

Acoustical Studies. IV. The Collision Efficiencies of Various Molecules in Exciting the Lower Vibrational States of Ethylene, Together with Some Observations Concerning the Excitation of Rotational Energy in Hydrogen

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Acoustical Studies. IV. The Collision Efficiencies of Various Molecules in Exciting the Lower Vibrational States of Ethylene, Together with Some Observations Concerning the Excitation of Rotational Energy in Hydrogen

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The velocity of sound in pure ethylene has been determined at various pressures, temperatures and frequencies. It is concluded that equilibrium is attained between the various states of the vibrational energy on every effective collision, but that a considerable activation energy of collision is required for the conversion of translational into vibrational energy. Collisions with argon, helium, and nitrogen molecules have no appreciable effect on the vibrational energy of the ethylene molecule. Collisions with hydrogen molecules are about ten times as effective

as ethylene-ethylene collisions in producing transitions in the lower vibrational energy states of ethylene. Hydrogen shows a dispersive region at ultrasonic frequencies which is apparently due to the failure of the rotational energy transitions to follow the acoustical cycle. It has been found necessary to suppose that ethylene-hydrogen collisions are about twenty times as effective as hydrogen-hydrogen collisions in exciting the rotational energy of hydrogen molecules.

INTRODUCTION

ONE of the outstanding unsolved problems in chemical kinetics is the mechanism of activation by collision. It has become increasingly apparent that great differences exist in the relative activation efficiencies of various types of molecules, but the theoretical approach to the problem is difficult, and it is apparently impossible at present to make quantitative predictions. The multiplication of suitably chosen experiments becomes therefore highly desirable.

Measurements on the dispersion and absorption of sound provide ready access to data concerning a somewhat analogous process: the excitation by collision of the lower vibrational energy states. This differs from the chemical activation of the molecule in several respects, but is even harder to describe from a theoretical standpoint because the interaction of the molecules must here be attacked by quantum mechanics, whereas there is every indication that in chemical activation the problem will ultimately yield to a classical dynamical treatment. Any final description of the mechanism by which translational energy is converted into vibrational energy must, however, be sufficiently general to embrace transitions between both the lower and higher vibrational states. A study of the collision efficiencies of various molecules in adjusting the

heat capacity cannot fail, therefore, to have ultimate bearing upon the chemical problem.

The first research of this character was undertaken by Abello,¹ who measured the absorption of ultrasonic energy in mixtures of carbon dioxide, hydrogen and nitrogen. The theoretical equipment necessary to interpret his results was provided shortly thereafter by Bourgin.² In 1932 Rogers³ reported briefly concerning the effect of water vapor on the absorption of sound in carbon dioxide, and an advance notice of the present work was published.⁴ During the past year Kneser has interpreted existing measurements on air and on oxygen-water-vapor mixtures,⁵ and Eucken and Becker⁶ have published conclusions from a few measurements on the velocity of sound in binary mixtures containing as one constituent either carbon dioxide or chlorine. This appears to complete the meager list of measurements which have been published to date.

¹ Abello, *Proc. Nat. Acad. Sci.* **13**, 699 (1927).

² Bourgin, *Nature* **122**, 133 (1928); *Phil. Mag.* **7**, 821 (1929); *Phys. Rev.* **34**, 521 (1929).

³ Rogers, *Phys. Rev.* **41**, 369 (1932).

⁴ Richards and Reid, *Nature* **130**, 739 (1932).

⁵ Kneser, *Ann. d. Physik* **16**, 337 (1933); *J. Acous. Soc. Am.* **5**, 122 (1933).

⁶ Eucken and Becker, *Zeits. f. physik. Chemie* **B20**, 467 (1933).

I. PURE ETHYLENE

A. The purity of the ethylene gas employed

The ethylene gas was obtained in compressed cylinders, which are supplied by the U. S. Industrial Chemical Company, and rated as about 99 percent pure. Four of these cylinders were employed, and of these three gave fairly reproducible results. The fourth gave values which varied from day to day, and all measurements on gas from this cylinder have been discarded. The cylinders were cooled to -20°C to liquefy the ethylene, and then "blown off" to remove any traces of non-condensing gases. Ethylene was then evaporated through phosphorus pentoxide into evacuated acoustical chambers of a design which has already been described.⁷ The apparatus was washed with gas several times before each measurement.

The measurements, combined by means of smoothed curves, permit comparison for theoretical purposes with an accuracy somewhat greater than 0.1 percent. It is not possible, however, to estimate here their absolute accuracy.

B. The low frequency terminal velocity

A measurement of the velocity of sound at 9 kc, 30°C , and 770 mm gave $332.8 \text{ m sec.}^{-1}$. In order to idealize this quantity it was multiplied by a factor of 1.0035, which was obtained from the van der Waals constants $a = 4.47 \times 10^6 \text{ cm}^6 \text{ atm. mole}^{-1}$ and $b = 57.14 \text{ cm}^3 \text{ mole}^{-1}$. The resulting figure is $333.9 \text{ m sec.}^{-1}$, which disagrees gravely with $336.1 \text{ m sec.}^{-1}$ calculated in a similar manner from the empirical equation given in the *International Critical Tables*. We cannot account for this discrepancy. It should be noted, however, that the equation given in the *International Critical Tables* results from a combination of the measurements of six different observers, who are in violent mutual disagreement.

No wholly satisfactory data on the heat capacity appear to be available. The most recent study has been made by Haas and Stegeman,⁸ who give values which are slightly lower than those reported by previous writers. Their results

are quoted without specification of the pressure, and are considered to vary linearly with temperature from 3° to 67°C ; both of these approximations leave much to be desired from the standpoint of the present work. If their empirical equation for the temperature coefficient is valid $(1/C_v)(dC_v/dT) = 2.5 \times 10^{-3}$, and if it is considered that the empirical equation refers to the heat capacity of the gas at zero pressure C_0 at 30°C is $8.20 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$. The corresponding ideal velocity is $334.2 \text{ m sec.}^{-1}$, whereas the idealized experimental velocity at 9 kc is $333.9 \text{ m sec.}^{-1}$. The agreement is better than that to be expected considering the various possibilities for error, and it is concluded that no important part of the heat capacity of ethylene is lacking in the adiabatic compressibility at 9 kc, 760 mm pressure and 30°C . No band spectral analysis of sufficient scope to confirm or to modify this conclusion is known to us.

C. The variation of the velocity of sound with pressure and frequency

The results of a study of the variation of the velocity of sound in the dispersive region with pressure at 30°C are reported in Table I. A large number of determinations were made at 790 mm because this measurement served as a test of the purity of the ethylene. The spread of points is great, being $\pm 0.45 \text{ m sec.}^{-1}$ for the 94 kc and $\pm 0.75 \text{ m sec.}^{-1}$ for the 451 kc points. It is to be noted, however, that the difference $V_{451} - V_{94}$ has a maximum variation of $\pm 0.35 \text{ m sec.}^{-1}$, which is less than half that of the 451 kc measurements.

TABLE I. The variation of the velocity of sound in ethylene with pressure and frequency at 30°C .

		At 451 kc				
P in mm	790	472	236	83	60	60
V in m sec. ⁻¹	335.4*	337.6	341.4	345.7	344.8	345.7
w	1.007	1.004	1.002	1.001	1.001	1.001
		At 94 kc				
P	790	472	236	83		
V	333.1*	333.9	334.5	339.5		
w	1.007	1.004	1.002	1.001		

* These figures are the average of the following determinations each pair of which was made on a separate sample of gas.

450 kc	335.9	335.6	335.8	335.3	334.7	335.4	336.2	334.9
94 kc	333.4	333.6	333.1	333.1	332.9	332.7	333.3	332.7

⁷ Richards and Reid, J. Chem. Phys. 1, 114 (1933).

⁸ Haas and Stegeman, J. Phys. Chem. 36, 2127 (1932).

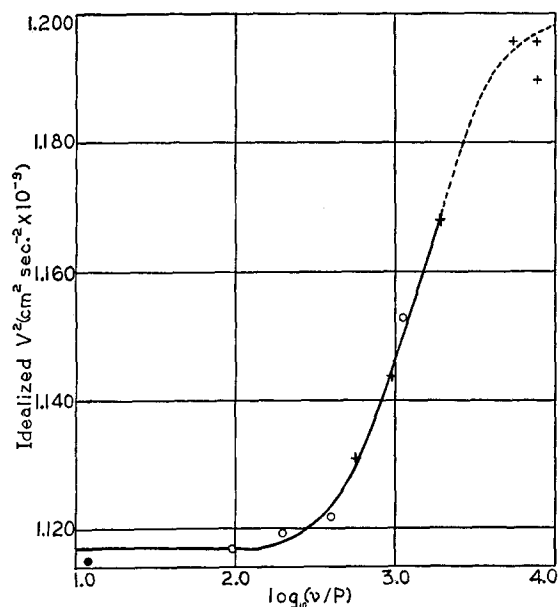


FIG. 1. The variation of the velocity of sound in ethylene with frequency and pressure at 30°C. 9 kc measurements indicated by black dots, 94 kc by circles, and 451 kc by plus signs. The line connecting the points is drawn from theoretical considerations discussed in the text.

Fig. 1 summarizes graphically the results of Table I by plotting, in the usual way, the square of the idealized velocity against the logarithm of the ratio of the acoustical frequency in Herzian cycles and the pressure in mm Hg equivalents. Several points in connection with this diagram should be noted. The S-curve has been drawn, according to the customary three-state approximation, from the points corresponding to $C_0 = 8.20$ cal. deg.⁻¹ mole⁻¹ and $C_\infty = 5.96$ cal. deg.⁻¹ mole⁻¹. The experimental values in the neighborhood of the supposed high frequency terminal velocity were made at very low pressures, and, because of the small mass reaction of the gas on the oscillator under these conditions, were of conspicuously less accuracy than the other determinations. An oscillator of higher frequency was not available, and no search for a constant velocity in the upper part of the dispersive region could therefore be undertaken. The moment of inertia of the hydrogen atoms around the carbon-carbon axis is so small that ethylene may enter a rotational dispersive region, analogous to that exhibited by hydrogen,⁹ before

⁹ Abello is apparently the discoverer of this dispersive region. Bourgin and Herzfeld and Rice (Phys. Rev. **31**,

the dispersive region due to the vibrations is wholly complete. The upper part of the S-curve has been drawn as a broken line to emphasize this uncertainty. No evidence for complexity of the dispersive region is, however, revealed by the measurements, since they fall uniformly on the S-curve within limit of experimental error.

D. The variation of the velocity of sound with temperature

A study of the temperature coefficient of the velocity at 94 and at 451 kc gave a series of measurements which are reported in Table II. The temperature coefficient was studied with somewhat more than the usual care, since by means of it certain conclusions may be reached which are directly serviceable in Section II.

TABLE II. The velocity of sound in ethylene at 790 mm pressure and various temperatures.

At 451 kc							
T°C	15.0	15.3	22.5	25.0	27.8	30.0	32.5
V m sec. ⁻¹	328.3	328.7	331.8	333.5	334.2	335.4*	336.3
T	35.0	35.0	37.5	40.0	40.0	42.0	45.0
V	336.8	337.1	338.6	340.1	340.0	340.5	341.7
At 94 kc							
T	15.0	15.3	20.0	22.5	25.0	27.8	30.0
V	325.5	325.7	328.1	329.4	330.7	332.0	333.1*
T	35.0	35.0	40.0	40.0	42.0	45.0	45.0
V	335.2	335.5	337.4	337.5	338.5	340.1	340.0

* Each of these values is the average of the eight determinations on different samples of ethylene gas which are quoted in Table I.

The continuous line connecting the 94 kc measurements is drawn from the data for the heat capacity quoted in *B* of this section, and from the equation $V_0 = \{(RT/M)(1 + R/C_0)\}^{1/2}$. It is to be noted that the disagreement of the points with the theoretical line is never greater than 0.3 m sec.⁻¹, which is well within a reasonable limit of absolute error for the velocity determinations. The theoretical line is, however, almost rectilinear, whereas a slight consistent tendency for the points to fall under this is observable both below and above 30°C. A dotted line has been drawn between the 451 kc measure-

691 (1928)) have attributed it to the failure of rotational energy adjustment; Kneser has recently supported this interpretation.

ments to give the most probable value of the velocity at this frequency at 790 mm pressure. The deviations of the experimental points from this average value is naturally somewhat greater than in the case of the 94 kc measurements.

E. Conclusions from the velocity of sound in pure ethylene

Owing to the lack of adequate band-spectral data it is not possible at present to describe the velocity of sound in the dispersive region in fundamental terms. The results may, however, be expressed in terms of numbers which will take on an exact meaning when the energy levels of the molecule are unequivocally defined.

From the ideal velocity of sound at a given temperature and various pressures and frequencies a characteristic time, ϑ , may be computed by the relationship

$$\vartheta = (C_0/\omega C_\infty) \{ (V_\omega^2 - V_0^2)/(V_\infty^2 - V_\omega^2) \}^{1/2}, \quad (1)$$

in which C_0 and C_∞ are the heat capacities when $\omega^2\vartheta^2 \cong 0$ and $\omega^2\vartheta^2 \cong \infty$, respectively, V_0 and V_∞ the corresponding ideal velocities, and V_ω the velocity at a circular frequency ω . This expression is approximate in several respects: notably a correction for the absorption has been neglected, and the time ϑ is without quantitative meaning in terms of specific transitions. The variations of ϑ with pressure and temperature, nevertheless, permit certain conclusions.

The conformity of experimental points to a symmetrical S-curve illustrated in Fig. 1 demonstrates, for example, that double collisions are the only appreciable means by which the various energy states which cause the dispersive region are excited. Similarly, since ϑ has been found to be independent of frequency and directly dependent upon the numerical density, the transition probabilities are sensibly equal from an acoustical standpoint for all of the contributing states. This strongly suggests that the vibrational energy attains equilibrium on every effective collision. The maximum acoustical absorption at 760 mm and 30°C evidently occurs at about 1.0×10^6 cycles sec.⁻¹. At this temperature and pressure the time ϑ has a value of 2.38×10^{-7} sec.

The activation energy of collision is evidently not great since the increase in $V_{451} - V_{94}$ is only 1.2 m sec.⁻¹ between 45° and 15°C (Fig. 2). In

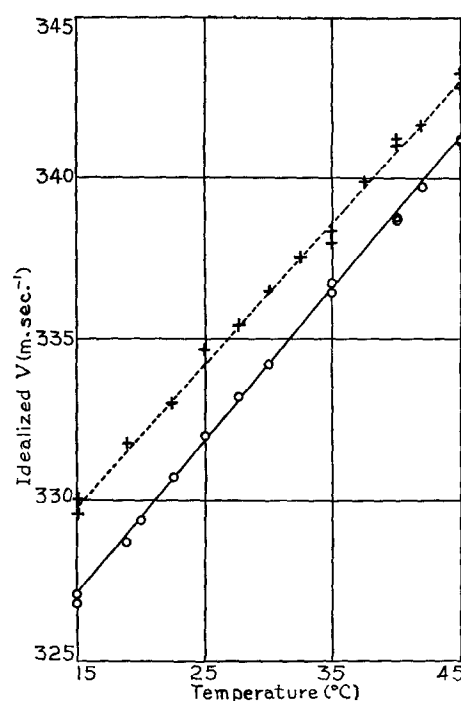


FIG. 2. The variation of the velocity of sound in ethylene with temperature at 780 mm. The line connecting the 94 kc points, which are indicated by circles, is the calculated ideal velocity. The dotted line connecting the 451 kc points, which are indicated by plus signs, assumes an activation energy of collision of 2800 cal. mole⁻¹.

such cases it is probable that the variation of the effective molecular cross section with temperature must be taken into account in the kinetic analysis of the transition probabilities. However, an upper limit for the activation energy of collision A may be simply obtained by writing, at temperatures T and T' ,

$$\vartheta'/\vartheta = (T'/T)^{1/2} e^{-(A(T'-T)/RTT')} \quad (2)$$

which involves the approximations that the cross section of the molecule is independent of the temperature, and that $(1+e^{-x})/(1+e^{-x'})=1$, where $x = h\nu_0/kT$. Since ϑ is 1.93×10^{-7} sec. at 45°C and 2.73×10^{-7} sec. at 15°C, the activation energy of collision is evidently about 2800 cal. mole⁻¹. If this value is substituted into the usual kinetic expression, it is found that the least separation of ethylene molecules on an effective collision is about 2×10^{-8} cm, which is only about a half of that found in ordinary kinetic processes. Since the measurements of the temperature coefficient of the velocity are unusually precise

and concordant, it is believed that the agreement of these two quantities is significant, and that no serious steric difficulty can be responsible for the failure of the vibrational energy to maintain its equilibrium distribution in the sound wave at high frequencies. A line drawn on the supposition that the activation energy of collision is

2800 cal. mole⁻¹ is identically the dotted line of Fig. 2.

II. BINARY MIXTURES OF ETHYLENE WITH OTHER GASES

The velocity of sound in a binary mixture of a gas *A* and a gas *B* will be approximately¹⁰

$$V^2 = \frac{P}{\rho_A m + \rho_B (1-m)} \left\{ 1 + R \frac{C_{0A}m + C_{0B}(1-m) + \omega^2 \vartheta^2 [C_{\infty A}m + C_{0B}(1-m)]}{[C_{0A}m + C_{0B}(1-m)]^2 + \omega^2 \vartheta^2 [C_{\infty A}m + C_{0B}(1-m)]^2} \right\}, \quad (3)$$

where ϑ is the characteristic time in the particular mixture, *P*, *C* and ρ refer to pressure, heat capacity, and density at *P* respectively, and *m* is the concentration of *A* expressed as a mole fraction. This expression is approximate in that it neglects absorption, and in that the characteristic time represents only roughly the reciprocal of the sum of the various transition probabilities involved in that part of the heat capacity (*C*_{0A} - *C*_{∞A}) which causes the dispersive region.

The velocity of sound in binary mixtures of ethylene with nitrogen, argon, helium and hydrogen has been measured, and the results and conclusions are reported below. The two gases were mixed under pressure in a reservoir and subsequently fed into the acoustical apparatus at a pressure of 780 mm. The gases were dried with phosphorus pentoxide, but not otherwise purified. The mixture was analyzed at the end of an experiment by absorbing the ethylene in fuming sulfuric acid, and measuring the residual volume of gas. This procedure was not of great accuracy, and a reproducibility of the measurements comparable to that obtained in the previous section is not to be expected. The temperature was uniformly maintained at 30°C.

Since the *P*, *v*, *T* relations of these mixtures have not been extensively studied, the procedure of idealizing the measured velocities of sound by the use of an acoustical equation which includes the second virial coefficient is not practicable. As an alternative the actual properties of the various gases, from data given in the *International Critical Tables*, were used for substitution into (3). They are summarized in Table III.

TABLE III. The acoustical constants of several gases.

Gas	A	C ₂ H ₄	He	H ₂	N ₂
ρ in g cm ⁻³ at 30°C and 780 mm	1.649 ×10 ⁻³	1.166 ×10 ⁻³	1.651 ×10 ⁻⁴	8.407 ×10 ⁻⁵	1.157 ×10 ⁻³
<i>C</i> ₀ / <i>R</i> at 30°C	1.5	4.115	1.5	2.46	2.504

A. Ethylene-argon, nitrogen, and helium mixtures

The various measurements at 94 and 451 kc are summarized in Table IV. In the case of nitrogen the results may be numerically reproduced by (3) only if ϑ is taken as being identical with ϑ obtained from the study of pure ethylene at a corresponding partial pressure. The agreement between the calculated and observed velocities is within experimental error, as a

TABLE IV. The velocity of sound at 780 mm and 30°C in various binary gaseous mixtures containing ethylene as one constituent.

Argon mixtures								
<i>m</i>	0.952	0.850	0.625	0.445				
<i>V</i> ₄₅₁	333.2	330.1	324.3	322.0				
<i>V</i> ₉₄	331.3	327.0	319.9	316.8				
Nitrogen mixtures								
<i>m</i>	0.970	0.959	0.895	0.870	0.851	0.800	0.635	0.500
<i>V</i> ₄₅₁	335.7	335.8	337.5	337.7	337.7	339.2	342.6	346.2
<i>V</i> ₉₄	333.8	334.1	335.2	335.3	335.8	343.1	339.5	—
Helium mixtures								
<i>m</i>	0.940	0.900	0.852	0.760				
<i>V</i> ₄₅₁	343.5	348.6	356.4	373.1				
<i>V</i> ₉₄	—	345.0	352.4	368.5				

¹⁰ This type of expression was first developed by Bourgin. The one here printed has been obtained from Einstein's treatment of the dispersion theory. See Richards, J. Chem. Phys. 1, 877 (1933).

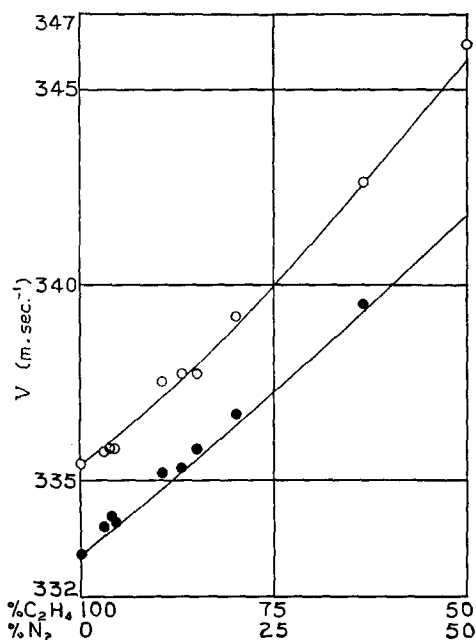


FIG. 3. The velocity of sound in nitrogen-ethylene mixtures at 780 mm and 30°C. The lines are calculated from the data in Table III; black dots indicate 94 kc and circles 451 kc.

glance at Fig. 3 demonstrates. With argon the agreement is not so satisfactory, since the experimental points lie increasingly above the calculated line with increasing concentrations of argon. A measurement on a sample of the argon employed gave a velocity of sound of 325.3 m sec.⁻¹ both at 451 and at 94 kc. Since this is conspicuously higher than the value 324.1 m sec.⁻¹ obtained from (3) when $m=0$ the discrepancy may safely be attributed to impurity of the argon.

With the helium measurements it is apparent that an even greater error due to impurity is present. At $m=0.75$, V_{451} calculated using the ϑ obtained from pure ethylene, is 386.7 m sec.⁻¹ and $V_{451 \text{ obs.}}$ read from a smoothed curve through the experimental points, is 375.0 m sec.⁻¹. Similarly, at $m=0.75$, $V_{94 \text{ calc.}}$ is 382.5 whereas $V_{94 \text{ obs.}}$ is only 370.3. It is to be noted, however, that $(V_{451} - V_{94})_{\text{calc.}}$ is 4.2 m sec.⁻¹ which agrees reasonably well with $(V_{451} - V_{94})_{\text{obs.}}$ which is 4.7 m sec.⁻¹. Similarly at $m=0.90$ the calculated difference is 3.0 m sec.⁻¹ and the experimental 3.6 m sec.⁻¹. There can be little question, therefore, that the cause of error is the inclusion

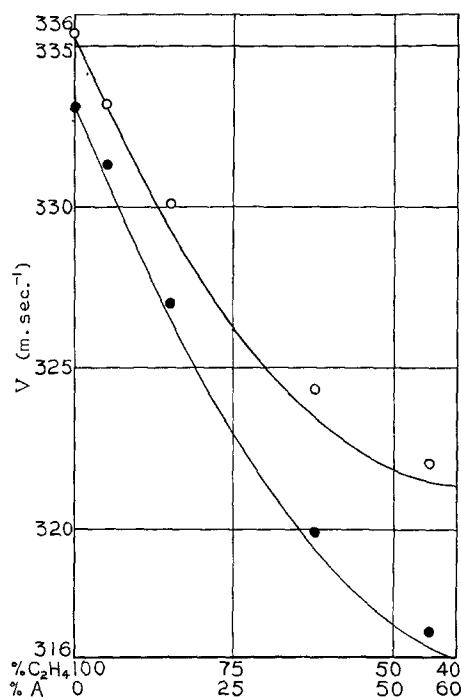


FIG. 4. A comparison of the measured and calculated velocities of sound in ethylene-argon mixtures at 780 mm and 30°C.

in the helium of a few percent of some denser impurity. Since *a priori* this is extremely likely, no serious concern is felt because of the lack of absolute agreement between the experimental and theoretical velocities.

Within experimental error, therefore, collisions of argon, nitrogen, and helium molecules fail entirely to bring about vibrational energy transitions in ethylene. It may roughly be estimated that their collision efficiencies must be less than a tenth that of the ethylene-ethylene collision.

B. Mixtures of hydrogen and ethylene

Measurements on hydrogen-ethylene mixtures are reported in Table V. It should be noted that the determinations at 94 kc which result in a velocity of sound greater than 400 m sec.⁻¹ are of

TABLE V. The velocity of sound in hydrogen-ethylene mixtures at 780 mm and 30°C.

m	0.950	0.940	0.890	0.780	0.51	0.306	0
V_{451}	342.5	345.3	354.0	376.4	462.9	584.2	1409
V_{94}	341.6	344.7	353.1	376.1	461.5	578.8	1319

considerably less accuracy than those below this figure. This is both because the tube-correction has not been determined for the apparatus at large velocities, and because the dimensions of the apparatus did not permit the detection of many points of maximum reaction when the wave-length was large. The agreement of the velocity at very low frequency calculated from (3) and that determined by experiment at 94 kc is in all cases satisfactory, however, and little hesitation is felt in basing approximate conclusions on the entire range of measurements.

It is at once apparent from an inspection of

$$V^2 = -\frac{P}{\rho} \left\{ 1 + \frac{R(1 - \omega^2 \vartheta_A \vartheta_B)(C_0 - C_\infty \omega^2 \vartheta_A \vartheta_B) + R\omega^2(\vartheta_A + \vartheta_B)[C_\infty(\vartheta_A + \vartheta_B) + C_A \vartheta_B + C_B \vartheta_A]}{(C_0 - C_\infty \omega^2 \vartheta_A \vartheta_B)^2 + \omega^2[C_\infty(\vartheta_A + \vartheta_B) + C_A \vartheta_B + C_B \vartheta_A]^2} \right\}. \quad (4)$$

In (4) subscript *A* refers to ethylene and subscript *B* refers to hydrogen, and

$$C_0 = C_{0A}m + C_{0B}(1-m),$$

$$C_\infty = C_{\infty A}m + C_{\infty B}(1-m),$$

$$C_A = (C_{0A} - C_{\infty A})m, \quad C_B = (C_{0B} - C_{\infty B})(1-m),$$

the heat capacities being expressed per mole and *m* indicating the mole fraction of *A*. As before $\rho_A m + \rho_B(1-m) = \rho$, ρ_A and ρ_B being, of course, the densities of *A* and of *B* at *P*. Finally

$$\vartheta_A = \vartheta_{AA}^0 / [m + \epsilon_B(1-m)],$$

$$\vartheta_B = \vartheta_{BB}^0 / [(1-m) + \epsilon_A m],$$

where ϵ_B is the relative efficiency, at *unit concentration*, of the ethylene-hydrogen collision and the ethylene-ethylene collision, and ϵ_A is the relative efficiency, at *unit concentration*, of the ethylene-hydrogen and the hydrogen-hydrogen collision. ϑ_{AA}^0 is the "relaxation time" of the ethylene-ethylene collision, and ϑ_{BB}^0 that of the hydrogen-hydrogen collision, both expressed at a numerical density corresponding to *P*. These are determined from the properties of the pure gases, and appropriate values of ϑ_A and ϑ_B found from gaseous mixtures containing small percentages of *A* and of *B* respectively.

In order to relate ϑ_A and ϑ_B to the relative efficiency of *A*-*B* and *A*-*A* or *B*-*B* collisions,

¹¹ This corresponds to Eq. (6.1) Richards, J. Chem. Phys. 1, 877 (1933).

Table V that two independent tendencies are at work, since $\Delta V (= V_{451} - V_{94})$ nearly vanishes in a mixture for which $m=0.75$, and increases markedly on either side of this composition. This behavior is plausibly explained if it is supposed that hydrogen-ethylene collisions are more efficient than ethylene-ethylene collisions in exciting the vibrational energy of ethylene, and that, conversely, ethylene-hydrogen collisions are more efficient than hydrogen-hydrogen collisions in exciting the rotational energy of hydrogen. A somewhat complicated situation results, which may most simply be described by the expression¹¹

expressed *per collision*, it is further necessary to consider the velocity and cross section of the *A* and *B* molecules. Ordinary kinetic considerations show that, at equal numerical densities, the factor relating number of collisions to concentration is $(\sigma_A + \sigma_B)^2 (M_A + M_B)^{1/2} / 2^{5/2} \sigma_A^2 M_B^{1/2}$, where σ indicates the kinetic diameter and *M* the molecular weight. By using σ_A (ethylene) = 4.3

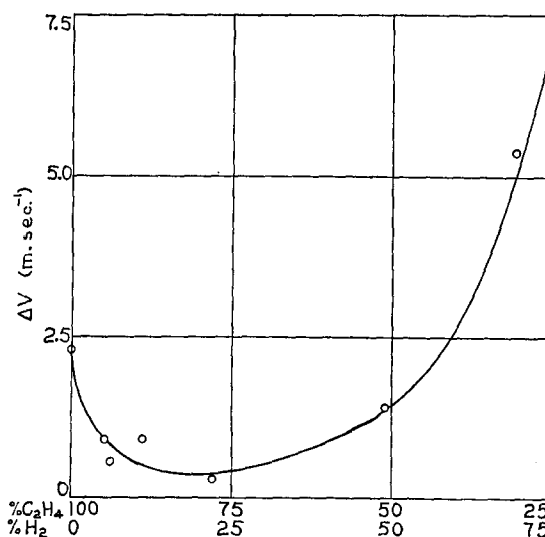


FIG. 5. A comparison of the measured difference in velocity of sound at 451 and at 94 kc. (ΔV) with that calculated on the assumption that an ethylene-hydrogen collision is twenty times as effective in causing transitions in the rotational energy of hydrogen as a hydrogen-hydrogen collision, and ten times as effective in causing transitions in the vibrational energy of ethylene as an ethylene-ethylene collision.

$\times 10^{-8}$ cm and σ_B (hydrogen) $= 2.2 \times 10^{-8}$ it is found that a molecule suffers 1.53 times as many collisions in a given concentration of hydrogen as in a given concentration of ethylene.

The results of the measurements at 780 mm and 30°C indicate that a hydrogen-ethylene collision is about 10 times as effective as an ethylene-ethylene collision in exciting the vibrational energy of ethylene, and that an ethylene-hydrogen collision is about 20 times as effective in giving rotational energy to hydrogen as a hydrogen-hydrogen collision. The correspondence of these assumptions with experiment is indicated by Fig. 5, where the heavy line indicates ΔV calculated from (4) on this basis and the circles are the experimental points. The agreement is within experimental error, and justifies the assumption, which is implicit in (4), that the adjustment of rotational energy in hydrogen is effected by a double-collision mechanism. It remains to attempt to reach an understanding of these findings.

III. DISCUSSION

It has been concluded in the previous sections that collisions with hydrogen are extremely effective in bringing about transitions between the lower vibrational energy states of ethylene, whereas collisions with argon, helium and nitrogen are virtually without effect. This raises the question which has been discussed in connection with the maintenance of the unimolecular decomposition rates of the paraffins by hydrogen. What advantage has the hydrogen molecule over other molecules (with the exception of the vibrating molecule itself and its close chemical analogs as, for example, its decomposition products) in effecting the conversion of translational energy into vibrational energy? We cannot attempt to answer this question here. A very brief review of several methods of attack will, however, be given in order to emphasize the necessity for further experiment.

It does not appear that the small mass of the hydrogen molecule can be of primary importance in this connection. If the laws of molecular impact are formulated in a purely classical

manner, after the method initiated by Oldenberg,¹² it is possible to imagine that a single hydrogen atom could give a part of its translational energy to a single more massive atom of some other molecule, and that all of the energy so imparted should appear as vibrational energy after the termination of the collision. The necessity for the conservation of linear momentum allows hydrogen a maximum advantage of a factor of less than two over helium in such a process. The experimental data, which indicate that this factor is in excess of 20, clearly demand another explanation.

The quantum mechanical approach to the problem leads to more promising conclusions. Zener¹³ and Rice¹⁴ have attempted solution by these means. Franck and Eucken¹⁵ have reduced this treatment to a qualitative picture which is more suitable for discussion here. It is supposed that the forces which ultimately make themselves felt by atomic exchange reactions are, with low relative translational energies, capable of causing small displacements of the nuclei in the colliding molecules. The efficiencies of various collisions are thus in a sense conditioned by the chemical reactivity of the participating molecules. In this respect hydrogen differs profoundly from helium, and a qualitative explanation for its advantage is found. A somewhat similar variant of the quantum mechanical treatment was suggested in Part II¹⁶ of this series when a mutual "bond-softening" of the colliding molecules was discussed. The great disadvantage of these methods of treatment is that they cannot, at present, supply numbers which may be compared with those obtained from actual measurement. The necessity for estimating the duration of the collision by the formulation of some dynamical mechanism of approach and separation of the molecules is a source of difficulty. It is not

¹² Oldenberg, *Phys. Rev.* **37**, 194 (1931); Heil, *Zeits. f. Physik* **14**, 31 (1932).

¹³ Zener, *Phys. Rev.* **38**, 277, 556 (1931).

¹⁴ Rice, *Phys. Rev.* **38**, 1943 (1931); *J. Am. Chem. Soc.* **54**, 4558 (1932).

¹⁵ Franck and Eucken, *Zeits. f. physik. Chemie* **B20**, 460 (1933).

¹⁶ Richards, *J. Chem. Phys.* **1**, 874 (1933).

possible, therefore, to accept this type of explanation without reserve in spite of its great plausibility.

Yet a third distinctive property of the hydrogen molecule, which has not been greatly stressed in this connection, arises from the smallness of its moment of inertia. As a result the rotational quanta for hydrogen are immense, and it has failed to attain a classical distribution of rotational energy even at room temperature. The occurrence of a dispersive region due to the failure of the rotational transitions to follow the acoustical cycle is surely due to this property; Zener has, indeed, essentially predicted such behavior.¹³ It is suggestive that, since ethylene is conspicuously more successful than hydrogen in giving rotational energy to hydrogen, it must also be that hydrogen can give its rotational energy to ethylene with relative ease. It appears at least possible that the magnitude of the rotational quanta which are so exchanged may be connected with the conspicuous effectiveness of the hydrogen molecule in exciting vibrational energy. If approximate "matching" or resonance occurred

between a hydrocarbon vibrational quantum and a hydrogen rotational quantum a fresh basis on which to build an explanation would appear.

Owing to the ill-defined condition of the present theoretical background it appears wiser to await an expansion of the very meager experimental material before attempting an explanation of the phenomena which have here been discussed. Comparative measurements of light and of heavy hydrogen at once suggest themselves as likely to provide desirable information. The chemical characteristics of the two are practically identical, and hence their behavior from the Franck-Eucken standpoint should be similar. The mass of the molecule of the heavy isotope is very near to that of helium, and any purely mass effects should, therefore, be readily separable. The larger moment of inertia of heavy hydrogen should on the other hand, profoundly alter any distinctive behavior which is due to rotational energy, and its smaller vibrational quantum should enhance any effects due to vibrational resonance. In this direction we hope for immediate progress.