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William T. Richards and James A. Reid

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Acoustical Studies. III. The Rates of Excitation of Vibrational Energy in Carbon Dioxide, Carbon Disulfide and Sulfur Dioxide¹

WILLIAM T. RICHARDS AND JAMES A. REID, *Princeton University*

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Measurements on these three gases at various pressures, temperatures and frequencies are reported. In all cases double collisions provide the predominant mechanism of excitation. The van der Waals or capillary forces follow the acoustical cycle without lag under the conditions of the experiments. The velocity of sound at 9 kc in carbon dioxide shows that a part of the heat capacity has already disappeared from the adiabatic elasticity at this frequency, and comparison with the measurements of other investigators leads to the belief that this term is missing even at considerably lower frequencies at ordinary temperatures. The remaining vibrational energy terms disappear together from the acoustical cycle, their rates of excitation being sensibly equal. There is a considerable activation energy necessary to excite the deformation vibration. The velocity of sound at 9 kc in carbon disulfide agrees well with that obtained by calculation from the results of band spectral analysis and hence no important energy terms appear to

be lacking at this frequency. The symmetrical linear ($S \leftrightarrow C \rightarrow S$) and the deformation ($S \downarrow C \uparrow S \downarrow$) vibrations leave the acoustical cycle together at high frequencies or at low pressures. A study of the dispersive region caused by this disappearance shows that the rates of excitation of the various energy states are identical within limit of error, and consequently that the activation energy of collision is uniform throughout the dispersive region. The velocity of sound at 9 kc in sulfur dioxide conforms reasonably well to the somewhat conflicting band-spectral data for the equilibrium heat capacity. There is a serious discrepancy between the results of the velocity measurements in the dispersive region here reported and the current interpretation of the few existing absorption measurements. A tentative argument is given whereby this discrepancy may be removed. Several theoretical questions which require further elucidation are discussed.

I. METHOD OF EXPERIMENT AND OF PRESENTATION

A. Apparatus

The measuring instruments were modifications of the sonic interferometer devised by Pierce.² Since they have already been described in a communication from this laboratory,³ only the briefest sketch is here necessary. Magnetostriction oscillators, cut from nichrome steel, were mounted in cylindrical tubes of Pyrex glass and driven by valve-tube circuits. Points of maximum reaction in the vibrating column of gas were explored with plane-ground Pyrex reflectors, and detected by means of a microammeter in the plate circuit of the driving oscillator. The displacements of the reflecting pistons were measured to 0.05 mm from 9 to 92

kc and to 0.005 mm from 94 to 451 kc. The frequency was measured to 0.05 percent at all temperatures; it is not necessary to quote here its exact value in each case. Determinations at 9 and 92 kc were made exclusively in Pyrex tubes of 2.5 cm internal diameter and of 1 mm wall-thickness. Determinations at 94 and 451 kc were made exclusively in Pyrex tubes of 1.0 cm internal diameter and 1 mm wall-thickness. The pressure and temperature control were suitable to reproduce the velocity of sound in a non-absorbing gas to ± 0.05 m sec.⁻¹.

The use of tubes of small diameter greatly simplifies the process of measurement, but necessitates a tube-correction to compensate for the retarding influence of the walls on the compressional wave. The tube corrections for this apparatus have already been defined by measurements in pentane and air at 9 and 92 kc and in pentane, propane and air at 94 and 451 kc. A number of measurements were made on other gases, but since they do not alter the previous values they will not be printed. In the meantime

¹ An advance notice of this work appeared in *Nature* **130**, 739 (1932). A few of the earlier conclusions have here been modified owing to the introduction of a more quantitative method for the analysis of experiment.

² Pierce, *Proc. Am. Acad. Sci.* **61**, 1 (1928).

³ Richards and Reid, *J. Chem. Phys.* **1**, 114 (1933).

a paper has appeared by Kaye and Sherratt⁴ and an investigation has been undertaken in the laboratory of Professor Pierce by Mr. G. A. Norton⁵ which very strongly support the Helmholtz-Kirchhoff reduction formula, and place measurements of the velocity of sound in small tubes in an extremely strong position.

As before the measurements at 9 and at 92 kc have been made compatible by a tube correction, and the measurements at 94 and 451 kc have been similarly adjusted to give mutual concordance. No attempt has been made to correlate the 92 and 94 kc measurements since a difference of a few tenths of a meter in the absolute velocities is considered of no importance. The tube corrections have already been applied to all the measurements quoted below.

B. "Idealization" of the measured velocity of sound

The velocity of a plane sinusoidal wave of infinitesimal amplitude propagated in an ideal, non-absorbing gas of molecular weight M and heat capacity at constant volume C is given by

$$V_{\text{ideal}} = \left\{ (RT/M)(1 + R/C) \right\}^{\frac{1}{2}} \quad (1)$$

This will be spoken of below as the *ideal velocity of sound*.

In interpreting measurements on the free-space velocity of sound in real gases it has been customary to make use of this expression, and consequently to neglect two sets of corrections. The first set deals with the acoustical conditions, and includes corrections for the finite amplitude of the wave, viscosity and heat conduction of the gas, and the like. No attempt to apply corrections of this character will be made, since it is believed that they are of secondary importance for the interpretation of the type of dispersive effect which is here discussed. The second set of corrections result from non-ideal behavior of the gas. Since it is expedient, in order to economize space, to plot measurements at various pressures and frequencies, or at various temperatures and frequencies, on a single Cartesian surface, corrections of the second type become imperative.

They will be introduced by means of a factor w which is to be applied in the sense $w = V_{\text{ideal}}^2 / V_{\text{real}}^2$. It has been obtained by the following argument.

If the van der Waals equation

$$(P + a/v^2)(v - b) = RT \quad (2)$$

is used for the description of a real gas of density ρ the velocity of sound is found to be

$$V = \left\{ \frac{RT + P(b - 2a/RT)}{M - \rho b} + \frac{R}{C} \cdot \frac{RT}{M - 2\rho b} \right\}^{\frac{1}{2}} \quad (3)$$

if appropriate derivatives for substitution into the equation $V = (\partial P / \partial \rho)^{\frac{1}{2}}_{\text{adiab}}$ are evaluated, neglecting terms in ρ^2 . Eq. (3) is suitable for the description of the velocity of sound at low frequency in a real gas, and may easily be adapted for use with a dispersive gas in which a part of the heat capacity $C_0 - C_\infty$ fails to follow the adiabatic acoustical cycle at high frequencies, if the assumption is made that the van der Waals forces remain in equilibrium. Since according to (2) $(\partial C_v / \partial v)_T = 0$, the heat capacity and the density remain independent variables, and the usual derivation according to the method of Einstein is not seriously disturbed. This yields

$$V_{\omega\mu}^{\frac{1}{2}} = \left\{ \frac{RT + P(b - 2a/RT)}{M - \rho b} + \frac{R(C_0 + \omega^2 \vartheta^2 C_\infty)}{(C_0^2 + \omega^2 \vartheta^2 C_\infty^2)} \cdot \frac{RT}{(M - 2\rho b)} \right\}^{\frac{1}{2}} \quad (4)$$

and is suitable for the description of a real dispersive gas which has a heat capacity of C_0 at equilibrium, of C_∞ at frequencies so high that $\omega^2 \vartheta^2 \cong \infty$, and in which the energy states contributing $C_0 - C_\infty$ to the heat capacity have identical approximate relaxation times ϑ . The factor μ is determined by the absorption.⁶

It is, therefore, the ratio of the squared velocity according to (1) and that calculated from (3) which determines the van der Waals correction factor w for the low frequency velocity of sound. Corresponding values of w in

⁴ Kaye and Sherratt, Proc. Roy. Soc. **A141**, 123 (1933).

⁵ G. A. Norton, private communication.

⁶ The significance of μ and of ϑ have been discussed by Richards in J. Phys. Chem. **1** (1933) on pages 865 (Eq. 1.8) and 876 (Eqs. 5.5 and 5.6), respectively.

the dispersive region may readily be obtained from the customary ideal dispersion equation developed from (1) and from its corrected equivalent (4). Measured velocities of sound which have been multiplied by a calculated quantity $w^{\frac{1}{2}}$ will be spoken of as *idealized measured values*.

A considerable advantage is gained by idealizing measured velocities if the energy levels of the molecule are known from band-spectral analysis. In this case (1) contains no unknown quantities, and the ideal value of the velocity of sound at very low frequency is defined with great accuracy. Any lack of correspondence with experiment at low frequencies becomes, therefore, of immediate interest.

In an ideal gas, the energy adjustments of which are effected by double collisions only, an increase of the acoustical frequency has the same effect on the velocity as a numerically equal decrease of pressure. This is, of course, the result of the fact that the number of double collisions per molecule is directly proportional to the pressure. Hence a given value of ν/P , where ν is the acoustical frequency, defines the velocity at any given temperature. A plot of V^2 against $\log_{10} \nu/P$ is a symmetrical *S*-curve if the gas has the dispersive properties described by (4). This is easily constructed and any experimental deviations from the regular function will be readily apparent.

C. The effect of traces of gaseous impurities

If there is a steric or energetic hinderance in the adjustment of vibrational energy by collisions between like molecules, very small traces of impurities may greatly affect the transition probability which is inferred from experiment. Since irregularities are reported below which appear to have this cause, it is perhaps worth while to cite a simplified specific example.

Let us consider a pure gas *A* at such a temperature and pressure that each molecule suffers on an average 10^{10} double collisions per second. Let us further suppose that on an average only one collision in 10^6 is effective in bringing about a given energy transition. This means that, for the transition in question, f_{AA} is 10^4 sec.^{-1} . Let us now introduce 0.1 percent of a gas *B* which has

approximately the same molecular weight and heat capacity as *A* and hence does not appreciably alter the measured value of the velocities at very low and at very high frequencies. The probability that the energy transition may be effected is now $f_{AA} + f_{AB}$. The number of collisions with *B* molecules suffered by an *A* molecule is about 10^7 per second. If each one of these is effective f_{AB} is 10^7 sec.^{-1} and is so far greater than f_{AA} which remains 10^4 sec.^{-1} that the dispersive region in the gas will shift to frequencies which are higher by almost three orders of magnitude. If, on the other hand, the efficiency of an *AB* collision is equal to or less than the efficiency of an *AA* collision f_{AB} becomes numerically far inferior to f_{AA} and the presence of the trace of gas *B* will cause no noticeable effect.

Traces of accidentally included impurities are, therefore, not likely to cause an apparent diminution of f_{AA} but may cause an enormous apparent increase. The lowest value observed for f_{AA} is, therefore, most likely to be correct if the gas is known to be reasonably pure.

Since an ordinary glass surface retains water in the adsorbed condition which will evaporate slowly into any pure gas in contact with the surface, irregularities are to be expected if water is an effective agent in bringing about energy transitions in the pure gas. Evidence is already at hand which indicates that collisions between water molecules and carbon dioxide molecules or oxygen molecules give rise to this effect.⁷ In such cases wholly trustworthy values of the *AA* probabilities may evidently be obtained only by the use of high vacuum technique.

II. MEASUREMENTS ON CARBON DIOXIDE

The carbon dioxide was prepared from calcium carbonate and a guaranteed brand of hydrochloric acid. It was passed through a drying train of calcium oxide and phosphorous pentoxide, and was, therefore, reasonably pure when admitted to the evacuated apparatus. An oil pump of conventional design was used for evacuation, and the apparatus was washed several times with pure gas before a series of measurements was

⁷ Carbon dioxide, Rogers, Phys. Rev. **41**, 369 (1932); Eucken and Becker, Zeits. f. physik. Chemie **B20**, 467 (1933); oxygen, Kneser, J. Acous. Soc. Am. **5**, 122 (1933).

made. It is significant that, even with these precautions, it was difficult to obtain reproducible results. Evidently traces of some substance which is extremely effective in adjusting the transverse vibration were not eliminated by this preliminary treatment.

A. The velocity of sound at 9 kc

The measured velocity of sound at 9 kc, 30°C, and 774 mm was 271.8 m sec.⁻¹, and at 403 mm was 272.2 m sec.⁻¹ at the same temperature. When idealized these yield an average of 272.5 m sec.⁻¹ at 9 kc, and show no trace of dispersion in this frequency and pressure region. The ideal velocity of sound at very low frequency from (1) may in this case be calculated with some precision, since the energy levels of the CO₂ molecule have been extensively studied. Strictly speaking the unperturbed Planck-Einstein φ -function for the vibrational energy

$$C_0/R = 5/2 + 2\varphi(\Theta_1/T) + \varphi(\Theta_2/T) + \varphi(\Theta_3/T) \quad (5)$$

must be modified, since the second energy state corresponding to the characteristic temperature $\Theta_1(O \downarrow C \uparrow O \downarrow)$ is so close to the first energy state of $\Theta_2(O \leftarrow C \rightarrow O)$ that a perturbation occurs in one of the three degenerate levels of the second state of the Θ_1 vibration. The heat capacity is somewhat larger than that given by (5) in consequence. The error is, however, small, and there is reason to believe it inappreciable at 30°C from the recent analysis of Adel and Dennison,⁸ and the approximate agreement at low temperatures of the measured heat capacity of carbon dioxide with that calculated from the Planck-Einstein function found by Eucken and Mücke.⁹ The value of C_0/R will, therefore, be considered to be 3.5116 at 30°C, which is the figure resulting from (5) if $\Theta_1 = 956^\circ$, $\Theta_2 = 1841^\circ$, and $\Theta_3 = 3331^\circ$. This corresponds to an ideal low frequency velocity of 271.2 m sec.⁻¹, and is significantly lower than the corresponding idealized experimental values at 9 kc. The discrepancy strongly suggests that a part of the heat capacity has already disappeared from the adiabatic cycle at acoustical frequencies considerably less and at frequencies of molecular

impact considerably greater than those of the 9 kc measurements here reported.

A certain amount of corroborative evidence for this conclusion is already at hand. *The International Critical Tables* give two empirical formulae for the velocity of sound in carbon dioxide over a range of temperatures, which were set up from the measurements of Buckendahl¹⁰ and of Dixon, Campbell and Parker¹¹ at atmospheric pressure. Both these agree that at 30°C and 760 mm the velocity of sound is 271.8 m sec.⁻¹, which corresponds to an idealized velocity of 272.5 m sec.⁻¹ under these conditions, and agrees satisfactorily with the 9 kc measurements reported above. The frequencies at which these measurements were made were evidently well within the audible range, and the conclusion follows that the missing energy terms have already disappeared at frequencies even below 9 kc at atmospheric pressure. Furthermore, Eucken and Mücke,⁹ on the basis of heat capacity measurements at equilibrium, were led to the conclusion that the term corresponding to the symmetrical linear ($O \leftarrow C \rightarrow O$) vibration was absent from the measurements on the velocity of sound at 3-4 kc made by Partington and Schilling and by Dixon. The missing term was believed to make a gradual reappearance only at high temperatures. On this assumption the ideal velocity at 9 kc should be 272.1 m sec.⁻¹ at 30°C, which agrees fairly well with the idealized measured value of 272.5 m sec.⁻¹. In view of considerations later to be discussed the conclusion of Eucken and Mücke will not be unconditionally supported, it being merely agreed that a term corresponding to about 1300 wave numbers is lacking at 9 kc and ordinary temperatures.

B. A revision of the customary notation

In view of the fact that several dispersive regions, which occur in quite separate ranges of frequency, must be distinguished, a point of notation arises. In writing V_0 for the velocity of sound corresponding to the equilibrium heat

¹⁰ Buckendahl, Diss. Heidelberg (1906). This paper was unfortunately not available, and the frequency at which the measurements were made is, therefore, unknown to us.

¹¹ Dixon, Campbell and Parker, Proc. Roy. Soc. A100, 1 (1921).

⁸ Adel and Dennison, Phys. Rev. 43, 716 (1933).

⁹ Eucken and Mücke, Zeits. f. physik. Chemie B18, 186 (1932).

capacity C_0 , and V_∞ corresponding to a high frequency heat capacity C_∞ it has already been stressed that the subscripts do not indicate zero and infinite acoustical frequencies, but are intended only to specify whether $\omega^2\vartheta^2 \leq 0$ or whether $\omega^2\vartheta^2 \leq \infty$ from the point of view of experiment. Since the values of the relaxation times of the excited states of the various modes of vibration may apparently be separated by many orders of magnitude, additional subscripts unfortunately become necessary in order to avoid ambiguity. For example the transverse ($O \uparrow C \downarrow O \uparrow$) vibration may maintain substantially its equilibrium distribution in the acoustical cycle at frequencies so high that the symmetrical linear ($O \leftarrow C \rightarrow O$) vibration is wholly absent from the effective heat capacity. In order to avoid multiple subscripts the following convention has been adopted, the terms "in" and "out" signifying equilibrium distribution and complete disappearance from the acoustical cycle respectively.

| Symbol | Mode of vibration | | |
|------------|--------------------------------------|--------------------------------|--|
| | $O \uparrow C \downarrow O \uparrow$ | $O \leftarrow C \rightarrow O$ | $O \rightarrow \leftarrow C \rightarrow O$ |
| V_∞ | out | out | out |
| V_6 | " | " | in |
| V_5 | in | " | out |
| V_4 | out | in | " |
| V_3 | " | " | in |
| V_2 | in | " | out |
| V_1 | " | out | in |
| V_0 | " | in | " |

These velocities designate a number of the possible terminal velocities of a colinear triatomic molecule, and may also be employed, by the usual conventions, to specify the corresponding quantities for any triatomic molecule. In this language the 9 kc velocity reported above corresponds approximately to both V_1 and to V_5 since the unsymmetrical linear ($O \rightarrow \leftarrow C \rightarrow O$) vibration is not appreciably excited at room temperatures.

C. The variation of the velocity of sound with pressure and temperature in the dispersive region

A detailed study was made of the variation of the velocity of sound with frequency and with pressure in the upper limit of the main vibrational dispersive region. This was undertaken because there is reason to believe that the $0 \rightarrow 1$ transition,¹² and the transverse vibration, which predominates in this dispersive region, has an appreciable fraction of its molecules in the second excited state at 30°C. The results of this study are presented in Table I, together with the appropriate van der Waals factors obtained from the constants $a = 3.61 \times 10^6 \text{ cm}^6 \text{ atm. mole}^{-1}$ and $b = 42.6 \text{ cc mole}^{-1}$. The idealized measurements have been graphed in Fig. 1 by plotting V^2 in $\text{cm}^2 \text{ sec.}^{-2} \times 10^{-8}$ as ordinates against $\log_{10} \nu/P$, where ν is the acoustical frequency in cycles per

TABLE I. Measurements of the velocity of sound in carbon dioxide at 30°C and various pressures and frequencies.

| At 450.7 kc | | | | | | | | |
|-----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| P in mm Hg | 70.5 | 116 | 237 | 408 | 431 | 602 | 604 | 774 |
| V in m sec. ⁻¹ | 283.7 | 283.6 | 283.6 | 283.4 | 283.5 | 283.2 | 283.4 | 283.0 |
| w | 1.0005 | 1.0007 | 1.0015 | 1.0026 | 1.0028 | 1.0039 | 1.0039 | 1.0050 |
| P | 776 | 777 | 778 | 800 | 880 | 935 | 1012 | 1180 |
| V | 283.1 | 282.9 | 283.1 | 282.8 | 282.8 | 282.9 | 282.7 | 282.4 |
| w | 1.0050 | 1.0050 | 1.0050 | 1.0052 | 1.0057 | 1.0060 | 1.0065 | 1.0076 |
| P | 1336 | 1640 | | | | | | |
| V | 282.2 | 281.5 | | | | | | |
| w | 1.0087 | 1.0108 | | | | | | |
| At 94.0 kc | | | | | | | | |
| P | 70.5 | 116 | 237 | 408 | 602 | 604 | 774 | 778 |
| V | 283.6 | 283.4 | 282.9 | 282.2 | 281.3 | 281.5 | 280.4 | 280.0 |
| w | 1.0005 | 1.0007 | 1.0016 | 1.0027 | 1.0040 | 1.0040 | 1.0052 | 1.0052 |
| P | 800 | 880 | 935 | 1012 | 1180 | 1336 | 1474 | 1640 |
| V | 280.3 | 280.0 | 279.7 | 279.3 | 278.4 | 277.0 | 276.7 | 275.6 |
| w | 1.0054 | 1.0060 | 1.0063 | 1.0068 | 1.0080 | 1.0091 | 1.0102 | 1.0114 |

¹² See for example, Richards, J. Chem. Phys. 1, 872 (1933).

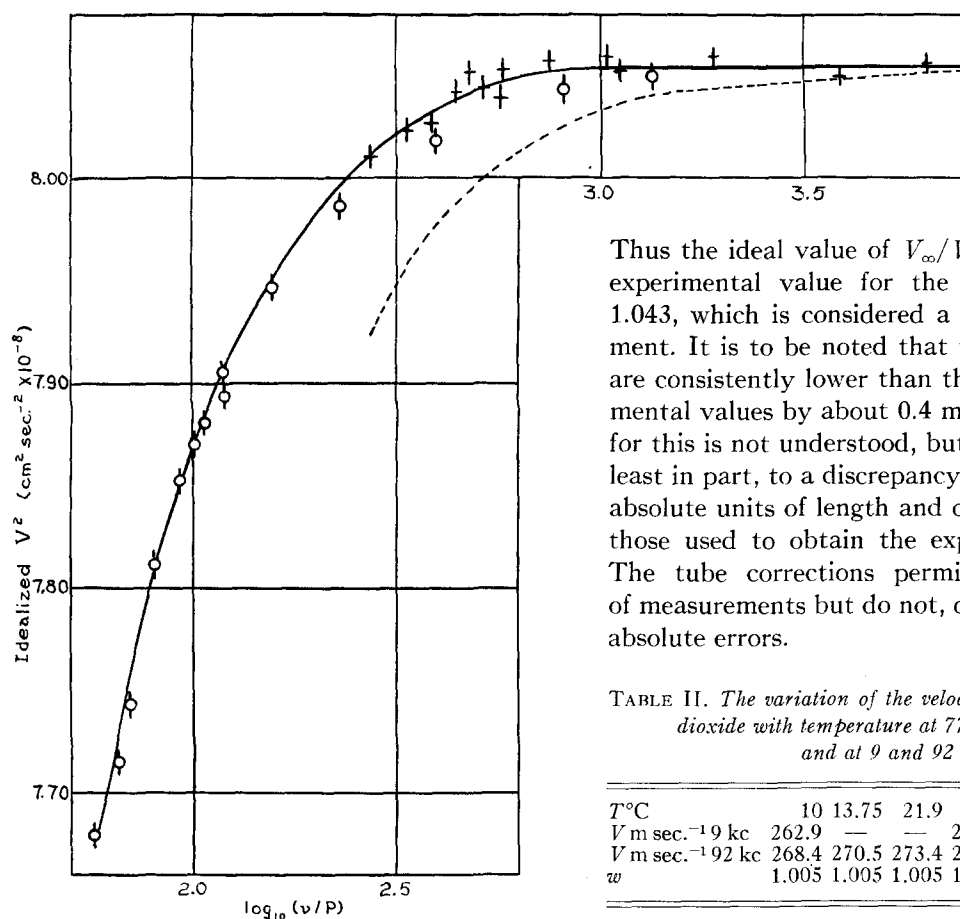


FIG. 1. The variation of the velocity of sound in carbon dioxide with frequency and pressure at 30°C. Experimental points are indicated by plus signs at 451 kc, and by circles with lines through them at 94 kc, the extension of the vertical line being equivalent to ± 0.1 m sec.⁻¹. The continuous line is drawn from theory, and the dotted line indicates the course of the experimental points at 451 kc if they are uncorrected for van der Waals forces.

second and P the pressure in mm of mercury, as abscissae. The solid line in Fig. 1 is the theoretical V^2 , $\log v/P$ curve for an ideal gas in which $V_\infty/V_1 = 1.042$, $f_{10} = f_{21}$ etc. $= 2.23 \times 10^5$ per molecule per second at 760 mm, and in which the excitation is brought about wholly by double collisions. The dotted line shows the course of the 45 kc measurements if they are uncorrected for departures of carbon dioxide from ideal behavior.

The idealized measured velocities average to give 283.7 m sec.⁻¹ as the terminal velocity. The ideal terminal velocity using an apparent heat capacity ratio of 1.400 is 283.2 m sec.⁻¹.

Thus the ideal value of V_∞/V_1 is 1.041 and the experimental value for the same quantity is 1.043, which is considered a satisfactory agreement. It is to be noted that the ideal velocities are consistently lower than the idealized experimental values by about 0.4 m sec.⁻¹. The reason for this is not understood, but it may be due, at least in part, to a discrepancy between the exact absolute units of length and of temperature and those used to obtain the experimental figures. The tube corrections permit intercomparison of measurements but do not, of course, eliminate absolute errors.

TABLE II. The variation of the velocity of sound in carbon dioxide with temperature at 774 mm pressure, and at 9 and 92 kc.

| T°C | 10 | 13.75 | 21.9 | 30.0 | 50.0 | 70.0 | 90.0 |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| V m sec. ⁻¹ 9 kc | 262.9 | — | — | 271.8 | 279.2 | 286.9 | 295.0 |
| V m sec. ⁻¹ 92 kc | 268.4 | 270.5 | 273.4 | 274.6 | 279.9 | — | — |
| w | 1.005 | 1.005 | 1.005 | 1.005 | 1.004 | 1.004 | 1.004 |

Measurements were made on the velocity of sound at 770–776 mm between 10°C and 90°C at 9 kc and between 10°C and 50°C at 92 kc. These are summarized in Table II, the van der Waals factors having been obtained from constants already given. The idealized measured velocities are plotted against temperature in Fig. 2. It is to be noted that the velocity at 30°C and 92 kc is 274.6 m sec.⁻¹ in Table II and at 94 kc and the same pressure is 280.2 according to Table I. Only a small part of this discrepancy is accounted for by the difference in frequency. This is unfortunate, for it indicates that the purity of the carbon dioxide used for the study of the temperature coefficient was not as great as that used for the study of the pressure coefficient. This is confirmed by the unsystematic character of the points in the dispersive region of the former study, as illustrated in Fig. 2. Calculation shows that the probability of the 1→0 transition has been increased by a factor of about 3.

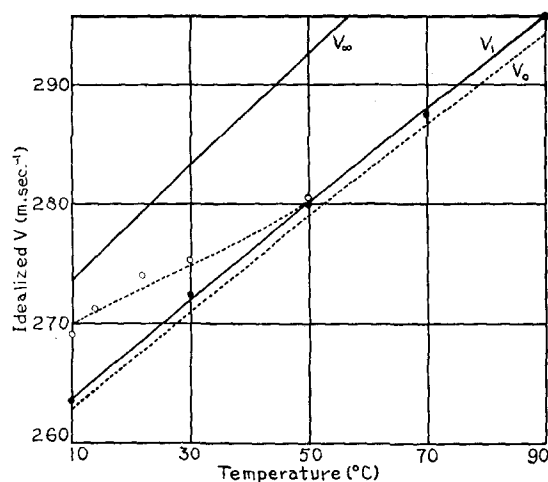


FIG. 2. The variation of the velocity of sound in carbon dioxide with temperature and frequency at 773 mm pressure. The various continuous and dotted lines conform to the convention explained in Section IIB with the exception of the dotted line connecting the 92 kc points, which have been indicated by circles. 9 kc points are indicated by black dots.

Whatever the impurity present, however, its effect on the 9 kc velocity was too slight to be experimentally manifest, for the 9 kc measurements could be reproduced quantitatively without difficulty.

D. Conclusions from the study of the velocity of sound in carbon dioxide

(1) The van der Waals forces follow the acoustical cycle quantitatively throughout the regions of pressure, temperature and frequency which were studied. This is based on the course of the dotted line in Fig. 1 and similar uncorrected constructions which have not been given to avoid confusing the diagrams.

(2) The mechanism by which excitation and de-excitation of the vibrational energy is effected is wholly that of double-collisions within the limit of error of experiment. This conclusion is based on the agreement of the 94 and 451 kc measurements at low pressures, and on the conformity of both to the fragment of a symmetrical S-curve drawn in Fig. 1. As a corollary it may be stated that the radiation life-time of the first excited state of the transverse vibration is greater than 10^{-4} seconds.¹³

¹³ An argument communicated to us privately by Professor E. U. Condon indicates that this lifetime is between 1 and 100 seconds.

(3) The velocity of sound at 9 kc and 774 mm pressure between 10°C and 90°C conforms closely to that calculated on the assumption that the symmetrical linear ($O \leftarrow C \rightarrow O$) vibration is absent from the heat capacity under these conditions. The reason for this conclusion has been discussed at some length above in connection with the 30°C velocity at 9 kc, at other temperatures it follows from a consideration of Fig. 2.

(4) The velocity of sound at the highest frequencies and lowest pressures employed in this study corresponds to a heat capacity in which the rotational terms are fully active and are classically excited. It is maintained constant for at least one order of magnitude of frequency or of pressure change. This statement is justified by measurements at large values of $\log \nu/P$ in Fig. 1. The magnitude of this terminal velocity corresponds to that measured by Kneser,¹⁴ Pielemeier,¹⁵ and Eucken and Becker,¹⁶ although none of these authors have demonstrated its constancy over so wide a range of conditions.

(5) The probability of the $1 \rightarrow 0$ transition of the transverse vibration is 2.23×10^5 per molecule per second at 760 mm and 30°C. This is reasonably in accord with the somewhat less carefully defined values given by Pierce,¹⁷ Kneser¹⁴ and Pielemeier.¹⁵ The chemical purity of the gas is so acutely important in determining the absolute value of this constant that exact agreement between different investigators is not to be expected at present.

(6) The probability of the $2 \rightarrow 1$ transition is equal to this within a factor of about 5. This follows⁶ from the correspondence of the experimental points and the continuous line in Fig. 1. A slight tendency for the points to fall under the continuous line may perhaps be imagined at large values of $\log \nu/P$, but it is certainly insufficient to justify quantitative conclusions.

(7) The temperature coefficient of the dispersion is adequately accounted for if it be assumed that the $1 \rightarrow 0$ transition of the transverse mode is effected only by molecules able to

¹⁴ Kneser, *Ann. d. Physik* **11**, 777 (1932); **12**, 1015 (1932).

¹⁵ Pielemeier, *Phys. Rev.* **41**, 833 (1932).

¹⁶ Eucken and Becker, *Zeits. f. physik. Chemie* **B20**, 467 (1933).

¹⁷ Pierce, *Proc. Am. Acad. Sci.* **60**, 271 (1925).

supply an activation energy of 6000 cal. mole⁻¹. On this assumption the relative translational energy for the 0→1 transition must evidently exceed 8000 cal. mole⁻¹. The probable error, of this determination is great, and an accuracy better than ±2000 cal. mole⁻¹ may not be claimed. The slope of the V_{92} curve against temperature is difficult to determine from the experimental points, and the presence of a trace of impurity may evidently also somewhat have obscured the result.

(8) The activation energy of the 2→1 transition can evidently not be far inferior to this figure, since no flattening of the S-curve in Fig. 1 is observed at large values of $\log \nu/P$.

(9) The effective collision diameter is found to have about one-fifth of its value for ordinary kinetic processes from the data given above. This conclusion is highly qualitative since the experimental determination of the activation energy is not exact.

III. MEASUREMENTS ON CARBON DISULFIDE

The carbon disulfide was obtained from the best certified commercial source. It was fractionated through phosphorous pentoxide, only the middle third being retained for study. The apparatus was pumped out and washed several times with pure vapor before each determination. It is apparent from the scattering of points in the dispersive region that this method of preparation was not wholly adequate. Additional difficulty in obtaining accurate measurements in the dispersive region was occasioned by the enormous acoustical absorption of carbon disulfide vapor. Absorption reduced the intensity of the electrical reaction to about 1 percent of its value after 5 wave-lengths in the center of the dispersive region. This is a somewhat greater effect than is to be expected from the magnitude of the acoustical absorption coefficient, although so large a part of the heat capacity disappears from the acoustical cycle with a hundred-fold change in frequency that outstanding absorptive properties must result.

Table III summarizes the measurements made at 30°C and various frequencies and pressures; they are presented graphically in Fig. 3, after being corrected for deviations from perfect

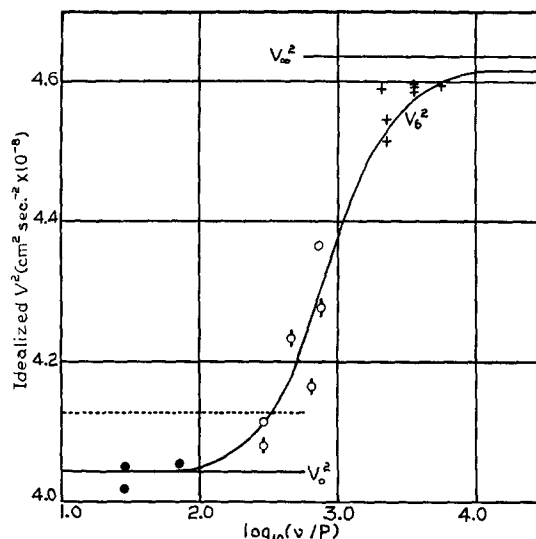


FIG. 3. The variation of the velocity of sound in carbon disulfide with frequency and pressure at 30°C. 451 kc measurements are indicated by plus signs, 94 kc by circles with lines through them, 92 kc by circles and 9 kc by black dots. The continuous line has been drawn from theoretical considerations. The measurements are not sufficiently accurate, however, to define unequivocally the high frequency terminal velocity, and the upper part of the S-curve must therefore be considered tentative.

behavior. The correction constants employed were $a = 11.61 \times 10^6$ cc² atm. and $b = 76.8$ cc per mole. The high frequency terminal velocity is in some doubt, since no oscillator above 451 kc was available, and it was found impossible to make reproducible measurements at pressures below 80 mm. That indicated in the figure, which corresponds to an apparent heat capacity including rotational terms and terms due to the unsymmetrical linear (S→←C→S) vibration in their equilibrium distributions, appears to accord well

TABLE III. The velocity of sound in carbon disulfide at 30°C and various frequencies and pressures.

| 451 kc | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|
| <i>P</i> mm | 215 | 200 | 200 | 128 | 128 | 128 | 80 |
| <i>V</i> m sec. ⁻¹ | 213.6 | 212.0 | 212.7 | 213.9 | 214.0 | 213.9 | 214.1 |
| <i>w</i> | 1.006 | 1.005 | 1.005 | 1.004 | 1.004 | 1.004 | 1.002 |
| 94 kc | | | | | | | |
| <i>P</i> mm | 321 | 200 | 128 | 128 | | | |
| <i>V</i> m sec. ⁻¹ | 201.0 | 205.1 | 203.6 | 206.4 | | | |
| <i>w</i> | 1.010 | 1.006 | 1.004 | 1.004 | | | |
| 92 kc | | | | 9 kc | | | |
| <i>P</i> | 309 | 128 | | 314 | 309 | 128 | |
| <i>V</i> | 201.8 | 208.5 | | 200.3 | 199.5 | 201.0 | |
| <i>w</i> | 1.010 | 1.004 | | 1.010 | 1.010 | 1.004 | |

TABLE IV. The velocity of sound in carbon disulfide at various temperatures.

| At 200 mm and 451 kc | | | | | | |
|-------------------------|-------|-------|-------|-------|-------|-------|
| $T^{\circ}\text{C}$ | 20.0 | 20.0 | 30.0 | 30.0 | 40.0 | 40.0 |
| $V \text{ m sec.}^{-1}$ | 210.0 | 209.8 | 212.0 | 212.7 | 214.7 | 214.7 |
| w | 1.006 | 1.006 | 1.005 | 1.005 | 1.005 | 1.005 |
| At 309–314 mm and 92 kc | | | | | | |
| $T^{\circ}\text{C}$ | 25.0 | 26.0 | 27.5 | 30.0 | 34.0 | 37.6 |
| $V \text{ m sec.}^{-1}$ | 200.6 | 200.7 | 201.8 | 201.8 | 202.9 | 203.9 |
| w | 1.012 | 1.012 | 1.011 | 1.010 | 1.010 | 1.009 |
| At 309–314 mm and 9 kc | | | | | | |
| $T^{\circ}\text{C}$ | 25.0 | 30.0 | 30.0 | 50.0 | 60.0 | 70.0 |
| $V \text{ m sec.}^{-1}$ | 198.7 | 200.3 | 199.5 | 206.5 | 209.6 | 212.5 |
| w | 1.012 | 1.010 | 1.010 | 1.009 | 1.008 | 1.007 |

with the measurements. The velocities at 9 kc correspond well with those calculated from band-spectral analysis for equilibrium conditions.¹⁸

Table IV summarizes in a similar manner measurements made on the temperature coefficient of the velocity under various conditions. Fig. 4 represents graphically the result of the measurements at 9 and 92 kc and 309–314 mm only.

These data are the justification of the following conclusions.

(1) The van der Waals forces follow the acoustical cycle without lag throughout the region experimentally investigated. This follows from the mutual discordance of measurements before the w correction has been applied.

(2) The transverse ($S \uparrow C \downarrow S \uparrow$) and symmetrical linear ($S \leftarrow C \rightarrow S$) vibration leave the acoustical cycle at the same frequencies of sound, and their characteristic adjustment rates are identical within limit of error. This follows from the conformity of the experimental points to the symmetrical S-shaped V^2 against $\log \nu/P$ curve which is illustrated by Fig. 3.

(3) The mechanism by which the excitation of these states is effected is one of double collisions only over the range and within the error of

¹⁸ The fundamental molecular frequencies were obtained from Villars, Chem. Rev. 9, 369 (1932). The empirical formula given in the *Int. Crit. Tables* for the velocity of sound does not agree either with our measurements or with the band-spectral results. Since the values are consistently too high, it may be assumed that a trace of some unknown impurity has been unintentionally included in the construction of the formula. Air, for example, owing to its smaller density and heat capacity could produce such an error if present even in very small quantities.

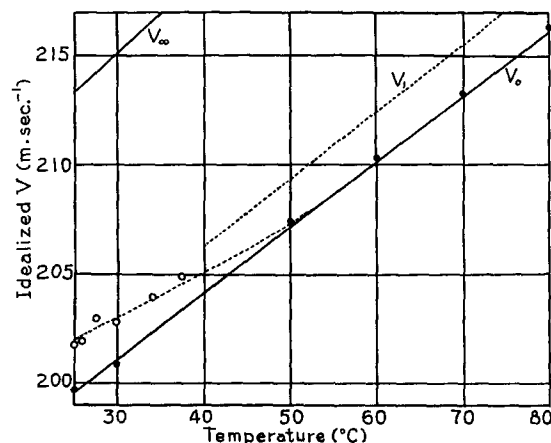


FIG. 4. The variation of the velocity of sound in carbon disulfide with temperature and frequency at 310 mm pressure. The conventions are the same as in Figs. 2 and 3.

experiment. Here, again, conformity to the S-curve in Fig. 3 is sufficient proof.

(4) The activation energy of collision for that process of excitation which dominates in the low frequency part of the dispersive region is about 5400 cal. mole⁻¹. The effective cross section appears to be of normal magnitude for this excitation process, although the error of the experiments is great enough to make this statement somewhat questionable. The activation energy and cross section have been obtained, as usual, from the slope of the line connecting 92 kc points in Fig. 4.

(5) The activation energy of collision and effective cross section for the excitation process which determines the upper part of the dispersive region are identical with those dominating the lower part within limit of experimental error.

There are two methods for justifying this statement. The measurements at 200 mm and 451 kc quoted in Table IV are in accord with the 92 kc measurements graphed in Fig. 4, but uncertainty concerning the high frequency terminal velocity somewhat obscures their significance. Also, the conformity of the 451 kc measurements plotted in Fig. 3 with the symmetrical S-curve may be used as a powerful supporting argument. A difference of 2000 cal. mole⁻¹ in the activation energy of collision between the processes determining the lower and higher parts of the dispersive region would result, with normal cross sections, in a difference of nearly thirty-fold

in rate. This difference would be manifest by a marked tendency of the S-curve to flatten in the high frequency region, and the measurements although inexact, are ample to demonstrate that no such effect is present.

(6) The probabilities of the $1 \rightarrow 0$, $2 \rightarrow 1$, etc., transitions of the deformation vibration are evidently about 7.8×10^5 per molecule per second at 30°C and 310 mm pressure. This is significantly greater than the corresponding probabilities for carbon dioxide which are 9.1×10^4 per molecule per second under these conditions.

IV. MEASUREMENTS ON SULFUR DIOXIDE

Relatively little attention has here been devoted to sulfur dioxide because the band spectral analysis appears to be controversial. The measurements reported below were, indeed, obtained merely during the process of defining the tube-correction. They are printed to permit a rough comparison with the absorption coefficients measured by Grossmann.¹⁹

The sulfur dioxide was obtained from tanks of the usual commercial product. It was dried by phosphorus pentoxide, but not further purified. The absolute values of the velocities are, therefore, not unassailable, and a scattering of experimental points is to be expected.

TABLE V. The velocity of sound in sulfur dioxide at 30°C and various frequencies and pressures.

| At 451 kc | | | | |
|----------------------------------|-------|-------|-------|-------|
| <i>P</i> in mm | 770 | 770 | 425 | 200 |
| <i>V</i> in m sec. ⁻¹ | 222.4 | 222.6 | 223.9 | 224.9 |
| <i>w</i> | 1.013 | 1.013 | 1.007 | 1.003 |
| At 94 kc | | | | |
| <i>P</i> | 770 | 770 | 425 | 200 |
| <i>V</i> | 221.9 | 221.1 | 222.8 | 223.7 |
| <i>w</i> | 1.013 | 1.013 | 1.007 | 1.003 |

Table V summarizes the measurements at 30°C at 94 and at 451 kc. The van der Waals factor was obtained from the constants $a = 6.7 \times 10^6 \text{ cm}^6 \text{ atm. mole}^{-1}$, $b = 56 \text{ cm}^3 \text{ mole}^{-1}$. A measurement at 9 kc, 30°C , and 480 mm gave a velocity of sound of 222.3 m sec.⁻¹, and requires multiplication by a factor of $(1.008)^{\frac{1}{2}}$ in order to give the corresponding idealized velocity.

¹⁹ Grossmann, Ann. d. Physik 5, 681 (1932).

The ideal velocity at very high frequencies of sound will be $(1.3333 RT/M)^{\frac{1}{2}}$ or 229.0 m sec.⁻¹ at 30°C if no vibrations contribute to the heat capacity, and if the rotations are classically excited and follow the wave without lag. At very low frequencies the heat capacity ratio from band spectra is 1.269 if the analysis of Bailey, Cassie and Angus,²⁰ which gives the fundamental frequencies of 610, 1164 and 1369 cm^{-1} is employed, and 1.263 using the more recent values of 510, 1150, and 1370 cm^{-1} due to Chow²¹ and Smyth.²² Thus the ideal velocity of sound at very low frequencies should lie between 223.5 and $222.9 \text{ m sec.}^{-1}$ at 30°C . This accords with the idealized measured 9 kc velocity.

In Fig. 5 the experimental data are sum-

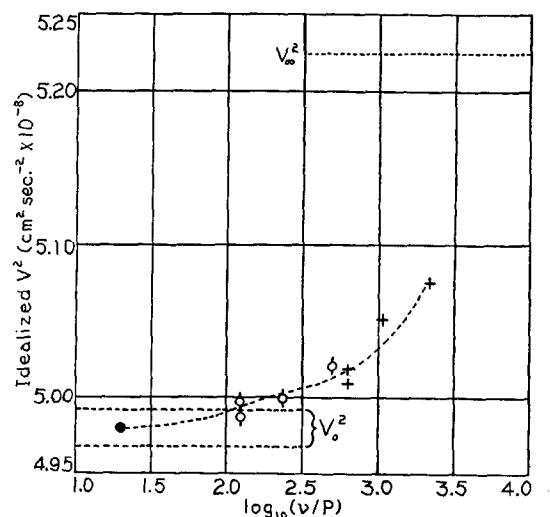


FIG. 5. The variation of the velocity of sound in sulfur dioxide with pressure and frequency at 30°C . The two dotted lines at low values of V^2 represent the low frequency velocity of sound according to two different band-spectroscopic analyses. The curved dotted line connecting experimental points is based on an unproved hypothesis which is tentatively advanced in the text.

marized graphically in the usual way. Several conclusions are clearly indicated by this diagram.

(1) The van der Waals forces follow the adiabatic cycle quantitatively at 30°C to frequencies of 450 kc and 400 mm pressure. This follows from a plot, which has not been repro-

²⁰ Bailey, Cassie and Angus, Proc. Roy. Soc. London A130, 142 (1930).

²¹ Chow, Phys. Rev. 44, 638 (1933).

²² Smyth, Phys. Rev. 44, 690 (1933).

duced, of $\log \nu/P$ against the non-idealized measured velocities.

(2) The dispersive region must be due, at least in part, to sluggishness in the adjustment of the energy states characterized by the fundamental frequency 510 cm^{-1} . Supposing that the two high frequency molecular vibrations disappear from the adiabatic cycle, leaving only the lowest in equilibrium, the ideal velocity of sound would be about $224.3 \text{ m sec.}^{-1}$ at very high frequencies, and this is significantly lower than the highest idealized measured value of $225.3 \text{ m sec.}^{-1}$.

(3) The position of the dispersive region in sulfur dioxide leads to the expectation that the absorption maximum will be in the neighborhood of $\log \nu/P = 3.5$ or about 2400 kc at atmospheric pressure.

The last of these conclusions permits a comparison with Kneser's prediction,²³ from the absorption measurements of Grossmann, that the absorption maximum must occur at about 20°C (the temperature is not exactly specified) and atmospheric pressure at about 1000 kc . A combination of these two figures yields an activation energy of $15,000 \text{ cal. mole}^{-1}$ by the approximate formula²⁴

$$\omega_{\max}/\omega'_{\max} = e^{-(A(T'-T)/RTT')},$$

So large an activation energy of collision cannot seriously be considered, since it implies a fantastically large effective molecular cross section in view of the rapid rate at which transitions occur. It is, therefore, necessary to supply an explanation for the discrepancy.

The argument given in the following paragraph is presented for this purpose, but it must be considered to be highly tentative in character.

If the dispersive or absorptive region is due to the concomitant dropping out from the acoustical cycle of a group of energy states which have identical rates of adjustment, the effect is normally complete in a frequency range the upper limit of which is a hundred times the lower limit. If, for example, dispersion first becomes manifest at 10 kc the high frequency

terminal velocity will usually have been sensibly attained at 1000 kc at constant temperature and pressure. It will be noticed by consulting Fig. 5 that although the velocity at $\log \nu/P = 2.0$ is sensibly greater than that at low frequencies, the dispersive region will not be complete at $\log \nu/P = 4.0$. Furthermore, a function of the type of the dotted line appears better suited to describe the experimental points than the conventional S-shaped curve. This suggests that one of the series of energy states corresponding either to 1160 cm^{-1} or to 1370 cm^{-1} is somewhat less readily adjusted by collisions than those states corresponding to the 510 cm^{-1} vibration. This is supported by the slight fall of the absorption coefficient measured by Grossmann at the beginning of the vibrational absorptive region. If this hypothesis is granted, the absorption maximum predicted by Kneser must be shifted to higher frequencies at 20°C and atmospheric pressure, and the magnitude of the activation energy of collision which must be assumed is very greatly diminished. Neither the velocity nor the absorption measurements are of sufficient accuracy to define the matter more exactly, but there appears at present no convincing ground for believing them incompatible.

Since the terminal velocity at high frequencies may be measured at 451 kc and 30°C only at pressures below 70 mm no quantitative statement of the transition probabilities of the various vibrational energy states may here be made. The predominant adjustment rate at 30°C is evidently about five times that of carbon disulfide, and about 15 times that of carbon dioxide.

V. DISCUSSION

It is apparent that at least one dispersive region in the range of acoustical frequencies now experimentally available is to be expected with polyatomic gases in which the vibrational heat capacity is appreciable. It is of little interest, therefore, merely to multiply the number of examples of dispersive gases, and attention is rather to be directed to the information which they provide concerning the mechanism of the transformation of kinetic to vibrational energy. Unfortunately, however, attempts to correlate experiment and theory must at present be highly speculative, since the descriptions of these

²³ Kneser, *Ann. d. Physik* **16**, 337 (1933).

²⁴ This is made on the basis of Eq. (15) of page 740, Richards and Reid, *J. Chem. Phys.* **1** (1933). The approximations are $f_{01}=f_{12}=\dots=0$, $(T/T')^{1/2}=1$, and $B_0/B_{\infty}Q = B'_0/B'_{\infty}Q'$.

phenomena in terms of quantum mechanical processes are so general that they do not lend themselves to the treatment of specific physical examples. In view of the predominantly experimental character of this study no theoretical discussion will here be attempted. The following paragraphs have been included to point out that our measurements are not at present unequivocal in their significance, and to indicate directions for further investigation.

Carbon dioxide and carbon disulfide so closely resemble each other in structure that it is surprising to find an appreciable part of the heat capacity failing to participate in the velocity of sound at audible frequencies in the former, whereas in the latter all of the heat capacity remains fully active well into the ultrasonic range. It is natural, in considering carbon dioxide alone, to follow Eucken and Mücke in supposing that the symmetrical linear vibration is that with the extremely low rate of adjustment. In searching for a kinetic mechanism by which such a mode of vibration may be excited a fortunate triple-collision of the type $A \rightarrow \text{OCO} \leftarrow A$ suggests itself; any bond-softening process or other double-collision mechanism seems inefficient in comparison. This supplies an excellent qualitative explanation for the behavior of carbon dioxide, but fails completely to account for that of carbon disulfide.

An examination of the quantitative differences in the structure of the energy levels of the two molecules serves only to make their difference in behavior more puzzling. It is probable, for example, that the various energy states in the symmetrical linear vibration and the deformation vibration "communicate" during the time that two colliding carbon disulfide molecules are effectively in contact. The equality of the rates of adjustment of these states, which has experimentally been established, can reasonably be explained only on the supposition that vibrational equilibrium between them has essentially been reached on every effective collision. Under these conditions all the "communicating" vibrations will, of course, fall out of the acoustical cycle with the rate of adjustment of the most readily excited member of the group, and the steric and energetic factors which are measured characterize the most probable transition. (This is sharply in

contrast to the behavior of nitrous oxide,²⁵ and may also differ from that of sulfur dioxide, where it appears that each of the vibrational modes is dropping out with a separate characteristic rate.) It is further apparent that the probability of "communication" between two vibrational modes increases greatly as the number of excited states in each is increased, since the matrix component connecting two widely separated energy levels is necessarily small. Since carbon disulfide contains a greater number of excited vibrational states at any given temperature than carbon dioxide, and since the duration of a collision between the heavier molecules is also probably greater, it would be natural to attribute their difference in acoustical behavior to the effect of "communication" alone. A serious difficulty to this interpretation results, however, from the perturbation of the first state of the linear vibration by one of the three levels corresponding to the second state of the transverse vibration. Perturbation indicates that one of these states may transform itself into the other during the course of a few vibrations without the intervention of a collision. It is, therefore, difficult to believe that the linear vibration alone drops out of the acoustical cycle at low frequencies while the deformation states remain in equilibrium well into the ultrasonic range.

It would be convenient, if it were possible, to discredit entirely the measurements at 9 kc on carbon dioxide, which are here reported, and obliterate the difference in behavior on *a priori* grounds. Unfortunately, however, they corroborate a considerable body of independent evidence, and only the case of carbon dioxide is difficult to interpret. It is necessary, therefore, to confess that the low frequency dispersive region in carbon dioxide is not understood by the writers, and to leave the matter in this highly unsatisfactory condition.

The situation is hardly more satisfactory when an explanation of the so-called activation energy of collision is sought. Three alternative hypotheses are at hand, and none of these may be eliminated with confidence.

(1) A bond-softening process has been suggested as the mechanism by which the excited state is reached. In this case the collision energy

²⁵ Kneser and Zühlke, *Zeits. f. Physik* **77**, 649 (1932).

must necessarily be greater than the energy available for the bond-softening process. This implies that the activation energy shall decrease roughly in proportion to the ratio between the energy of the state to be excited and the zero point energy. The experimental evidence fails to show this effect either with carbon dioxide or with carbon disulfide, since in neither gas is the symmetry of the S-shaped V^2 , $\log \nu/P$ curve appreciably disturbed. If, however, equilibrium between the vibrational states may be established during the time of a collision, as has been supposed above, this difference cannot be detected by experiment.

(2) Heil has suggested that, because of the comparatively small rigidity of the bonds attaching the oxygen atoms to the carbon, a broadside collision of the type $\rightarrow \cdots : \leftarrow$ would result in the transference of only about a third of the relative translational energy of the molecules into the vibration if the requirements of the law of conservation of linear momentum are to be satisfied. On this basis he has successfully predicted the order of magnitude of the activation energy of collision and the effective cross section of carbon dioxide from Kneser's measurements at atmospheric temperatures. A similar argument applies equally well to carbon disulfide: the available energy is smaller, but the rigidity of the bond is also less, and an activation energy of about the same magnitude is to be expected. The situation is somewhat complicated, however, by the rotation of the molecules during a collision. The activation energy represents, of course,

predominantly the minimum potential energy which must be available in order to de-excite a given state, and there appear to be several configurations of rotating molecules more favorable for the process than that which Heil has described. An explanation based on a dynamic mechanism of this kind has, however, the advantage that it implies approximately equal activation energies for the various states of a vibrational mode, and this is in accord with experiment.

(3) It is also possible that a molecule which is vibrating has an advantage over a molecule which contains only its zero point energy in bringing about transformations of the relative kinetic energy into vibrational energy by collision. If, for example, it is supposed that only the states 0 and 1 are present, and that a molecule in the state 1 is far more effective per collision in causing the transitions $1 \rightarrow 0$ and $0 \rightarrow 1$ than a molecule in the state 0, the transition probability f_{10} will not be proportional to the total number of collisions but to the number of 1-1 collisions. The relation between the number of molecules in the 0 and in the 1 states is of course $n_1 = n_0 e^{-h\nu_0/kT}$ and consequently, for gases like carbon dioxide and carbon disulfide at ordinary temperatures, n_1 will increase exponentially with temperature, and an apparent activation energy will be observed which has no relation to the activation energy ordinarily discussed in chemical kinetics. This possibility may also seem remote, but it is difficult to devise an experiment by which it may convincingly be eliminated.