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Several types of dispersion of sound which may be manifest in a dissociating gas are discussed. Of these only the heat-capacity dispersion and the dissociation dispersion need be considered under suitable experimental conditions. The expression derived by Einstein for the velocity of sound in a dissociating gas has been modified to include heat-capacity dispersion. The experimental procedure indicated by this for obtaining significant dissociation rate constants is outlined. Measurements on the velocity of sound in nitrogen tetroxide which have been made with apparatus of special design, are reported. The range of temperature studied is 0°C to 30°C, the range of pressure 132 mm to 670 mm, and the range of frequency 9 kc to 451 kc. The velocity of sound has been thus defined with an estimated error of ±0.1 m·sec.$^{-1}$. The maximum dispersion which has been observed is about 5 m·sec.$^{-1}$. From these measurements it appears that the rate constant of the dissociation reaction is $4.8 \times 10^4 \pm 0.5 \times 10^4$ at 25°C and 260 mm. The activation energy obtained for the dissociation reaction is 13.9 ± 0.9 kg·cal. The rate constant appears to diminish slightly as the pressure is reduced. Since an upper limit for the heat capacity of nitrogen tetroxide is fixed by experiment, it is necessary to suppose that the effective molecular diameters for the activation process are at least three times those for ordinary kinetic collisions.

INTRODUCTION

MEASUREMENTS of the velocity of sound in nitrogen tetroxide date from the pioneer researches of the Natansons[1] who were concerned with the reaction $N_2O_4 \rightleftharpoons 2NO_2$ as an example of chemical equilibrium. More recently, following a suggestion of Nernst and Keutel[2] and its incorporation into a quantitative theory by Einstein[3] several attempts have been made to detect a variation in the phase velocity with frequency in the hope of obtaining information concerning the rate of the dissociation reaction. The most recent of these[4] reported that the dispersion of sound at 25°C, 250 mm and 80 kc was no greater than an experimental error of 0.5 percent. This was believed to set a lower limit for the dissociation rate which closely approached the maximum unimolecular rate to be expected from the kinetic theory of gases. The present communication describes an attempt to obtain more positive information by increasing the precision of the acoustical method for corrosive gases, and by using lower temperatures and higher frequencies than have hitherto been employed in this connection. Measurements have been obtained which show unquestionable dispersion and, if interpreted in terms of a reaction rate, give a reasonable and self-consistent kinetic picture. An objection may, however, be raised to this interpretation which was not foreseen in the treatment of Einstein. It has become apparent that some non-dissociating gases show dispersion of sound similar both in its magnitude and in its dependence on pressure, temperature and frequency[5] to that which is here considered due to a reaction rate. Since only these quantities may conveniently be varied in the study of the dispersion of sound no straightforward experimental distinction between dispersion due to heat capacity and that due to reaction rate appears possible at present. It is necessary, therefore, to examine

* An advance notice of this communication has been published in J. Am. Chem. Soc. **54**, 3014 (1932).

[1] Ed. and Lad. Natanson, Wiedemann Ann. d. Physik und Chemie **24**, 454 (1885).

[2] Keutel, Inaug. Diss. Berlin (1910).

[3] Einstein, Sitz. Ber. Akad. 380 (1920).

[4] Kistiakowsky and Richards, J. Am. Chem. Soc. **52**, 4661 (1930). A more complete historical survey is given in this paper.

[5] Herzfeld and Rice (Phys. Rev. [2], **31**, 691 (1928)) base an explanation of this dispersion, which was first observed by Pierce (Proc. Am. Acad. Sci. **60**, 269 (1925)) on a lag between translational and internal energy adjustment. Kneser has recently (Ann. d. Physik **11**, 761 (1931)) treated this from the standpoint of Einstein's dispersion theory, and has explored the case of carbon dioxide over a considerable frequency range. Measurements in this laboratory on carbon dioxide and carbon disulfide at various frequencies, temperatures, and pressures provide additional authority for this statement.

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from a theoretical standpoint a system in which the heat capacity work and the dissociation work are covarient with frequency. For this purpose a brief review of the method used by Einstein becomes imperative. In order to conserve space this discussion will be given in qualitative terms as far as possible, and Einstein's equations, when rewritten, will be expressed in his notation.

The dispersion theory of Einstein

When a damped plane sound wave of phase velocity V and frequency ω is propagated in the direction x in a dissociating gas the pressure impulse may be written $\pi = \pi_0 e^{i[\omega(t-x/V)]+i\varphi-\beta}$ and the condensation impulse $\Delta = \Delta_0 e^{i[\omega(t-x/V)]-\beta}$ where the real parts of π and Δ represent pressure and density increments, t refers to time, and β is the damping coefficient. The substitution of these equations, after appropriate differentiation, into a wave equation of the usual form leads to the evaluation of the phase angle φ:

$$\frac{\omega^2}{V^2} - \beta^2 = \frac{\Delta_0}{\pi_0} \omega^2 \cos \varphi \qquad \frac{2\beta\omega}{V} = \frac{\Delta_0}{\pi_0} \omega^2 \sin \varphi. \quad (1)$$

Considerations apart from these give for a gas in which sound is transmitted adiabatically

$$\frac{\pi}{\Delta} = \frac{P}{\rho} \left(1 - \frac{\Delta(Pv)}{P\Delta v} \right) \qquad (2)$$

when P is pressure, ρ density, v volume, and Δ in the final term refers now to a small change. The real part of (2) is equal to the squared phase velocity of sound modified by absorption.

By means of (1) and (2) it is possible to compute the angle φ for any gas with completely determined properties or, conversely, to determine a single unknown property of the gas from measurements of the velocity of sound. The case of interest here is a dissociating gas for which the equilibrium constant is K, the heat of dissociation D, and the heat capacity at equilibrium C_0. It is further postulated that the gas contains n_1 double and n_2 single molecules, the decomposition of the double molecules having a unimolec-

ular rate constant k_1, and the association a bimolecular rate constant k_2. From chemical considerations it follows that

$$[C + C_\omega f(\omega)]\Delta T + P\Delta v - D\Delta n_1 = 0$$
$$R(n_1+n_2)\Delta T - RT\Delta n_1 = \Delta(Pv) \quad (3)$$
$$\frac{KDn_1}{RT^2} \Delta T + \left(\frac{n_2}{v}\right)^2 \Delta v + \left(K + \frac{4n_1}{v} + \frac{d}{k_2 dt}\right) \Delta n_1 = 0$$

where T refers to temperature. These equations differ from Einstein's only in the substitution of $C + C_\omega f(\omega)$ for the heat capacity C_0 which he considers constant. For the present purpose it will be sufficient to define $C_\omega f(\omega)$ as a part of the heat capacity which equals C_ω at very low frequencies and vanishes at very high frequencies. Since translational energy adjustments must be rapid in order that the gas may retain the elasticity necessary for the transmission of sound, the condition $C_0 - C_\omega \geqq 3/2R$ is apparent. Each of the variable quantities in (3) is undergoing cyclic adiabatic changes of the type

$$\zeta = \zeta_0 e^{i\omega t} \qquad (4)$$

where $\zeta = \Delta T$, Δn_1, Δv. The time derivative of (4) enters (3) for the quantities $C_\omega f(\omega)\Delta T$ and Δn_1, since it is postulated that these quantities depend on frequency. Differentiation of (4) gives directly the relation between Δn_1 and frequency. The dependence of $C_\omega f(\omega)$ on frequency must be inferred by postulating some mechanism by which this part of the heat capacity is excited. Kneser,[5] on the reasonable assumption that a double collision may degrade an excited molecule, or excite a molecule which is in a low energy state, arrives at a result which may be written

$$C_\omega f(\omega) = C_\omega/(1+i\omega\vartheta) \qquad (5)$$

if ϑ is a time characteristic of the duration of vibrational energy in the molecule. The general form of (5) is independent of the assumptions used in its derivation, and it may, therefore, be employed with some confidence. If now (3) is solved for $-\Delta(Pv)/P\Delta v$ and the result substituted in (2) a complex is obtained which has the form

$$\frac{\pi}{\Delta} = \frac{P}{\rho} \left\{ 1 + \frac{k_1[A_1 - A_3 \bar{C}_\omega(1+i\omega\vartheta)^{-1}]+i\omega R}{k_1[A_2 + A_4 \bar{C}_\omega(1+i\omega\vartheta)^{-1}]+i\omega[\bar{C}+\bar{C}_\omega(1+i\omega\vartheta)^{-1}]} \right\} \qquad (6)$$

where $\bar{C}$ and $\bar{C}_\omega$ represent the parts of the average | heat capacity of the mixed gases which are re-

spectively independent of and dependent on the frequency, and

$$A_1 = \left(\frac{2D}{T} - \overline{C}\right)\frac{n_1}{n_1+n_2} + R\left(1 + \frac{4n_1}{n_2}\right)$$

$$A_2 = \frac{D^2}{RT^2}\frac{n_1}{n_1+n_2} + \overline{C}\left(1 + \frac{4n_1}{n_2}\right)$$

$$A_3 = \frac{n_1}{n_1+n_2} \qquad A_4 = \left(1 + \frac{4n_1}{n_2}\right). \qquad (7)$$

Following the method of Einstein it will be supposed that the real part of (6) is equal to the squared phase velocity of sound modified only by absorption as indicated by (1). This gives the solution

$$V^2\frac{1 - \beta^2 V^2/\omega^2}{(1+\beta^2 V^2/\omega^2)^2} = \frac{P}{\rho}\gamma \qquad (8)$$

where γ, the ratio of adiabatic to isothermal compressibilities is given by,

$$\gamma = 1 + \frac{k_1{}^2[A_1A_2 + \overline{C}_\omega(A_1A_4 - A_2A_3) - \overline{C}_\omega{}^2 A_3A_4] + \omega^2[R(\overline{C}+\overline{C}_\omega) + k_1\vartheta\overline{C}_\omega(\overline{C}A_3 - RA_4 + A_1) + k_1{}^2\vartheta^2 A_1A_2] + \omega^4\vartheta^2 R\overline{C}}{k_1{}^2(A_2 + A_4\overline{C}_\omega)^2 + \omega^2[(\overline{C}+\overline{C}_\omega)^2 + 2k_1\vartheta\overline{C}_\omega(A_2 - A_4\overline{C}) + k_1{}^2\vartheta^2 A_2{}^2] + \omega^4\vartheta^2\overline{C}^2}.$$

When ϑ is very small (8) reduces to the case $C_0 = \overline{C} + \overline{C}_\omega$ treated by Einstein; when ϑ is very large a corresponding reduction for the case $\overline{C}_0 = \overline{C}$ is obtained. If in a nonassociated' gas double collisions are considered molecular associations, k_1 becomes very large, and n_1 very small, and the expression given by Kneser emerges. Finally, when ϑ and n_1 are very small or, conversely, when ϑ and k_1 are very small, the well-known expression due to Laplace results.[6]

The effect of uncertainties concerning the heat capacity

The influence of heat capacity variations on the dispersion of sound in a dissociating gas may now be calculated. For this purpose it will be convenient to consider a gas at 280°K for which $P/\rho = 3\times10^8$ cm^2 sec.$^{-2}$, $D = 14$ kg·cal. per mole and $k = 1\times10^4$ in rough analogy to nitrogen tetroxide. To make the case somewhat more unfavorable than may reasonably be expected in practice it will further be supposed that only 10 percent of the double molecules are dissociated

at this temperature, and that half the molecular heat capacity at equilibrium may drop out of the adiabatic elasticity at high frequencies, leaving only 5 calories due to the translational and rotational freedom of rectilinear molecules. This makes $\overline{C}_0 = 10$ cal·deg.$^{-1}$ and $\overline{C}_\omega = 5$ cal·deg.$^{-1}$ per mole at constant volume. The velocity of sound in this gas, calculated from (8) for the circular frequencies of 10^5 sec.$^{-1}$ and 5×10^5 sec.$^{-1}$ and various values of ϑ is illustrated in Fig. 1. The velocity of sound at these frequencies
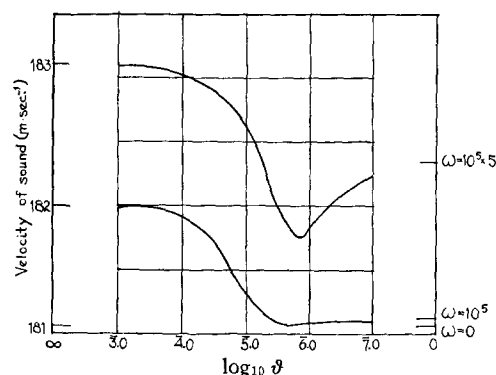
FIG. 1. Variation of the velocity of sound of various frequencies with the characteristic excitation time ϑ of the vibrational heat capacity in a dissociating gas having properties closely analogous to those of nitrogen tetroxide.

for a gas of the same properties except that $k_1 = 1\times10^8$ is given by Fig. 2. When the rate constant is small with respect to the frequency the situation need not here be considered.

If ϑ may be neglected in comparison with ω and k_1, and absorption is neglected, (8) may be rewritten in the more convenient approximate form

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[6] The transition from (6) to (8) is unfortunately not as straightforward as it may at first sight appear. Indeed it is unwise to state unequivocally that (8) is the physically significant part of (6) until the development of (8) has been achieved with real quantities and an identical result obtained. This is difficult because when $C_\omega f(\omega)$ is introduced into (3) a harmonic of ω results which is not written in the original pressure and condensation waves. It is considered, however, that 'since (8) reduces to the forms given by Einstein, Kneser, and Laplace, all of which may readily be obtained with real quantities, the interpretation of (6) which is here adopted is justifiable.

$$k_1 = \omega \left\{ \frac{\overline{C_0} R T^2 \alpha [2 + \alpha(1-\alpha)]}{(2-\alpha)[\overline{C_0} R T^2 + D^2 \alpha(1-\alpha)]} \right\} \left\{ \frac{V_\infty^2 - V_\omega^2}{V_\omega^2 - V_0^2} \right\}^{1/2} \tag{9}$$

when α is the degree of dissociation, and V_∞,[7] V_ω, and V_0 the phase velocities at high frequency, at the frequency ω, and at very low frequency respectively. For the case here under discussion V_∞^2, and V_0^2 are 36,000 and 32,780 m²·sec.⁻² from (8). When the assumption that ϑ is very small is not justified the value of k_1 calculated from (9) will not yield the true rate of dissociation. The magnitude of the error so introduced may easily be found by interpreting the dispersion sketched in Figs. 1 and 2 as wholly due to reaction rate.
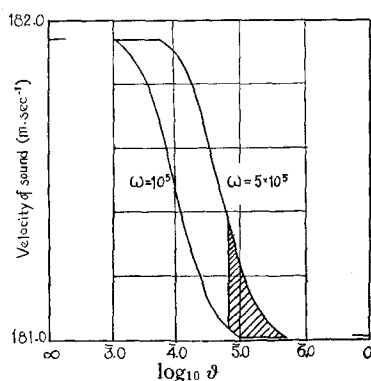

Fig. 2. Variation of the velocity of sound of various frequencies with the characteristic time ϑ in a dissociating gas having ten thousand times the dissociation rate constant of nitrogen tetroxide.

When k_1 is actually 1×10^4 sec.⁻¹ the rate constant calculated from (9) has a maximum value at $\vartheta = 1.8 \times 10^{-6}$ sec. of 1.76×10^4 sec.⁻¹ for $\omega = 1 \times 10^5$ sec.⁻¹ and of 1.34×10^4 sec.⁻¹ for $\omega = 5 \times 10^5$ sec.⁻¹. Although not exact, these rate constants may be considered reasonably satisfactory. When k_1 is again actually 1×10^4 sec.⁻¹ and ϑ is actually not small, but very large, the rate constant calculated from (9) is more seriously in error; it is 2.28×10^3 sec.⁻¹ for 1×10^5 cycles and 7.47×10^3 sec.⁻¹ for 5×10^5 cycles. A discrepancy of this magnitude will be apparent from experiment, and may easily be corrected by an appropriate change of $\overline{C_0}$ in (9). If, therefore, the dispersion which is observed is partly due to

change from the equilibrium heat capacity and partly to lag in the dissociation work, no grave difficulty in its interpretation need be anticipated.

When, however, the reaction rate constant is far greater than the frequency as pictured in Fig. 2, dispersion may be found in which the reaction rate plays no part, and its interpretation by means of (9) will then be wholly in error. In the region shaded in Fig. 2, which will be determined in extent by the magnitude of experimental error, an apparent rate constant will be found which is independent of frequency over a small range. This will change with temperature and pressure as ϑ changes, and hence may plausibly represent a dissociation reaction. Fortunately, the total increase of sound velocity which is to be anticipated from this cause is small in a gas for which the dissociation heat is greater than 10 kg·cal. In nitrogen tetroxide between 273° and 303°K, and from 150 to 600 mm pressure any velocity of sound which differs from that at any very low frequency by 1 m·sec.⁻¹ or more may safely be attributed in part to lag in the dissociation work.

One further point should be made concerning the heat capacity which is not related to its possible variation with frequency. The heat capacities of the constituent molecules in a dissociating mixture cannot at present be obtained more than approximately either experimentally or from theoretical considerations. For this reason an uncertainty due to heat capacity is introduced into the calculated value of the dissociation rate constant even when ϑ is small and (9) is applicable. The influence of the heat capacity in (9) is strongly felt for two reasons, first, because it affects the compression work, and second, because it determines the value of V_∞. For reasons given above it is unlikely that experiment will yield a trustworthy value of V_∞, and this quantity must therefore be calculated by assuming a plausible $\overline{C}$. Thus uncertainty in k_1 due to heat capacity vanishes in a region of dispersion which is determined in extent by the experimental error, and which lies near the velocity at very low frequency. The accuracy of the rate constant obtained from (9) will, therefore, be in-

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[7] The subscript ∞ means only that the frequency is much larger than k_1 and ϑ^{-1}. It may be shown by the kinetic theory that all gases become opaque to sound at very high finite frequencies.

creased if it is calculated from cases where $V_\omega - V_0$ is small, provided that it has been shown that ϑ may be neglected.

The experimental determination of the rate constant

If the argument given above is accepted, it is possible by suitable measurements to obtain values for the rate constant of the dissociation reaction which are free from error due to heat capacity uncertainties. Only the simplest case, in which the heat of dissociation is large, need here be considered.

No measurement of the dispersion of sound at a single frequency is sufficient to determine the rate constant. If .the principles set down above are strictly applied it is necessary to employ two frequencies at each temperature and pressure, and it is further necessary that the higher of these frequencies should in each case show a dispersion significantly greater than the maximum which can be produced by heat capacity change. If, under these conditions, the rate constants given by both frequencies are the same, the effect on the rate constant of uncertainty concerning the equilibrium heat capacity may be eliminated by interpreting very small dispersions, measured with lower frequencies, as due wholly to change in dissociation work with frequency. The enormous labor involved in this procedure may greatly be reduced in the case of nitrogen tetroxide between 0°C and 30°C by a single assumption concerning the temperature coefficient of the mean lifetime of the excited molecule. This quantity may vary greatly with temperature only if a relatively small proportion of the total number of double collisions results in molecular excitation. Whatever the nature of $\overline{C}_\omega$ it is hardly conceivable that the "activation energy" required for its excitation should be very much greater in order of magnitude than that of the chemical reaction if, at a particular temperature, $\overline{C}_\omega$ is to participate in the adiabatic cycle. Hence it is permissible to assume that the temperature coefficient of ϑ^{-1} is equal to or less than that of k_1. When this is the case any change in $\overline{C}_\omega f(\omega)$ from the value $\overline{C}_\omega$ will be most apparent at the highest of the temperatures at which observations are made. If concordant values of k_1 are obtained from (9) at this temperature with two widely

separated frequencies it may be concluded that $\overline{C}_\omega f(\omega) = \overline{C}_\omega$. In a small range of temperature below this the same conclusion will be justified if ϑ^{-1} conforms to the assumption made above that its temperature coefficient is not inordinately large. A procedure of this kind may be applied only, however, when the dissociation work in the sound wave is far greater than that due to $\overline{C}_\omega f(\omega)\Delta T$; it must be regarded with suspicion when applied to dissociating gases for which the heat of dissociation is small, or in which the degree of dissociation is near to unity. An additional sense of security will independently be gained if, at the lowest of the temperatures which are to be considered, a dispersion is obtained which far exceeds that possible from the change $\overline{C}_\omega f(\omega) = \overline{C}_\omega$ to $\overline{C}_\omega f(\omega) = 0$.

In the following sections very small dispersions, which have been shown to represent reaction rates by this argument, will so be interpreted without further discussion.

EXPERIMENTAL METHOD[8]

In view of the convenience with which magnetostriction oscillators of various frequencies may be prepared, they were used throughout this investigation. The electrical circuit for driving them has been described by Pierce[9] and the analysis of the frequencies so produced has been treated, following Pierce, in the previous communication from this laboratory. No change in this aspect of the magnetostriction method was found necessary.

The tube-dispersion

It has long been known that dispersion of sound appears when its velocity of propagation is measured in small cylindrical tubes. Since it is of secondary interest in this communication, it will be treated as an experimental tube-correction. A brief discussion of its nature, magnitude, and dependence on frequency will be given at this point in order to separate it from the wholly different and unpredictable dissociation-dispersion.

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[8] In this and the succeeding sections the abbreviation kc will denote kilocycles sec.$^{-1}$, and will refer always to linear frequencies.

[9] Pierce, Proc. Am. Acad. Sci. **63**, 1 (1928).

Helmholtz and Kirchhoff[10] have developed an expression which describes with fair success the dispersion of sound in cylindrical tube. This may be written

$$V_\omega = V_0 \left(1 - \frac{(\gamma\eta)^{1/2} + (\kappa/C_v)^{1/2}(\gamma-1)}{2r(\gamma\omega\rho/2)^{1/2}} \right) \quad (10)$$

in which the quantities not previously defined are η, the viscosity, r, the radius of the tube, and κ, the thermal conductivity. According to this the velocity of sound in a particular gas in a tube of finite radius at a finite frequency should always be less than that at zero frequency in free space, and the difference between the two should increase as the wave-length increases or the radius diminishes. With a dissociating gas this difference increases sharply in the region of dissociation-dispersion[11] for, although the decrease in apparent C_v to be expected from Einstein's theory is almost exactly balanced by a corresponding decrease in κ, $\gamma-1$ may change from 0.08 to 0.25. Adequate values for η, κ, and C_v are lacking for nitrogen tetroxide, and the exact extent of the change to be expected under a given set of experimental conditions is, therefore, not accessible, but an exceedingly rough calculation shows that the tube-correction will approximately double when the dissociation work has been eliminated at very high frequency. Since, however, this change is only of the order of 5 percent of the dissociation-dispersion under the experimental conditions outlined below, the small correction which should be added to the observed dissociation-dispersion has here been neglected. The reaction rate constants calculated from (9) are then somewhat too large, but the error so introduced is believed to be considerably inferior to that due to other causes.

The dispersion produced in free space by the viscosity and heat-conduction of the gas should also be taken into account in any comprehensive theoretical treatment. This alters the phase velocity in the opposite sense to the tube-correction. Under the experimental conditions described below, however, its influence is far inferior to that of the tube walls, and may be wholly neglected with safety.

Apart from uncertainty concerning the damping constants of nitrogen tetroxide it appears unwise to apply (10) literally for the evaluation of the tube-correction under the experimental conditions herein employed. The measurements reveal, in common with all piezoelectric or magnetostrictive determinations, slight variations in the average half-wave-length with the distance from oscillator to reflector. These may be attributed, at least in part, to path differences between the main compressional impulse emitted by the oscillator and its subsidiary parts, with consequent interference and slight displacement of the points of maximum reaction measured in the acoustical chamber. Thus the assumption of a pure phase sinusoidal wave from which (10) was developed is violated, and simultaneously a number of variables are introduced about which little exact information is available, such as the reflection coefficients, amplitudes, and mass reactions of the various parts of the wave. For this reason it was considered expedient to calibrate the tube and oscillator with various nondissociating gases, and to apply the tube-correction indicated by these to the measurements on nitrogen tetroxide. Great confidence may be placed in the tube corrections so found, for they accord with (10) not only in sign, but also in magnitude as nearly as an estimate may be formed from the somewhat uncertain properties of the various gases. The tube-corrections indicated below are not, however, to be considered as tests of the Helmholtz-Kirchhoff theory, for they contain also corrections for the standard procedure used in measuring and averaging the various sound velocities.

A new and startling type of tube-dispersion, which has recently been discovered by Boyle and his co-workers[12] in liquids, is due to the absorption of longitudinal vibration and its transference into radical vibration at resonant frequencies of

[10] Helmholtz, Gesam. Wiss. Abh. Leipzig I, 383 (1882). Kirchhoff, Pogg. Ann. 134, 177 (1868). More recent information on this subject may be found in Cornish and Eastman, Phys. Rev. [2], 33, 90 (1929); Henry, Proc. Phys. Soc. 43, 341 (1931).

[11] This statement is made on the assumption that (10) may be applied literally at any frequency to any gas whatever. A theoretical investigation of this assumption would be of interest, but could scarcely lead to corrections of magnitude which need here be considered.

[12] Boyle, Froman and Field, Canadian J. Research 6, 102 (1932). Field and Boyle, ibid. 6, 192 (1932).

the latter. While this is not specifically excluded for gases by the theory of Field,[13] it has been proved absent in the present work by the calibration of the tubes with gases of almost identical acoustical properties to those of nitrogen tetroxide, and by obtaining velocities of sound at the same frequency in two vessels of different diameter which differ only by the Helmholtz-Kirchhoff correction.

Apparatus for measuring the velocity of sound as a function of temperature

The problem of measuring velocities of sound at temperatures far from that of the room centers about the design of a suitable acoustical chamber. It is necessary that this be wholly immersed in the thermostating fluid to prevent temperature gradients. The oscillators must be supported rigidly to prevent change of position, and yet delicately to insure a large amplitude of oscillation. All materials of which the chamber is constructed must be highly resistant to the corrosive action of nitrogen tetroxide. Finally, the position of the movable reflector must be measurable with a high degree of precision. These conditions are satisfied by the acoustical chamber illustrated in Fig. 3.

The high- and low-frequency oscillators are marked A and B respectively. The ends of both measured 2.4 cm. The high-frequency oscillator operated at about 92 kc and was made of nichrome steel. It was supported on its dynamical center in alignment with the axis of the tube by means of a stout tungsten rod, C, sealed into the glass of the chamber itself. The low-frequency oscillator was a nickel tube of 2.2 cm outside, and 1.6 cm inside diameter. At each end of this solid nickel disks were fastened with gold solder; these served for the actual transmission of the sound impulse to the gas. This structure, being too heavy for support on a tungsten rod, was held free from constraint and in alignment by a sleeve of glass tubing fitted closely both to the interior of the acoustical chamber and to the exterior of the nickel tube.

The reflecting piston D was made entirely of glass, and enclosed a small bar of soft iron. Since the faces of the reflector must be normal to the axis of the acoustical chamber, they were ground

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[13] Field, Canadian J. Research 5, 131 (1931).

on a glass lathe of special design. The position of the reflector was changed by means of a laminated-core magnet diagrammatically represented as E in Fig. 3, and changes were measured with a cathetometer to 0.005 cm. The magnetic field was
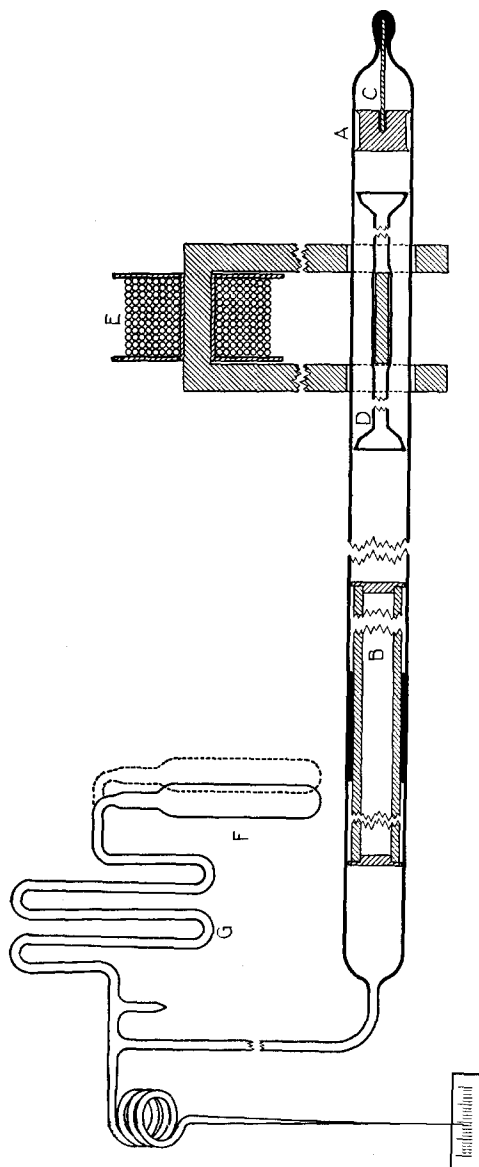

FIG. 3. Apparatus for measuring the velocity of sound in a corrosive dissociating gas as a function of temperature.

first adjusted to "float" the reflector in the acoustical chamber, and the magnet was then moved on a runway by means of a small-pitch driving screw. This secured great precision of movement, eliminated the packed joint neces-

sary with a thread drive, and made possible the use of two oscillators in the same tube. The response of the reflector to small impressed forces was so sensitive that it often migrated automatically to points of minimum motion in the standing-wave pattern. If its motion was not sufficiently smooth the faint vibration given by a small electric buzzer mounted on a remote part of the apparatus was sometimes helpful.

The Pyrex tubing of which the acoustical chamber was constructed had an internal diameter of 2.5 cm and was especially selected from a large stock for uniformity of bore and smoothness of internal wall.

The thermostat employed was filled with kerosene and provided with powerful stirrers. The temperature was regulated by hand to the precision necessary to define the velocity of sound. Irregularities of temperature at once manifested themselves by irregularities in the wave-pattern at points distant from the face of the oscillator. In general, the required accuracy was 0.05°C. Low temperatures were secured by circulating kerosene from the bath through a copper coil immersed in calcium chloride solution at $-25°$C. Condensation of moisture from the air, with consequent power loss in the oscillators, necessitated frequent changes of the bath liquid.

Pressure regulation in the acoustical chamber was secured by a small bulb F which was immersed in a large water-filled Dewar flask at an appropriate temperature. The bulb was kept in mechanical agitation to secure pressure equilibrium at all times. The glass spring G prevented the transmission of this impulse to the acoustical chamber. The pressure was read with a quartz spiral manometer.

The nitrogen tetroxide employed was made by heating lead nitrate in a stream of oxygen. It was then distilled with oxygen through phosphorous pentoxide, and finally distilled in vacuum before being distilled into the apparatus. These precautions, while in general adequate for the exclusion of the lower oxides of nitrogen and the permanent gases, were not sufficient wholly to eliminate small quantities of nitric acid.

The tube-correction for this apparatus was small and easily defined by the measurements with nondissociating gases summarized in Table I. Each value given is the average of at least

three independent determinations of the velocity of sound with the same filling of gas. Since the difference between the velocity at 9 kc and at 92 kc was alone the quantity of importance, no attempt was made to eliminate small traces of impurities from the gases. The absolute velocities hence may be slightly in error. The tube-correction for this apparatus for nitrogen tetroxide is evidently $+0.4$ m·sec.$^{-1}$ at 9 kc. At 92 kc it may, therefore, be neglected according to the equation of Helmholtz and Kirchhoff. The velocity of sound in 99.98 percent argon at 92 kc was found to be 324.0 meters·sec.$^{-1}$ at 30°C and 760 mm pressure. This accords well with the velocity 324.2 meters·sec.$^{-1}$ calculated for these conditions from data found in the *International Critical Tables*, and substantiates the conclusion that the tube-correction may be neglected with this oscillator.

TABLE I. *Determination of the tube-correction for 9 and 92 kc 2.4 cm oscillators in a 2.5 cm glass acoustical chamber.*

Gas	P mm	T°C	V_9 m·sec.$^{-1}$	V_{92} m·sec.$^{-1}$	Tube-correction $V_{92}-V_9$
Pentane	342	30.2	190.16	190.62	$+0.46$
	343	30.2	190.25	190.62	0.37
	342	30.2	190.26	190.65	0.39
Air	760	30.0	349.42	350.02	0.60
	760	18.9	342.60	343.13	0.53
	140	30.0	349.40	350.04	0.64

Apparatus for measuring the velocity of sound at frequencies above 90 kc

At frequencies much above 92 kc the use of oscillators of 2.45 cm cross section becomes impractical owing both to mechanical difficulties of support and alignment, and to the inaccuracy of the cathetometer in estimating half-wave-lengths corresponding to very small displacements. An acoustical chamber suitable for use with oscillators of 0.933 cm cross section was, therefore, constructed. Although of more conventional design it has been diagrammatically illustrated in Fig. 4. The micrometer head A serves to determine the displacement of the polished glass reflecting surface B. The two are connected by means of an "invar" steel rod C, uncertainties in contact being prevented by the nichrome springs DD'. The rod passes through a packing of asbestos and graphite at F. Since this packing is not wholly gas-tight, an outer jacket G, which is kept at a pressure below that in the acoustical chamber, is

necessary to prevent contamination of the nitrogen tetroxide. Any nitrogen tetroxide lost by diffusion is automatically replaced from a mechan-
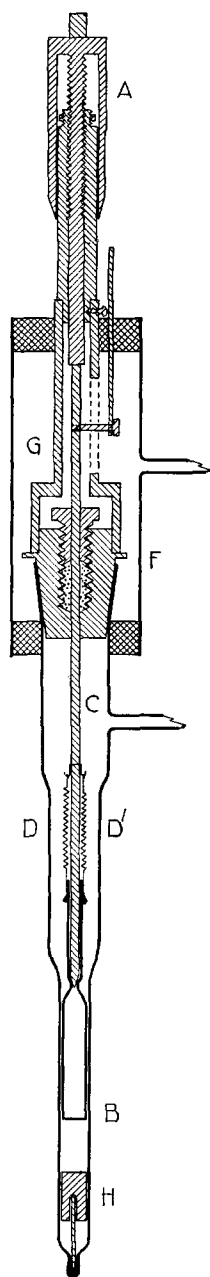
ically agitated reservoir. The oscillator H is supported vertically on its dynamical center by means of a suitably fitted tungsten rod. The smallest oscillators gave, however, satisfactory

results if laid on their sides horizontally without further support. The chamber itself was made of Pyrex glass, and the male member of the ground union at F of nichrome steel. Phosphoric acid served as a cement. The acoustical chamber was thermostated in a bath of transformer oil.

This apparatus functioned satisfactorily from 92 to 451 kc and probably would have served even to higher frequencies had this been necessary. It was used only at 30.0°C in order to avoid the construction of an elaborate thermostat, and because at this temperature all necessary information had been obtained. With suitable precautions the reproducibility obtainable with this apparatus was fully as great as that described in the preceding section. Two oscillators of different frequencies in separate acoustical chambers were invariably used with each filling of gas, and the difference between the two observed velocities was, therefore, almost independent of small quantities of accidentally included impurities.

The tube-correction in this apparatus was somewhat larger owing to its small diameter. It was determined with three nondissociating gases as indicated by Table II. Here also the sign and

TABLE II. *Determination of the tube-correction for 94 and 451 kc 0.93 cm oscillators at 30°C in a 1.0 cm glass acoustical chamber.*

Gas	P mm	V_{94} m·sec.$^{-1}$	V_{451} m·sec.$^{-1}$	$V_{451} - V_{94}$
Air	760	348.6	350.4	1.8
	760	348.5	350.3	1.8
	240	348.5	350.3	1.8
Propane	760	251.8	252.8	1.0
	760	251.7	252.8	1.1
Pentane	183	191.2	191.9	0.7
	187	191.1	191.8	0.7

magnitude of the correction accords with that to be expected from the Helmholtz-Kirchhoff theory. A tube-dispersion of 0.8 m·sec.$^{-1}$ is evidently to be expected with nitrogen tetroxide in this apparatus.

Measurements of the velocity of sound in nitrogen tetroxide

Measurements on nitrogen tetroxide were confined to isobaric or isothermal lines. Those at 260 mm are summarized in Table III, and those in which the pressure was varied in Table IV. In both cases the method of presentation is the

same; the sound velocities recorded have been fully corrected, and are those used for calculations in the succeeding section. The corrections applied were: 9 kc, $+0.4$ m·sec.$^{-1}$; 92 kc, 0; 94 kc, $+0.6$ m·sec.$^{-1}$; 451 kc, -0.2 m·sec.$^{-1}$. If these are algebraically subtracted from the various velocities quoted the actual experimental velocities will be obtained. It is encouraging to

TABLE III. *The temperature dependence of the velocity of sound of various frequencies in nitrogen tetroxide at 260 mm pressure.*

$T°C$	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Corr. $V_\omega - V_0$
1.0	9.265	170.8	92.07	172.8 ⎱	1.8
1.0	9.341	171.4	92.14	173.0 ⎰	
7.0	9.343	176.4	92.07	177.2	0.8
8.0	—	—	92.06	178.3	
8.1	9.340	177.5	—	—	0.8
10.0	9.331	179.2	92.02	179.9	0.7
13.9	9.336	183.05	92.00	183.6	0.55
25.0	9.298	195.3	91.89	195.7	0.3
25.0	9.298	194.8	91.89	195.0	
30.0	9.213	202.4	91.73	202.6	0.2
30.0	94.00	201.5	450.7	205.8	3.5
	94.00	201.4	450.7	205.7	3.4
	94.00	201.6	450.7	205.6	3.3

TABLE IV. *The pressure dependence of the velocity of sound in nitrogen tetroxide at various frequencies and temperatures.*

P_{mm}	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Corr. $V_\omega - V_0$
		30.0°C			
342	94.00	197.8	450.7	200.9	2.3
260	94.00	201.5	450.7	205.6	3.4
235	94.00	202.8	450.7	208.1	4.5
		25.0°C			
668	9.301	184.8	91.89	185.3	0.1
260	9.301	194.7	91.89	195.4	0.3
162	9.301	201.6	91.89	202.5	0.5
		1.0°C			
260	9.340	170.7	92.10	172.9	1.8
156	9.340	175.0	92.10	179.1	3.7
132	9.340	176.3	92.10	181.0	4.3

note that an independent concordant determination of the tube-correction results from these measurements.

Although the reproducibility of measurements is shown by Tables I and II to be about ±0.05 m or ±0.03 percent, the measurements in Tables III and IV are scattered over a much wider range of ±0.3 m·sec.$^{-1}$ or ±0.15 percent, and the difference between high- and low-frequency veloci-

ties cannot be read from a smoothed curve to better than ±0.1 m·sec.$^{-1}$ with confidence. This is not due to uncertainties concerning frequency, since it was measured after each experiment to ±0.05 percent. The variability of frequency shown by the 9 kc oscillator in Table III is real and not a matter of experimental uncertainty. Since each velocity quoted in Table III is, with one or two exceptions, the result of a series of measurements on a separate filling of the apparatus, it is probable that slight variations in the composition of the nitrogen tetroxide are responsible for the lack of reproducibility. Small quantities of air and nitric acid, which are involuntarily included or released from the extensive glass and metal surfaces of the apparatus are indicated as a reasonable explanation.

INTERPRETATION OF THE MEASUREMENTS IN TERMS OF DISSOCIATION RATE

Calculation of the velocity of sound at low frequency

The application of (8) to the interpretation of the velocity of sound in a real dissociating gas involves the justification of a number of assumptions and approximations. It has been supposed, to name a few of these, that the wave is plane, its amplitude small, and its form purely sinusoidal. The dissociating gas has been supposed to be perfect, non-absorbing, and non-conducting to heat. The second equation of (3) neglects the influence of temperature and pressure on the degree of dissociation. No one of these approximations is easy to justify on direct experimental grounds, and together they may conveniently be treated only by the comparison of the measured velocity of sound at low frequencies with that calculated from (8) when ω and ϑ are both negligible. This comparison is made in Table V.

In order to calculate the velocity of sound at low frequencies from (8) values for the dissociation heat, dissociation constant at constant volume, average heat capacity at constant volume, and density of the gas at various pressures and temperatures are necessary. The dissociation heat is given by Verhock and Daniels[14] as 14.6 kg·cal. and by Bodenstein[15] as 13.0 kg·cal. An error of

[14] Verhock and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).
[15] Bodenstein, Zeits. f. physik. Chem. **100**, 68 (1922).

1 kg·cal. in this quantity causes an error of about 0.4 percent in the velocity of sound calculated at low frequency, too high a dissociation heat yielding, of course, too low a velocity. For the sake of consistency 14.6 kg·cal. will be used throughout the remainder of this communication. Verhock and Daniels give the dissociation constant at 25°C and at 35°C, and at 30° a satisfactory value has been obtained by the van't Hoff isochore. The average heat capacity at constant volume is given by the expression

$$\bar{C}_0 = \frac{(2\alpha C_{NO_2} + (1-\alpha)C_{N_2O_4})}{(1+\alpha)}.$$

Since the heat capacities of the component molecules are unknown the calculation has been carried through in duplicate, using the minimum ($C_{NO_2} = 6$, $C_{N_2O_4} = 10$) and the maximum ($C_{NO_2} = 8$, $C_{N_2O_4} = 16$) values which the heat capacity may reasonably be expected to assume. The densities have been obtained at 25° and 35° and, by interpolation, at 30°C from Verhock and Daniels; at 15° and 1° they have been calculated, through the dissociation constant, from the degree of dissociation and the ideal gas laws. The observed velocity of sound at 15° has been interpolated from Table III.

It is considered that the agreement obtained in Table V is sufficiently good, in view of the uncertainties in the data upon which the calculated values are based, to justify the approximations in (8) for nitrogen tetroxide at 260 mm. It is noteworthy that γ_0 is almost independent of temperature at constant pressure, and not greatly sensitive either to the value of $\bar{C}_0$ or the dissociation heat. Since P is fixed by the nature of the experiments it follows that a large part, at least, of the deviation of calculated and observed velocities must be due to uncertainties concerning the density.

The agreement at higher pressures is unsatisfactory, owing probably to failure of the ideal gas laws. The measurements at lower pressures will be discussed below.

Calculation of the reaction rate constants

The agreement of measured and calculated velocities of sound at very low frequencies removes a large number of objections from the use of (9) to evaluate dissociation rate constants. The fundamental reasoning underlying (8) from which (9) is derived should be in general valid at any frequency, for the characteristics of the gaseous system are unaltered by the sound wave. All the approximations necessary for the calculation of the velocity of sound at very low frequency are then equally justified at high frequency save only those concerning tube-dispersion, heat capacity and absorption. In view of the extended discussion in the introduction concerning the first two of these, it will be sufficient here to show that the rate constants obtained under various conditions are harmonious. That absorption must increase in the region of dispersion is implied by (2) and that it may alter the velocity appreciably follows from (8) when β^2 is not negligible with respect to ω^2/V^2. Since no means by which an irreproachable numerical magnitude may be assigned to the absorption coefficient is at present available it is believed preferable to explore the region in which the velocity of sound is close to that at very low frequency, rather than to attempt corrections for absorption at high frequencies.

The absorption coefficients obtained by measuring the mass reaction of the gas on the electrical circuit do not at present appear worthy of great confidence. The main kinetic conclusions which

TABLE V. *Comparison of observed and calculated velocities of sound in N_2O_4 at 260 mm and low frequency.*

T°C	K_p l·atm.	α	$\rho \times 10^4$ g·cm^{-1}	Estimated $\bar{C}_0$ cal·deg.$^{-1}$	γ_0	Calc. V_0 m·sec.$^{-1}$	Obs. V_0 m·sec.$^{-1}$
30.0	0.2025	0.3591	9.32	11.77 / 7.88	1.081 / 1.086	200.5 / 201.0	202.4
25.0	0.1344	0.2991	9.94	12.31 / 8.16	1.080 / 1.086	194.1 / 194.6	195.1
15.0	0.0572	0.2003	11.10	13.33 / 8.67	1.078 / 1.085	183.5 / 184.1	184.2
1.0	0.0155	0.1058	12.66	14.47 / 9.24	1.078 / 1.087	171.8 / 172.5	171.1

are reached in this communication are based on differences between the velocity of sound at 9 and 92 kc, where the dispersion is small, and are believed independent of error due to absorption. The error in the rate constant due to neglecting absorption is in any case partly neutralized by that due to neglecting the tube-correction change when the dispersion is large.[16]

Two further points should be mentioned before (9) is applied to the calculation of rate constants. The quantity k_1 is defined as the number of associated molecules decomposing per second divided by the total number present. This will be a constant in the chemical sense only if the reaction is unimolecular, that is, if k_1 is independent of pressure. The sense of the dispersion theory of sound demands only that k_1 be independent of frequency. When k_1 diminishes with diminishing pressure a bimolecular or a quasi-unimolecular reaction is indicated: This will cause no difficulty in the theoretical treatment, and will indicate merely that the chemical characteristics of the reaction are not what it was simplest to assume.

A glance at (9) will show that k_1 is determined only by the differences between squared veloci-

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[16] The absorption of sound in a dissociating gas has recently been suggested by Luck (Phys. Rev. 40, 440 (1932)) as a means of determining dissociation rates. Absorption is discussed in some detail from the standpoint of Einstein's theory in his communication. Recent comment by Teeter (J. Am. Chem. Soc. 54, 4111 (1932)) on the advance notice of this work necessitates a brief addition. The velocity of sound as determined above involves the examination of relatively few wave-lengths, which are chosen near the source to avoid possible effects of radial resonance. Under these conditions a small increase in the absorption coefficient at the edge of the dispersive region passes unnoticed. The absorption coefficient enters Einstein's expression for the velocity in the second approximation, but when the dispersion is small its effect on the calculated rate constant may be neglected in view of other uncertainties of calculation and experiment. In the center of the (first) dispersive region the correction due to absorption becomes considerable but there, for other reasons, acceptable values for the rate constant cannot at present be obtained. Absorption coefficients for the intensity may easily be evaluated by means of the velocities here reported and the expression given by Luck for the amplitude coefficient, but it is felt that their present value is small since their connection with any measurable quantity is not clear. The effect of absorption on the measured velocity of sound is also believed to require more detailed treatment than it has at present received, and references above to the interrelation of the two are intentionally vague.

ties, two of which are measured and the third of which, V_∞, must be calculated. Since a part of the heat capacity will almost certainly not participate in the adiabatic cycle at very high frequencies even if it remains active at frequencies where the chemical reaction begins to fall out, it appears unwise to attempt the measurement of V_∞. In the calculations which are reported below V_∞ has been considered an ideal quantity which is defined by $V_\infty = (V_0\gamma_\infty/\gamma_0)^{1/2}$ when the ratios γ_0 and γ_∞ are calculated from (8) for the real case $\omega \doteq 0$, $\bar{C} + \bar{C}_\omega = \bar{C}_0$, and for the ideal case $\omega \doteq \infty$, $\bar{C} + \bar{C}_\omega = \bar{C}_0$, respectively. This definition is justified only when k_1 as defined by (9) has been proved independent of frequency within limit of error. When permissible it has the advantage of further diminishing uncertainties in k_1 due to changes in heat capacity with frequency, and of almost wholly eliminating errors in k_1 due to failure of the ideal gas laws, or uncertainties concerning density and exact absolute velocity at very low frequency.

The rate constants obtained from (9) in the manner described above are collected in Table VI. The difference $V_\omega - V_0$ is obtained from experiment at 1° and at 30°, and has been interpolated at 15° from a plot of these differences given in Table III against temperature. The necessary values of α, γ_0, and $\bar{C}_0$ (which has been used with its maximum and minimum values as before) are quoted in Table V for the appropriate temperatures.

The accuracy of the rate constants in Table VI must now be considered. It may be shown from

TABLE VI. *The dissociation rate constant of nitrogen tetroxide at 260 mm.*

T °C	$V_\omega - V_0$ m·sec.$^{-1}$	Linear frequency kc	Estimated $\bar{C}_0$ cal·deg.$^{-1}$	Ideal V_∞ m·sec.$^{-1}$	$k_1 \times 10^{-3}$
30.0	3.4	450.7	11.77	208.5	63
			7.88	215.8	70
30.0	0.2	91.9	11.77	208.5	70
			7.88	215.8	66
15.0	0.5	92.0	13.33	189.7	26
			8.67	195.5	26
1.0	1.8	92.1	14.47	175.3	6.3
			9.42	180.5	7.7

these by (9) that the velocity of sound at very low frequencies at 1°C is less than 0.1 m·sec.$^{-1}$ below that quoted at 9 kc. Error from this cause, is,

therefore, eliminated. The rate constant obtained at 30°C and 91.9 kc is open to objection on the ground that 0.2 m·sec.$^{-1}$ is scarcely greater than experimental error for the quantity $V_\omega - V_0$; it is nevertheless considered significant because it coincides with that obtained by extrapolation from $V_{92} - V_9$ at lower temperatures by the use of an experimentally determined activation energy. The coincidence of the rate constant from measurements at 30° and 450.7 kc with that at lower frequencies is well within experimental error, and must be considered accidental. A detailed examination of the various sources of error leads to the conclusion that accuracy better than 10 percent cannot be claimed for the rate constants in Table VI, and that experimental uncertainties in the quantity $V_\omega - V_0$ are of more importance than uncertainties in the thermodynamic properties of nitrogen tetroxide.

If precise data for comparison with these rate constants were available the research would not have been undertaken. The highest published lower limit for the reaction rate set by the acoustical method is 5×10^4 at 25° and 250 mm[4], which agrees reasonably well with the positive constant 4.8×10^4 resulting from these experiments. Brass and Tolman[17] by a quite different method have obtained positive evidence of the dissociation rate which indicates the limits of 2.4 to 8.4×10^4 at 25°, a conclusion which is in accord with the result here supported.

The activation energy of dissociation

The activation energy required by the dissociation process is easily obtained by the Arrhenius isochore from the rate constants in Table VI. Between 1° and 15° this is 15.7 kg·cals. if the "maximum" heat capacity is used and 13.6 kg·cals. using the "minimum." An uncertainty of 0.1 m·sec.$^{-1}$ in $V_\omega - V_0$ at either temperature would alter these values about 1 kg·cal. The activation energy appears to be 13.6 to 13.2 kg·cals. from the measurements at 1° and 92 kc and at 30° and 451 kc; this is far less sensitive to slight errors in $V_\omega - V_0$ than the preceding values. A survey of all the various activation energies obtainable from these experiments and all sources of error leads to the average value 13.9 ± 0.9 kg·cals. Since this agrees well with esti-

mates of the dissociation heat (13.0 to 14.6 kg·cals.) it may reasonably be supposed that the activation energy for the association of two nitrogen dioxide molecules is small.

The order of the dissociation reaction

If k_1 is independent of pressure the dissociation reaction may be considered unimolecular; if it depends directly on pressure it may be considered bimolecular. The rate constants obtained by applying (9) to the measurements in Table IV are given in Table VII. Some increase in the dispersion of sound with decreasing pressure is of course to be expected from the increased dissociation of the gas.

The interpretation of these measurements is less secure than the interpretation of those used to obtain the activation energy, for several uncertainties eliminated at 260 mm reappear as possible sources of error at pressures other than this. Chief among these is the heat capacity, which is particularly important when the dispersion is large. Any conclusion based on Table VII must, therefore, be tentative. It appears that the rate constant decreases with pressure, particularly at low pressures, and this effect is believed to be real although the course of k_1 with P may not be precisely indicated by Table VII.

THE KINETICS OF DISSOCIATION AND ASSOCIATION

If the interpretation given in the last section of the velocity of sound in nitrogen tetroxide is accepted it may be supposed that the dissociation process has an activation energy of 14 kg·cal., and a rate constant of 4.8×10^4 at 25°C and 260 mm. It may further be granted that the rate constant varies somewhat with pressure, at least below about 300 mm at this temperature, and that the activation energy is equal to the dissociation heat. With these data it is possible, by the application of standard relationships, to form a reasonably clear kinetic picture of the reaction.[18]

The number of nitrogen tetroxide molecules decomposing cc^{-1} sec.$^{-1}$ is $k_1 n_1$, and at 25°C and

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[17] Brass and Tolman, J. Am. Chem. Soc. **54**, 1003 (1932).

[18] The kinetic formulae employed have been adapted from the article by Herzfeld and Smallwood in Taylor's *Treatise on Physical Chemistry* (Van Nostrand) 1931, and from Kassel's Monograph, *The Kinetics of Homogeneous Gas Reactions*, (Chem. Cat. Co.) 1932.

TABLE VII. *Variation of the velocity constant of dissociation with pressure at various temperatures.*

$T°C$	P_{mm}	n_1+n_2 $\times 10^{-18}$	n_1 $\times 10^{-18}$	Estimated $\overline{C}_0$ cal·deg.$^{-1}$	Ideal V_∞ m·sec.$^{-1}$	$k_1 \times 10^{-3}$
30.0	342	10.97	6.61	12.16	205.9	72
				8.07	212.3	78
30.0	260	8.34	3.94	11.77	208.5	63
				7.88	215.8	70
30.0	235	7.54	3.41	11.62	211.5	49
				7.81	218.5	60
25.0	668	21.79	15.09	13.53	190.4	61
				8.76	196.3	60
25.0	260	8.48	4.58	12.31	201.9	49
				8.16	208.0	47
25.0	162	5.28	2.41	11.63	210.2	45
				7.90	216.6	43
1.0	260	9.02	7.29	14.47	175.3	6.3
				9.24	180.5	7.2
1.0	156	5.53	4.21	14.08	180.2	4.2
				9.04	185.8	6.1
1.0	132	4.68	3.47	13.93	181.6	3.4
				8.97	187.2	5.6

260 mm is evidently 2.2×10^{23}. Assuming cross-sections $\sigma_1 = 5.3 \times 10^{-8}$ and $\sigma_2 = 4.2 \times 10^{-8}$ cm, the number of double collisions suffered by nitrogen tetroxide molecules is

$$Z_{11, 12} = 2n_1^2 \sigma_1^2 \left(\frac{\pi RT}{M_1}\right)^{1/2}$$
$$+ 2n_1 n_2 \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \left[\left(\frac{M_1 + M_2}{M_1 M_2}\right) 2\pi RT\right]^{1/2}$$

when M_1 and M_2 refer to molecular weights. $Z_{11, 12}$ is, therefore, 9.1×10^{27} cc^{-1} sec.$^{-1}$. The fastest rate at which the dissociation reaction may proceed is given by

$$k_1 n_1 = Z_{11, 12} e^{-E/RT} \sum_{m=0}^{m=\frac{1}{2}s-1} \frac{1}{m!} \left(\frac{E}{RT}\right)^m$$

where s is the number of classical squared terms which contribute to the internal heat capacity. If s is taken as 12 to 13 agreement is obtained with the measured reaction rate within limit of error. Experiment, however, excludes a value as large as this. It will be seen from Tables IV and VII that at 1°C and 132 mm the measured velocity of sound at 92 kc is within 0.6 m·sec.$^{-1}$ of the idealized velocity at infinite frequency if this is calculated on the basis that $C_{N_2O_4} = 16$. Even granting considerable uncertainty in the significance of this measurement it appears unlikely, from the way in which the dissociation work must disappear as the pressure is lowered, that a higher value for the heat capacity at 1°C is permissible. Very similar conclusions may be drawn from the corresponding values at 30.0° and 235 mm in the same tables. Hence, at 25°, the maximum dissociation rate permissible with normal cross sections would appear to be

$$9.2 \times 10^{27} \times 10^{-10} (23.5^4/4\,!) + (23.5^3/3\,!)$$
$$= 2.2 \times 10^{22} \text{ molecules cc}^{-1} \text{ sec.}^{-1}$$

which is inferior to the measured value. If the responsibility for this discrepancy is attributed to the cross section chosen, it is necessary to suppose $Z_{11, 12}$ larger by about one order of magnitude, and hence to increase the kinetic cross sections by about three-fold. This result finds an analogy in the behavior of nitrogen pentoxide. The heat capacity of nitrogen pentoxide is not, however, known even to the rough approximation employed above, and hence the limit to the number of vibrational terms which may be supposed active is more flexible.

The rate of the association reaction is less illuminating. If it is supposed that the association reaction occurs by suitable triple collisions, the number of which is $Z_{112, 111}/Z_{22, 12} = \sigma_2/\Lambda$ where Λ, the mean free path, is defined as

$$\frac{1}{\Lambda} = \pi(2)^{1/2} n_2 \sigma_2^2 + \pi n_1 \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2}$$

there is obtained, using normal kinetic cross sections, $\sigma_2/\Lambda = 3.6 \times 10^{-3}$ and $Z_{111, 112} = 2.8 \times 10^{25}$. Calling ϵ the fraction of all triple collisions which are effective it follows that $Z_{111, 112}$ $\epsilon = (k_1/K)n_2$ and $\epsilon = 5.0 \times 10^{-2}$. The association reaction requires no activation energy, and consequently, might be expected to occur on every suitable triple collision. The value of ϵ indicates that this is roughly the case, but little significance may safely be attributed to this coincidence since nothing is known concerning the steric factor or directional specificity of the collision process, and the duration of the triple collision is ill-defined. Furthermore, a certain number of association reactions are now known which do not appear to require a third body. In view of these uncertainties it is considered unwise to base definite conclusions on the rate constant of the association reaction.

The large molecular diameters which it is necessary to assume for the activation process raise at once the question of the effectiveness of various types of collision in provoking dissociation. An expression for the velocity of sound in a mixture of gases one of which is dissociating has been developed, and a few observations already collected dealing with this matter. They are not included here because it is felt that this communication, even when confined to a pure dissociating gas, is excessively long and detailed. It is hoped that conclusions along these lines, and also a report of the extension of the acoustical method to other dissociating gases may be presented for publication in the near future.