρ for $H=20{,}000$ oersteds. The results are probably not accurate to less than 0.1 percent, but appear to lie on a smooth curve. The explanation of the shape of the curve is not apparent. On the one hand one might expect the effect to be large when the curie point is low, as it is at each end of the range of alloys studied, because there the change in spontaneous magnetization with field is relatively large. On the other hand, near 70 to 75 percent nickel the crystal anisotropy is zero, and order-disorder phenomena are observed, and there may be some connection, not now established, between these and the effect of spontaneous magnetization on resistivity.

I am indebted to Dr. C. L. Dolph and Miss C. L. Froelich for assistance with the mathematics and computations involved in the solution of the energy equation.

---

[19] E. Englert, Ann. d. Physik **14**, 589–612 (1932).

PHYSICAL REVIEW VOLUME 70, NUMBERS 11 AND 12 DECEMBER 1 AND 15, 1946

The Velocity of Sound in Hydrogen when Rotational Degrees of Freedom Fail to Be Excited

J. Elmer Rhodes, Jr.*
Rowland Physical Laboratory, The Johns Hopkins University, Baltimore, Maryland

(Received August 21, 1946)

The velocity of sound in parahydrogen, normal hydrogen, and 50 percent para-50 percent orthohydrogen mixtures has been observed at several temperatures, and over a range of frequency to pressure ratio from one to 60 megacycles per atmosphere. Dispersion attributed to failure of the rotational degrees of freedom to follow the temperature associated with the translational degrees of freedom has been observed with all mixtures and at every temperature at which observations were made. Measurements at two different frequencies for similar samples at the same temperature indicate that frequency and pressure affect the velocity of sound only as the quotient, frequency/pressure, with the exception of small corrections that must be applied because hydrogen is not a perfect gas. Experiments indicate that the dispersion occupies a greater range of frequency to pressure than would be expected if the rotational specific heat behaved as a simple relaxation phenomenon. It is shown that a simple relaxation phenomenon is not to be expected, and that the dispersion in parahydrogen can be characterized, approximately, by two relaxation frequency to pressure ratios, one for the rotational transition 0–2, and another for the transition 2–4. An expression for these relaxation frequency to pressure ratios, that roughly fits the observations, is derived on the basis of some assumptions about the collision process.

CHANGES of sound velocity in some gases with variation of the frequency to pressure ratio have been known for a number of years. These have been attributed to failure of the internal degrees of freedom of the molecules to follow temperature changes in the sound wave. The first phenomenon of this type to be observed was associated with vibrational degrees of freedom. In this respect carbon dioxide has been extensively investigated.[1]

Recently in this laboratory E. S. Stewart[2] observed a similar phenomenon associated with

---

* Now at Georgia School of Technology, Atlanta, Georgia.

[1] W. T. Richards, Rev. Mod. Phys. **11**, 59 (1939).

[2] E. S. Stewart, Phys. Rev. **69**, 632 (1946). See also, E. S. Stewart, J. L. Stewart, and J. C. Hubbard, Phys. Rev. **68**, 231 (1945).

the rotational degrees of freedom of hydrogen. This had been sought for by others,[3] but their work was not done at a sufficiently high ratio of frequency to pressure.

MEASUREMENTS AND APPARATUS

Measurements of sound velocity in parahydrogen and in mixtures of ortho- and parahydrogen were made at different frequency to pressure ratios. The results of the measurements are recorded in the curves of Fig. 1.

The velocity measurement was made by measuring the wave-length with a sonic interferometer and at the same time measuring the frequency. The interferometer was the one described by J. L. Stewart[4]; however, the electrical circuits were different. No separate oscillator was used to drive the quartz crystal of the interferometer; rather, the crystal was employed as one of the tuned circuits in the oscillator. Resonance of the gas column was indicated by a sensitive vacuum tube voltmeter that indicated change of the radiofrequency voltage across the quartz crystal.

The interferometer was inverted in a large Dewar flask which contained a liquid bath to maintain constant temperature. Water and ice were used for measurements near zero degrees Centigrade; dry ice and alcohol, near 200 degrees absolute; and water, near room temperature. The temperature of the bath was measured with a calibrated thermocouple.

The hydrogen was purified by slowly passing it through a trap surrounded by liquid hydrogen. Parahydrogen (99.8 percent) and 50 percent para-50 percent orthohydrogen were prepared at the temperatures of liquid hydrogen and of liquid air, respectively, by adsorbing hydrogen onto activated charcoal.[5]

RELATION BETWEEN THE VELOCITY OF SOUND AND THE RATE OF ROTATIONAL TRANSITIONS

If the effects depending upon the first and third derivatives of the displacement of an element of mass (heat conduction and viscosity) are neglected, Newton's laws of motion and the principle of conservation of mass yield for the velocity of plane waves of sound in a homogeneous isotropic medium:

$$V=\left[\left(\frac{\partial p}{\partial \rho}\right)_T+\frac{MT}{C\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho^2\right]^{\frac{1}{2}}, \tag{1}$$

where M is the molecular weight of the material; ρ, the density; T, the absolute temperature; C, the specific heat per mole at constant volume;

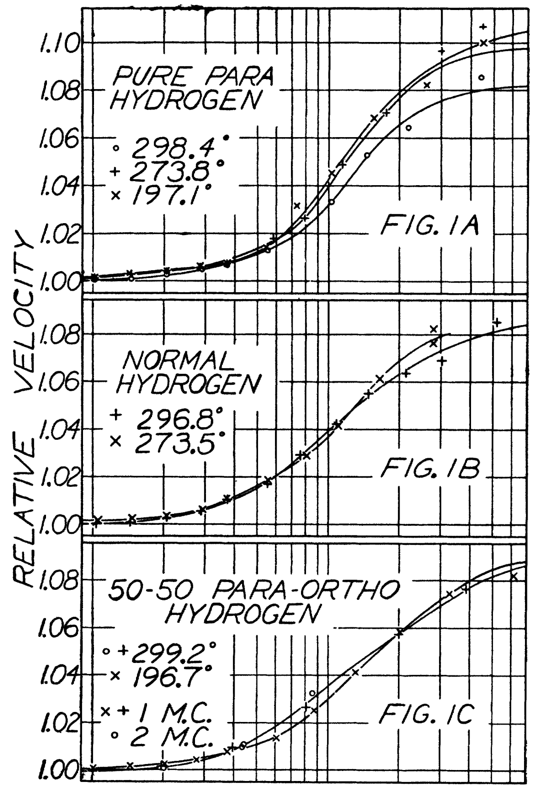

FIG. 1. The velocity of sound in hydrogen as a function of f/p, the frequency to pressure ratio; f/p is on a logarithmic scale. Velocity is shown in units equal to the calculated low frequency velocity for the temperature indicated. Figure 1A is for pure parahydrogen; 1B for normal (25 percent para-, 75 percent ortho-) hydrogen, and 1C is for a 50 percent para-, 50 percent orthohydrogen mixture. All experimental points were observed at a frequency of one megacycle except those in 1C indicated by *o*'s, which were observed at a frequency of two megacycles. That both one and two megacycle observations lie on the same curve indicates that frequency and pressure affect the velocity only through the quotient, f/p, except for small correction terms that depend upon the second virial coefficient. The experimental errors are greater the greater the value of f/p.

---

[3] A. S. Roy and M. E. Rose, Proc. Roy. Soc. London **A149**, 511 (1935).

[4] J. L. Stewart, Rev. Sci. Inst. **17**, 59 (1946).

[5] A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions* (The Macmillan and Company, Limited, London, 1939), p. 154.

p, the pressure; and V, the complex velocity of sound.

In (1) M is constant; T and ρ are average temperature and density and are considered constant. Both partial derivatives are associated with the translational degrees of freedom. Consequently, they should be real in a sound wave whose period is long compared to the relaxation time for translational motion. All sound waves to be considered here have periods far longer than the relaxation time for translational motion. Only C is associated with internal degrees of freedom. When excitation of any internal degree of freedom lags behind the temperature change in the sound wave associated with the translational degrees of freedom, then C becomes complex. Then V also becomes complex, and it is the real part of V that represents the phase velocity, the quantity that one measures with a sonic interferometer.

If V^2 is expressed as $\alpha+i\beta$ and V as $v+iu$, where v is the phase velocity, then,

$$V^2=v^2-u^2+2iuv=\alpha+i\beta; \tag{2}$$

from which,

$$v^2=\tfrac{1}{2}\alpha[1+(\beta^2/\alpha^2+1)^{\frac{1}{2}}]. \tag{3}$$

If β/α is small compared to one, as it proves to be in the experiments considered here, then,

$$v^2\cong\alpha[1+\tfrac{1}{4}\beta^2/\alpha^2]. \tag{4}$$

An empirical equation of state for hydrogen is[6]

$$p=RT\rho/M+\rho^2B/M^2, \tag{5}$$

where R is the universal gas constant, and B is the second virial coefficient for hydrogen. This function for p inserted into (1) gives, after dropping second-order terms,

$$V^2=\frac{RT}{M}\left\{1+2pB\frac{T_0^2}{T^2}+\frac{R}{C}\left(1+2p\frac{T_0^2}{T}\frac{dB}{dT}\right)\right\}. \tag{6}$$

T_0 is 273.1 degrees absolute.

The theory of the effective specific heat for a two level gas has been carried through in great detail by Rutgers[7] for the case when the levels are associated with molecular vibrations. His approach applied to molecular rotations follows: Consider a gas transmitting a sound wave of angular frequency ω. Suppose some internal degree of freedom has only two levels, a and b, with energy difference ΔE between them. Let n be the number of molecules per mole, n_a the number in state a, and n_b the number in state b. Then $n_a+n_b=n$, and $dn_a=-dn_b$. The reaction equation is,

$$dn_b/dt=k_{ab}n_a-k_{ba}n_b, \tag{7}$$

where k_{ab} and k_{ba} are probabilities per second per molecule of the transitions $a-b$ and $b-a$, respectively. At equilibrium $dn_b/dt=0$, so,

$$k_{ba}=k_{ab}n_a/n_b. \tag{8}$$

For a rotator

$$\frac{n_a}{n_b}=\frac{2J_a+1}{2J_b+1}e^{\Delta E/kT}, \tag{9}$$

where

$$\begin{aligned}\Delta E/kT&=\sigma[J_b(J_b+1)-J_a(J_a+1)];\\ \sigma&=h^2/8\pi^2IkT;\end{aligned} \tag{10}$$

J is the rotational quantum number; k is Boltzmann's constant; I is the moment of inertia of the molecule. Suppose T varies periodically so that $T=T_0+\Delta Te^{i\omega t}$, and suppose $n_b=n_b^0+\Delta n_be^{i\omega t}$. Then $n_a=n_a^0-\Delta n_be^{i\omega t}$. After dropping second-order terms, so long as $\Delta n_a\ll n_a$, $\Delta n_b\ll n_b$, $\Delta T\ll T$, these suppositions lead to,

$$\begin{aligned}i\omega\Delta n_b=&-k_{ab}\Delta n_b-k_{ba}\Delta n_b\\ &+(n_a^0\Delta k_{ab}-n_2^0\Delta k_{ba}).\end{aligned} \tag{11}$$

$$\begin{aligned}(n_a^0\Delta k_{ab}-n_2^0\Delta k_{ba})=&\,\Delta k_{ab}n_a^0\\ &-n_b^0\left(\Delta k_{ab}\frac{n_a^0}{n_b^0}-k_{ab}\frac{2J_a+1}{2J_b+1}e^{\Delta E/kT}\Delta T\right),\end{aligned}$$

$$\frac{\Delta E\Delta n_b}{\Delta T}=k_{ab}\frac{n_a^0}{n_b^0}\frac{(\Delta E)^2}{kT^2}\bigg/(i\omega+k_{ab}+k_{ba}). \tag{12}$$

The term on the left is the effective rotational specific heat, and the expression on the right reduces to the statistical mechanical equation for the specific heat of a rotator with two levels if ω is set equal to zero. The general statistical mechanical equation for the specific heat of a rotator is Eq. (21) below. Thus the effective specific heat associated with levels a and b is

$$C_R'=\frac{C_R}{1+i\omega/\omega_0}, \tag{13}$$

---

[6] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 221–223.

[7] A. J. Rutgers, Ann. d. Physik **16**, 350 (1933).

where

$$\omega_0 = k_{ab} + k_{ba} = k_{ab}\left(1 + \frac{2J_a+1}{2J_b+1} e^{\Delta E/kT}\right), \qquad (14)$$

and where C_R is the rotational specific heat when $\omega = 0$. For a non-radiating rotator, rotational transitions are effected only by molecular collisions. The rate of collisions is proportional to the pressure, p. Thus, k_{ab} contains p as a factor, and (13) and (14) may be written,

$$C_R' = C_R \Big/ \left(1 + i\frac{f/p}{(f/p)_0}\right); \qquad (15)$$

$$(f/p)_0 = \frac{k_{ab}}{2\pi p}\left(1 + \frac{2J_a+1}{2J_b+1} e^{\Delta E/kT}\right). \qquad (16)$$

If the specific heat obeys (15), it is said to exhibit simple relaxation phenomena.

That frequency and pressure enter the dispersion only as f/p is shown by Fig. 1c. The ratio $(f/p)_0$ will be referred to as the relaxation frequency to pressure ratio.

To analyze such phenomena in a three level gas, one must solve three differential equations simultaneously. If n_a, n_b, n_c are the numbers of molecules per mole in levels a, b, and c, then $n = n_a + n_b + n_c$, and the three equations are

$$\begin{aligned} dn_a/dt &= -k_{ab}n_a + k_{ba}n_b; \\ dn_b/dt &= -\frac{dn_a}{dt} - \frac{dn_c}{dt}; \qquad (17) \\ dn_c/dt &= k_{bc}n_b - k_{cb}n_c. \end{aligned}$$

This development neglects the possibility of transitions $a-c$ and $c-a$. As before, $k_{ba} = k_{ab}(n_a/n_b)$; $k_{cb} = k_{bc}(n_b/n_c)$. The assumption of harmonic variation of n_a, n_b, n_c, and T gives, after dropping second-order terms,

$$\begin{aligned} i\omega\Delta n_a &= -k_{ab}\Delta n_a + k_{ab}(n_a^0/n_b^0)\Delta n_b + P_1\Delta T; \\ \Delta n_b &= -\Delta n_a - \Delta n_c; \qquad (18) \\ i\omega\Delta n_c &= k_{bc}\Delta n_b - k_{bc}(n_b^0/n_c^0)\Delta n_c + P_2\Delta T; \end{aligned}$$

where the P's contain n's and k's as in Eq. (11). Elimination of Δn_b in (18) leaves,

$$\begin{aligned} i\omega\Delta n_a &= -k_{ab}[\Delta n_a + (n_a^0/n_b^0)(\Delta n_a + \Delta n_c)] + P_1\Delta T; \\ & \qquad (19) \\ i\omega\Delta n_c &= -k_{bc}[(\Delta n_a + \Delta n_c) + (n_b^0/n_c^0)\Delta n_c] + P_2\Delta T. \end{aligned}$$

If there were some simple relation between k_{ab} and k_{bc}, then (19) might be reduced to the form of (15), with the specific heat exhibiting a simple relaxation frequency to pressure ratio. With the help of some plausible assumptions, such a relation has been found for a vibrating molecule with many levels.[8] A simplifying factor in the case of a vibrator is the fact that energy levels are equally spaced. This is not the case with a rotator. If there are appreciable numbers of molecules in more than two levels, there is no simple relaxation frequency to pressure ratio for rotational specific heat.

Parahydrogen at room temperature is essentially a three level gas with most of its molecules in rotational levels with $J = 0$, 2, and 4. One may associate 0, 2, and 4 with a, b, and c in (19). The $0-2$ transition fails to follow the sound wave at a lower f/p than the $2-4$ transition. Most of the rotational specific heat is associated with the $0-2$ transitions; thus Δn_a is much greater than Δn_c at low f/p. As f/p increases, (19) describes Δn_a and Δn_c. To a good approximation, at low f/p, Δn_c may be neglected in the first equation of (19). Then (19) becomes identical with (11). As f/p continues to increase Δn_a becomes smaller, and the approximation ceases to be valid. At sufficiently high f/p, Δn_a becomes small enough to be neglected when compared to Δn_c. Then the second equation of (19) becomes equivalent to (11). Thus at sufficiently high and at sufficiently low f/p hydrogen may be treated as a two level gas.

The total effective specific heat for a two level gas is,

$$C_E = C_\infty + (C_0 - C_\infty) \Big/ \left(1 + i\frac{f/p}{(f/p)_0}\right), \qquad (20)$$

where the second term is obtained from (15). C_0 is the specific heat when transitions between the two levels concerned follow the sound wave and C_∞ is the specific heat when no transitions between these levels occur. The rotational specific heat can be calculated by the methods of statistical mechanics for any number of levels. Its value is[9]

---

[8] L. Landau and E. Teller, Physik. Zeits. Sowjetunion **10**, 34 (1936).

[9] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, New York, 1940), Chap. 6.

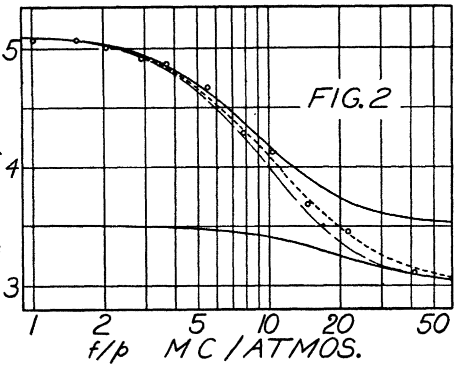

FIG. 2. The solid curves show C_ω calculated from Eq. (24). The upper curve has $(f/p)_0=7.2$ megacycles per atmosphere; the lower one, 20 megacycles per atmosphere. The asymtotic values for these curves, C_0 and C_∞, were calculated by Eq. (21). The dotted curve is the resultant of the two solid curves, and the o's are experimental points calculated by Eq. (23) from velocity measurements. The dashed curve shows what would be expected if the whole rotational specific heat showed a simple relaxation frequency to pressure ratio. The value of $(f/p)_0$ for the dashed curve was chosen to be 7.3 megacycles per atmosphere. The experimental points occupy a greater range of f/p than this curve, indicating that the rotational specific heat does not exhibit simple relaxation phenomena.

$$C_R=\frac{R}{Q}\left\{\sum_J (2J+1)[\sigma J(J+1)]^2e^{-\sigma J(J+1)} -\frac{1}{Q}\left[\sum_J (2J+1)\sigma J(J+1)e^{-\sigma J(J+1)}\right]^2\right\}, \quad (21)$$

where Q is the partition function for a rotator,

$$Q=\sum_J (2J+1)e^{-\sigma J(J+1)}. \quad (22)$$

If some rotational transitions are considered as not occurring, the levels from which no molecules enter or leave are omitted from the sums in (21) and (22). The total specific heat is the effective rotational specific heat plus the translational specific heat which is $3R/2$.

Equations (20) and (6) substituted into (4) give

$$v^2=\frac{RT}{M}\left\{1+2pB\frac{T_0^2}{T^2}+\frac{R}{C_\omega}\left[1+2p\frac{T_0^2}{T}\frac{dB}{dT}\right]\right\} \times\left\{1+\frac{1}{4}\frac{\beta^2}{\alpha^2}\right\}, \quad (23)$$

where

$$C_\omega=\left(C_0^2+C_\infty^2\frac{(f/p)^2}{(f/p)_0^2}\right)\Big/\left(C_0+C_\infty\frac{(f/p)^2}{(f/p)_0^2}\right) \quad (24)$$

and

$$\frac{\beta}{\alpha}=\frac{R(C_0-C_\infty)\dfrac{f/p}{(f/p)_0}}{R\left[C_0+C_\infty\dfrac{(f/p)^2}{(f/p)_0^2}\right]+C_0^2+C_\infty^2\dfrac{(f/p)^2}{(f/p)_0^2}}. \quad (25)$$

Relaxation frequency to pressure ratios were obtained for the $0-2$ and $2-4$ transitions of parahydrogen at 298.4 degrees absolute. For the $0-2$ transition, which has the lower $(f/p)_0$, observed values of v were put into (23). The last factor of (23) was first treated as one, and first approximations for C_ω were obtained. The value of $(f/p)_0$ that made (24) best fit these values was then obtained by trial. This approximation to $(f/p)_0$ was used in (25) to obtain β/α, which was subsequently used in (23) to obtain final values for C_ω. (These values for β/α were all less than 0.08, and the corrections on C_ω were less than 0.02 percent.) A final value of $(f/p)_0$ was obtained to make (24) best fit the final experimental values of C_ω for low values of f/p. The value of σT used in all of these calculations was 82.6 degrees.[10]

For the $2-4$ transition the same procedure was carried out: (24) was made to fit the experimental C_ω's at high values of f/p rather than at low ones.

Figure 2 shows how (24) for the final $(f/p)_0$'s chosen fits the experimental points.

At lower temperatures parahydrogen is so nearly a two level gas that no reliable figures could be obtained for the $2-4$ transition. The $(f/p)_0$'s for the $0-2$ transition were obtained. Results are tabulated in Table I.

CALCULATION OF k_{ab}

After an inelastic collision in which masses M and m collide with relative velocity v_r, some of

TABLE I. Relaxation frequency to pressure ratios for parahydrogen.

Transition between rotational levels:	Temperature (deg. abs.)	Relaxation frequency to pressure ratio, $(f/p)_0$ (m.c./atmos.) Observed	Calculated
0–2	197.7	6.6±0.3	6.13
0–2	273.8	6.9±0.3	6.98
0–2	298.4	7.2±0.3	
2–4	298.4	20. ±5.	22.0

---

[10] P. S. Epstein, *Textbook of Thermodynamics* (John Wiley and Sons, New York, 1937), p. 305.

the energy of their relative motion appears as a subsequent relative velocity, and the rest goes into the internal energy of the colliding bodies. Momentum and energy are conserved. In order to conserve energy and the component of momentum in the direction of v_r, the maximum energy of relative translational motion that can go into internal energy is

$$E_{\mathrm{max}}=\frac{1}{2}\frac{mM}{m+M}v_r^2. \tag{26}$$

If the colliding bodies are two hydrogen molecules, then $M=m$, and $E_{\mathrm{max}}=\frac{1}{2}(\frac{1}{2}mv_r^2)=\frac{1}{2}E_r$, or half the kinetic energy of their relative motion.

In considering the probability that a molecule in rotational level a will be left in level b after collision with another molecule, one need consider only those collisions for which

$$E_{\mathrm{max}}+\Delta E_2 \overline{\overline{>}} \Delta E_{ab}, \tag{27}$$

where ΔE_{ab} is the energy required for the transition $a-b$, and ΔE_2 is the amount of internal (rotational) energy the colliding molecule might possibly lose. In the calculations that follow ΔE_2 is taken as the energy given up by the colliding molecule in undergoing a transition from its initial rotational level to its next lower allowed level. When the colliding molecule is initially in its lowest level, ΔE_2 is zero.

The number of collisions per second per molecule in a gas with magnitude of initial relative velocity between v_r and (v_r+dv_r) is[11]

$$dz=\tfrac{1}{2}\pi^{\frac{1}{2}}D^2N(m/kT)^{\frac{1}{2}}v_r^3 \times\exp\left[-mv_r^2/4kT\right]dv_r, \tag{28}$$

where N is the molecular density, D the collision diameter of the molecule.

If (28) is integrated over all relative velocities, one obtains the rate of occurrence of collisions. Consider one molecule in rotational level a that collides with a second molecule with an initial relative velocity, v_r. Let W be the probability that the first molecule will undergo a transition during the collision to its next higher allowed level b. W multiplied by (28), and then integrated gives k_{ab}, the rate per molecule in state a of the transition $a-b$. Thus:

$$k_{ab}=\int_{v_r=0}^{\infty} Wdz. \tag{29}$$

Calculation of W requires the evaluation of the expression for such a probability:

$$W=\left[\frac{2\pi}{h}\int\int\Psi_b^* V_c\Psi_a dxdt\right]^2. \tag{30}$$

Ψ_a and Ψ_b are the rotational wave functions of the molecule: Ψ_a in rotational level a, and Ψ_b in level b. All coordinates of the rotator are included in x; t is time. V_c is the potential energy of the rotator resulting from the presence of the colliding molecule. In classical mechanics one can express any impulse on a rigid body by an equivalent impulse applied to the center of mass of the body plus an equivalent impulsive torque. V_c corresponds to the potential energy associated with this impulsive torque during the collision. Necessary information about the molecular forces during the collision for obtaining V_c as a function of the coordinates of the rotator and time are lacking so (30) cannot be evaluated.

Some properties of W are available. Unless condition (27) is satisfied, W is certainly zero. One would expect that as the left side of (27) becomes larger compared to the right side, W would increase. An attempt was made to express W as a function of $(E_{\mathrm{max}}+\Delta E_2-\Delta E_{ab})$, for positive values of this quantity. Several simple functions were tried, and it was found that

$$W\propto E_{\mathrm{max}}+\Delta E_2-\Delta E_{ab} \tag{31}$$

best fitted observations. It is possible that W can be accurately represented by a rapidly converging power series in $(E_{\mathrm{max}}+\Delta E_2-\Delta E_{ab})$.

To calculate k_{ab} on the basis of this assumption, one puts (31) and (28) into (29). Since W is zero for negative values of $(E_{\mathrm{max}}+\Delta E_2-\Delta E_{ab}) =(\frac{1}{4}mv_r^2+\Delta E_2-\Delta E_{ab})$, the integration is carried out only from $v_r^2=(4/m)(\Delta E_{ab}-\Delta E_2)$ to ∞, when this lower limit is greater than zero. If $\Delta E_2>\Delta E_{ab}$, then the integration is carried out from zero to ∞. The result is

$$\begin{aligned} k_{ab}'&=\lambda p'T^{\frac{1}{2}}(X+2)e^{-X}, \quad X\geqq 0;\\ k_{ab}'&=\lambda p'T^{\frac{1}{2}}(-X+2), \quad X\leqq 0, \end{aligned} \tag{32}$$

where $X=(\Delta E_{ab}-\Delta E_2)/kT$. In obtaining (32), the molecular density, N, has been given its

---

[11] R. B. Lindsay, *Physical Statistics* (John Wiley and Sons, New York, 1941), pp. 87–88.

value for a perfect gas, $N=p'/kT$, where p' is the partial pressure of the molecules in the level that corresponds to ΔE_2. All multiplying constants, including the proportionality constant for W, are included in λ. In calculating k_{ab} by (32), one must calculate a term for the fraction of the molecules in each rotational level, as ΔE_2 is different for each level. Thus the final k_{ab} is a sum of terms like (32).

From k_{ab}, the relaxation frequency to pressure ratio, $(f/p)_0$, is determined by (16). The observed $(f/p)_0$ for the $0-2$ transition in parahydrogen at 298.4 degrees absolute was used in (16) and (32) to find λ. Values for the other $(f/p)_0$'s calculated from this λ are in the last column of Table I.

Properly chosen assumptions about the quantities in (30) can lead to (31). One such set includes the assumption that the collision occupies only a small region of the coordinates, so that the product of the Ψ s can be replaced by an average value; (30) then takes the form:

$$W=\left[\frac{2\pi}{h}\langle\Psi_b{}^*\Psi_a\delta x\rangle_{\text{Av}}\int V_c dt\right]^2,$$

or $W\propto[\int V_c dt]^2$. If V_c is assumed to have a maximum value proportional to $(E_{\max}+\Delta E_2-\Delta E_{ab})$; if a coordinate ξ is zero just as the molecules "contact" and increases as they move closer together; and if the molecular force associated with V_c is a rapidly increasing function of the positive values of ξ, $e^{a\xi}$ or ξ^n, with n large, for example, then (31) results.

CONCLUSION

Dispersion of the velocity of sound in hydrogen has been observed at several temperatures; the frequency to pressure ratio at which the dispersion occurs shows no strong temperature dependence.

The excitation of rotational degrees of freedom in hydrogen is shown to have no simple relaxation frequency to pressure ratio; however, each rotational transition can be assigned a ratio that approximates a true relaxation frequency to pressure ratio. The range of frequency to pressure ratio over which the velocity of sound changes is greater for hydrogen than that called for by the law for a simple relaxation.

PHYSICAL REVIEW VOLUME 70, NUMBERS 11 AND 12 DECEMBER 1 AND 15, 1946

Frequency Dependence of the Properties of Sea Echo*

HERBERT GOLDSTEIN
Department of Physics, Harvard University, Cambridge, Massachusetts

(Received September 3, 1946)

The properties of sea echo—a radar echo associated with surface of the sea—have been measured at wave-lengths of 9.2, 3.2, and 1.25 cm, for grazing angles of incidence about 1° and over a wide range of sea states. The measurements, which are given in terms of a suitably defined cross section per unit area of the sea, were obtained with three experimental truck-borne systems. Details of these systems, and of the measuring techniques, are described. The troublesome rapid fluctuations of the sea echo signals were eliminated by an electrical averaging scheme. A discussion of the possible errors in the determination of the absolute cross sections leads to an estimated uncertainty of ±2 db on 9.2 and 3.2 cm and ±4 db on 1.25 cm. The results have been interpreted in the light of possible theories of the scattering mechanism responsible for the echo. Assuming the scatterers to be spray drops small compared to λ, the wave-length dependence of the cross section should be between λ^{-4} and λ^{-8} whereas the observed variation is between λ^0 and λ^{-4}. While these results are in better accord with the hypothesis of scattering from irregularities on the surface, the observed large changes of the cross section with polarization seem explainable only by some form of the drop theory. A modification of the drop theory is proposed, which assumes the presence of drops of diameter of the order of λ. The consequences of such a theory are examined and found to be in rough agreement with experiment.

INTRODUCTION

At certain times, depending upon the state of the sea, microwave radar systems will receive echoes associated with the sea surface and commonly known as "sea echo." Large areas on the indicators are often covered by the echo, seriously interfering with the usefulness of airborne radar systems. The fundamental scattering

---

* This paper is based on work done while at the Radiation Laboratory, M.I.T.