

The Rate of Dissociation of Nitrogen Tetroxide

Charles Edwin Teeter Jr.

Citation: [The Journal of Chemical Physics](#) **1**, 251 (1933); doi: 10.1063/1.1749281

View online: <http://dx.doi.org/10.1063/1.1749281>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Multiphoton ionization/dissociation of osmium tetroxide](#)

J. Chem. Phys. **98**, 951 (1993); 10.1063/1.464258

[ShockTube Measurement of the Rate of Dissociation of Nitrogen](#)

J. Chem. Phys. **44**, 1378 (1966); 10.1063/1.1726870

[Determination of the Equilibrium Constant for the GasPhase Dissociation of Nitrogen Tetroxide by Infrared Absorption Techniques](#)

J. Chem. Phys. **37**, 2445 (1962); 10.1063/1.1733025

[Ultrasonic Dispersion in Dissociating Dinitrogen Tetroxide](#)

J. Acoust. Soc. Am. **34**, 129 (1962); 10.1121/1.1908997

[The Dispersion of Sound in Nitrogen Tetroxide and Its Interpretation in Terms of Dissociation Rate](#)

J. Chem. Phys. **1**, 114 (1933); 10.1063/1.1749212



The Rate of Dissociation of Nitrogen Tetroxide¹

CHARLES EDWIN TEETER, JR., *Research Laboratory of Inorganic Chemistry, Massachusetts Institute of Technology,**
Department of Chemistry, University of California†

(Received January 17, 1933)

It has long been supposed that the rate of dissociation of nitrogen tetroxide could be calculated from observations of the dispersion of the sound in the gas. Einstein's equations gave the velocity constant in terms of the dispersion and the properties of the substances, regarded as ideal, acoustically transparent gases. Dispersion has been reported and rate constants calculated by several observers. On the other hand an equal number of negative results have been reported. Recently the theory has been examined critically by D. G. C. Luck and modified to take account of the absorption of sound and the deviations from the gas laws. Moreover dispersion has been observed for nondissociating gases, particularly carbon dioxide. In this gas, time lag in the equilibrium between vibrational and translational-rotational degrees of freedom causes an increase of velocity exactly parallel with that caused by dissociation. Indeed any type of equilibrium in the system may be expected to produce a dispersion of sound in some frequency region related to its own frequency, and it is not possible to distinguish between the types of equilibrium by sound measurements. The use of very small measuring

tubes also produces a dispersion of somewhat smaller magnitude. Under these circumstances it is difficult to see how any interpretation can be made or conclusions drawn. In a series of measurements made during the last five years, the author has found no measurable dispersion of sound in N_2O_4 up to 53.8 kc. The velocity of sound at this frequency agreed closely with that determined by Grüneisen and Goens at audible frequencies, although high absorption made observation difficult. At higher frequencies no evidence of transmission could be obtained although sound up to 860 kc was employed. This increasing absorption shows that we are entering a dispersive region but it is not possible to say whether dissociation, time lag, or a combination of both is responsible for the dispersion. This applies equally to the velocity increases found by Richards and Reid in the same frequency region. Hence it seems that the sonic method for measuring rates of dissociation is not likely to fulfill the hopes of its proponents, and further experimental work will not be fruitful.

I. THEORY OF THE CALCULATION OF THE RATE CONSTANT

The dispersion equations of Einstein

The speed at which the reaction $N_2O_4 \rightleftharpoons 2NO_2$ attains equilibrium has been a subject of investigation for the last forty-seven years. Ordinary methods are useless for so rapid a reaction, and attempts have been made to determine the rate by measurements of the velocity of sound in the gas.

The theory upon which this work was based

was proposed by Einstein² in 1920. Equations were derived for the propagation of sound of different frequencies in a system of ideal, acoustically transparent gases one of which was the dissociation product of the other. At either very high or very low frequencies the velocity of sound is given by an exact equation not involving either the frequency or the rate constant of dissociation. At frequencies of the order of magnitude of the dissociation frequency dispersion sets in, and the velocity is given by an approximate relation involving both the sound frequency and the rate constant. These equations are:

at low frequencies, $V_0 = [(p/\rho)(1+A/B)]^{\frac{1}{2}}$ (1)

at high frequencies, $V_\infty = [(p/\rho)(1+R/\bar{C}_v)]^{\frac{1}{2}}$ (2)

and at intermediate frequencies, $\nu = \omega/2\pi$,

$$V_\nu = \left[\frac{p}{\rho} \left(1 + \frac{k_1^2 AB + \bar{C}_v R \omega^2}{k_1^2 B^2 + \bar{C}_v \omega^2} \right) \right]^{\frac{1}{2}}. \quad (3)$$

* Contribution No. 26.

† This investigation was suggested by A. R. Olson, and the early portion of the work was carried out at the University of California with his counsel and cooperation. The author is indebted to the Parker Fund of Harvard University for a Fellowship in 1927-8, and to the National Research Council for a National Research Fellowship in 1928-9.

¹ A preliminary notice of this communication has already appeared. (J. Am. Chem. Soc. 54, 4111 (1932).)

² A. Einstein, Sitzungsber. d. Berl. Akad. 1920, 380.

By solving (3) for k_1 and substituting (1) and (2) for their values we can obtain

$$k_1 = (2\pi\nu\bar{C}_v/B)[(V_\infty^2 - V_r^2)/(V_r^2 - V_0^2)]^{1/2}. \quad (4)$$

Applied to the N_2O_4 dissociation, p is the pressure, ρ the density, k_1 the rate constant of dissociation,

$$A = \left(\frac{2D}{T} - \bar{C}_v \right) \frac{1-\alpha}{1+\alpha} + R \frac{2-\alpha}{\alpha},$$

$$B = \frac{D^2}{RT^2} \frac{1-\alpha}{1+\alpha} + \bar{C}_v \frac{2-\alpha}{\alpha},$$

D is the heat of dissociation at constant volume, α the degree of dissociation, \bar{C}_v is the weighted average of the heat capacities of N_2O_4 and NO_2 , $\bar{C}_v = [C_v''(1-\alpha) + 2\alpha C_v']/(1+\alpha)$, and R is the gas constant.

Several of the early experimenters^{3, 4, 5, 6} thought they had reached the dispersive region at audible frequencies. From some measurements completed in 1929 the author⁷ believed he had found dispersion at 51.7 kc. Richards and Reid⁸ report that they have found measurable

dispersion from 92 to 450 kc and calculate rate constants.

On the other hand Grüneisen and Goens⁹ found no dispersion up to 15.6 kc. Kistiakowsky and Richards¹⁰ extended this to 80 kc. In the present paper new experiments are described which show no measurable dispersion up to 53.8 kc, but do show the presence of strong absorption, increasing greatly up to 860 kc. This indicates the advent of dispersion, without affording quantitative evidence.

The dispersion equations of Luck

It seems a particularly bad approximation to apply the ideal gas laws to a system such as $N_2O_4-NO_2$, where both gases deviate from ideality, but one (N_2O_4) deviates much more than the other. It becomes important therefore to examine D. G. C. Luck's¹¹ modification of Einstein's theory to apply to real gases and at the same time to take account of sound absorption. Since no equation of state was known for the gas mixture, Luck used a functional form, $p=f(\rho, T, \alpha)$. Following the general method of Einstein, he obtained

$$\frac{V_r}{V_0} = \left[\frac{1+\epsilon^2 X^2}{1+X^2} \right]^{1/2} \left(\frac{1+\theta^2}{(1-\theta^2)^{1/2}} \right) \quad \text{for velocity}, \quad (5)$$

$$\text{and} \quad \theta = \frac{\lambda}{2\pi l} = \left[1 + \frac{(1+\epsilon^2 X^2)^2}{(\epsilon^2 - 1)^2 X^2} \right]^{1/2} - \frac{1+\epsilon^2 X^2}{(\epsilon^2 - 1)X} \quad \text{for absorption}. \quad (6)$$

In these equations X (termed the relative frequency) $= 2\pi\nu/bk_1$, $\epsilon = V_\infty/V_0$, $V_0 = \partial p/\partial \rho(1+ga/b)$, $V_\infty = \partial p/\partial \rho(1+g)$,

$$a = \frac{2-\alpha}{\alpha} + (1-\alpha) \frac{\partial p/\partial \alpha}{\partial p/\partial \rho} \frac{\partial \ln K}{\partial T} + \frac{(1-\alpha)\rho^2 C_v}{pM} \frac{\partial p/\partial \alpha}{\partial p/\partial T} - \frac{D}{C_v} \left(\frac{\partial \ln K}{\partial \rho} - \frac{1}{\rho} \right),$$

$$b = \frac{2-\alpha}{\alpha} + (1-\alpha) \frac{D}{C_v} \frac{\partial \ln K}{\partial T}, \quad g = \frac{\partial p/\partial T}{\partial p/\partial \rho} \frac{Mp}{\rho^2 C_v},$$

³ E. and L. Natanson, Wied. Ann. **24**, 454 (1886); **27**, 606 (1886).

⁴ Argo, J. Phys. Chem. **18**, 438 (1914).

⁵ F. Keutel, Inaug. Diss., Berlin (1910).

⁶ H. Selle, Zeits. f. physik. Chemie **104**, 1 (1923).

⁷ A. R. Olson and C. E. Teeter, Jr., Nature **124**, 444 (1929).

⁸ W. T. Richards and J. A. Reid, J. Chem. Phys. **1**, 114 (1933).

$C_v = (1-\alpha)C_v'' + 2\alpha C_v'$ = heat capacity/mole of mixture, M = molecular weight, l is the distance in which the amplitude of the sound is reduced by

⁹ E. Grüneisen and E. Goens, Ann. d. Physik **72**, 193 (1923).

¹⁰ G. B. Kistiakowsky and W. T. Richards, J. Am. Chem. Soc. **52**, 4661 (1930).

¹¹ D. G. C. Luck, Phys. Rev. **40**, 440 (1932).

the factor e^{-1} , and K is the dissociation constant. The equations reduce to the form given by Einstein if the equation of state becomes $p/M \cdot RT(1+\alpha)$ and θ becomes negligible. By assuming values of ϵ , Luck is able to show the form of the velocity and absorption curves but application to the calculation of rate constants cannot as yet be made, since the differential coefficients, $[\partial p/\partial \rho]_{\alpha, T}$, $[\partial p/\partial T]_{\alpha, \rho}$, and $[\partial p/\partial \alpha]_{\rho, T}$ are at present unknown and not measurable, and there is no equation of state from which they may be computed. The curve for V_r/V_0 differs in position but not in shape from that plotted from Einstein's equation. That for absorption rises rapidly in the dispersive region and attains a maximum at $X=1/\epsilon$, thereafter dropping off again.

If Luck's equations are solved for k_1 the relation

$$k_1^L = \frac{2\pi\nu}{b} \left[\frac{V_\infty^2(1+\theta^2)^2 - V_r^2(1-\theta^2)}{V_r^2(1-\theta^2) - V_0^2(1+\theta^2)^2} \right]^{\frac{1}{2}} \text{ is obtained.}$$

This is seen to reduce to the form derived from Einstein's equations,

$$k_1^E = \frac{2\pi\nu\bar{C}_v}{B} \left[\frac{V_\infty^2 - V_r^2}{V_r^2 - V_0^2} \right]^{\frac{1}{2}} \text{ if the gases are ideal,}$$

and to the form $k_1^L = (2\pi\nu/b) \cdot (1+\theta)/(1-\theta)$ at the absorption maximum. If a value of ϵ is assumed, θ and V_r/V_0 at the absorption maximum can be calculated, while b and \bar{C}_v/B follow from the dissociation data. It is thus seen that a rough notion of the separate effects of the deviation from the gas laws and the absorption of sound can be obtained, if for K the variable $K_p = F(p, T, \alpha)$ is used. The chief uncertainties are in the values of ϵ , α , and $\partial K/\partial T$, in the case of ϵ since V_0 and V_∞ calculated from Luck's equations may not be the same as the values from Einstein's equations. At the absorption maximum $X=1/\epsilon$ and $\theta = (\epsilon-1)/(\epsilon+1)$. Also $V_r/V_0 = (1+\epsilon)/2$ (approximately, if ϵ is near 1). Using values of V_0 and V_∞ calculated from Einstein's equations, we find that ϵ varies from about 1.04 to 1.06 at 25°. With $\epsilon=1.05$, $V_r/V_0=1.025$ and $\theta=0.024$. This means that the amplitude will be diminished 1/e in 6.6 wave-lengths. By substituting in the two equations for k_1 , $k_1^L = 2\pi\nu/b \times 1.050$ and k_1^E

$= 2\pi\nu\bar{C}_v/B \times 1.012$, a difference of about 3.8 percent. If $\epsilon=1.06$, $\theta=0.029$ and $k_1^L = 2\pi\nu/b \times 1.060$, $k_1^E = 2\pi\nu\bar{C}_v/B \times 1.015$, a slightly greater difference. The other factors b and B/\bar{C}_v may be calculated to show the effect of the deviations from ideality. At 25° and 565 mm pressure $b=86.1$ and $b'=B/\bar{C}_v=77.5$, a difference of about 10 percent. At this same temperature and 260 mm $b=75.7$ and $b'=65.3$, and at 106 mm $b=58.1$ and $b'=49.9$, differences of roughly 14 and 13 percent, respectively. At lower temperatures the calculation becomes too uncertain as the values for α and K were experimentally determined¹² only at 25°, 35° and 45°.

Unfortunately no more information can be gleaned from Luck's equations in the present state of our knowledge. It might be possible to guess at the values of the constants for an equation of state, but the accuracy would not be sufficient to justify a calculation from Luck's equations. We may state, however, that at the absorption maximum the values of k_1 from Einstein's equations may be about 4 percent too low on account of absorption and perhaps 15 percent too high because of deviations from the gas laws.

The dispersion equations of Kneser

At the end of Luck's paper it was pointed out that dispersion due to other causes than dissociation might render invalid any conclusions drawn from acoustic data. Such dispersion was observed for air and carbon dioxide by Pierce¹³ and Reid,¹⁴ and it was attributed by Herzfeld and Rice¹⁵ to a time lag in energy transfer from translational to internal molecular degrees of freedom. More lately Kneser¹⁶ studied this dispersion both theoretically and experimentally, and found an effect closely analogous to and of nearly the same magnitude as that predicted by the Einstein theory for the dissociation dispersion. In CO₂ the velocity rose about 3.5 percent in the frequency

¹² F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. 53, 1250 (1931).

¹³ G. W. Pierce, Proc. Am. Acad. Sci. 60, 27 (1925).

¹⁴ C. D. Reid, Phys. Rev. 35, 814 (1930).

¹⁵ K. F. Herzfeld and F. O. Rice, Phys. Rev. 31, 691 (1928).

¹⁶ H. O. Kneser, Ann. d. Physik (5) 11, 761 (1931); 11, 777 (1931).

region 100–600 kc and again became constant at higher frequencies. It is instructive to compare the equations Kneser derived for the velocity at different frequencies (which gave curves checking his data closely) with the corresponding equations of Einstein. For very low frequencies he found $V_0 = [(p/\rho)(1+R/C)]^{1/2}$, and for very high frequencies, $V_\infty = [(p/\rho)(1+R/C_a)]^{1/2}$. For intermediate frequencies in the dispersive region he obtained

$$V_v = \left[\frac{p}{\rho} \left(1 + R \frac{C + C_a \beta^2 \omega^2}{C^2 + C_a^2 \beta^2 \omega^2} \right) \right]^{1/2} \quad (7)$$

In these equations C is the total heat capacity per mole and C_a is the part of the heat capacity due to translational and rotational degrees of freedom. The symbol β represents the time characteristic of excitation of the vibrational degrees of freedom. If Kneser's equation for V_v is rewritten

$$V_v = \left[\frac{p}{\rho} \left(1 + \frac{RC + RC_a \beta^2 \omega^2}{C^2 + C_a^2 \beta^2 \omega^2} \right) \right]^{1/2}, \quad (7')$$

and Einstein's equation is written

$$V_v = \left[\frac{p}{\rho} \left(1 + \frac{AB + R\bar{C}k_1^{-2}\omega^2}{B^2 + \bar{C}^2 k_1^{-2}\omega^2} \right) \right]^{1/2}, \quad (3')$$

the close similarity between the two dispersion formulas may be seen. By a fortunate choice of constants it would be possible to explain a given dispersion either as dissociation or as time lag.

It should be pointed out that Kneser, like Einstein, used the ideal gas laws and neglected sound absorption in his derivation. Hence his equations should be modified in the same way to take account of deviations from these ideals. This would not be expected to alter the similarity of the two corrected formulas.

It can be readily seen that any type of equilibrium in the system, whether in the intermolecular forces, in a chemical reaction, or in the states of the molecules themselves would be expected to give a dispersion in some frequency region related to its own frequency. If the dispersive regions overlap or coincide it is very difficult to see how any clear interpretation can be made or conclusions drawn.

The dispersion equations of Richards and Reid

Nevertheless an attempt has been made by Richards and Reid to modify the Einstein theory to include the "heat capacity" dispersion of Pierce, Reid and Kneser as well as the dissociation dispersion. The resulting equation however is used only to try to justify their neglect of the heat capacity effect. In their derivation, an absorption term is included, but this also is neglected in all calculations. The ideal gas laws are still assumed throughout. With this procedure the equation

$$V_v^2(1 - \beta^2 V_v^2/\omega^2)/(1 + \beta^2 V_v^2/\omega^2)^2 = (p/\rho)\gamma \quad (8)$$

is obtained. Here β , the "damping coefficient" used by Richards and Reid, is nearly identical with the " l " used in Luck's equations, and $\gamma (= C_p/C_v)$, which is also the ratio of isothermal to adiabatic compressibilities (Richards and Reid seem to have this ratio inverted), is given by a complex involving the different heat capacities, the frequency, and also the time lag θ (Kneser's β). When absorption and time lag are negligible (8) should reduce to the form given by Einstein. It is evident that there is an algebraic error in the reduction as carried out by Richards and Reid. Their Eq. (9) should read

$$k_1 = \omega \left\{ \frac{C_0 RT^2 \alpha [2 + \alpha(1 - \alpha)]}{(2 - \alpha)[C_0 RT^2 (2 + \alpha(1 - \alpha)) + D^2 \alpha(1 - \alpha)]} \right\} \left\{ \frac{V_\infty^2 - V_v^2}{V_v^2 - V_0^2} \right\}^{1/2},$$

which readily reduces to our Eq. (4) above, instead of

$$k_1 = \omega \left\{ \frac{C_0 RT^2 \alpha [2 + \alpha(1 - \alpha)]}{(2 - \alpha)[C_0 RT^2 + D^2 \alpha(1 - \alpha)]} \right\} \left\{ \frac{V_\infty^2 - V_v^2}{V_v^2 - V_0^2} \right\}^{1/2},$$

which is used in all their calculations. Fortunately, this error is independent of frequency and affects only the first or smaller term of the denominator. The rate constants calculated in Tables VI

and VII, however, should be decreased by about 5 percent on this account.

The tube dispersion

A somewhat smaller change of velocity with frequency is caused, as has long been realized, by the use of very small tubes as the measuring chambers. The effect of small tubes is quite complicated. In the first place the close proximity to the walls causes side reflections which break up and distort the sound pattern and cause the appearance of spurious nodes and antinodes. If an attempt to avoid these disturbances is made by examining only the region close to the source of sound, the anomalies noted by Pierce and Reid are likely to vitiate the results. In the second place the velocity, according to the Helmholtz-Kirchhoff formula, will decrease as the sound frequency or the radius of the tube diminishes. In a region of dissociation dispersion this change of velocity would be expected to increase greatly as Richards and Reid pointed out. At the most they suggested that the correction might double. This will not be very significant if the dispersion observed is large and the tube dispersion only a small proportion of the total. However if the two are of nearly the same order of magnitude it becomes extremely important to know the tube dispersion very accurately in order that the corrected value for the dissociation dispersion may not be meaningless.

II. EXPERIMENTS

Preliminary experiments

The apparatus was particularly designed to avoid the complications caused by the use of small tubes. Sound waves were produced in a chamber, made as large as possible to cut down wall effects, and standing waves were set up between the crystal which was the source of sound and a plane reflector. A sketch of the apparatus is given in Fig. 1 and a diagram of the electrical circuit in Fig. 2. The sound chamber was a bell of Pyrex tubing five inches in diameter, the open end of which was closed by a brass plate heavily coated with paraffin. The crystal, *c*, was contained in the male part of a $1\frac{1}{2}$ inch ground joint; the female part of which was sealed in a hole in the center of the brass plate. The lower electrode was a gold plate resting on a block of paraffin, the upper a square of platinum foil pressing lightly on the crystal. The seals *s*, *s* were made vacuum tight by applying beeswax and rosin and shellac on the outside. The reflector, *r*, was a lantern slide cover supported by a glass tube and moved by a calibrated screw *S*. A vacuum-tight movable joint, *j*, was made by stretching a piece of Gooch rubber tubing between rubber stoppers. To protect the rubber and to prevent it from collapsing under vacuum the tube was partly filled with a mixture of paraffin and vaseline. The chamber, itself thermostated, was in communication with a

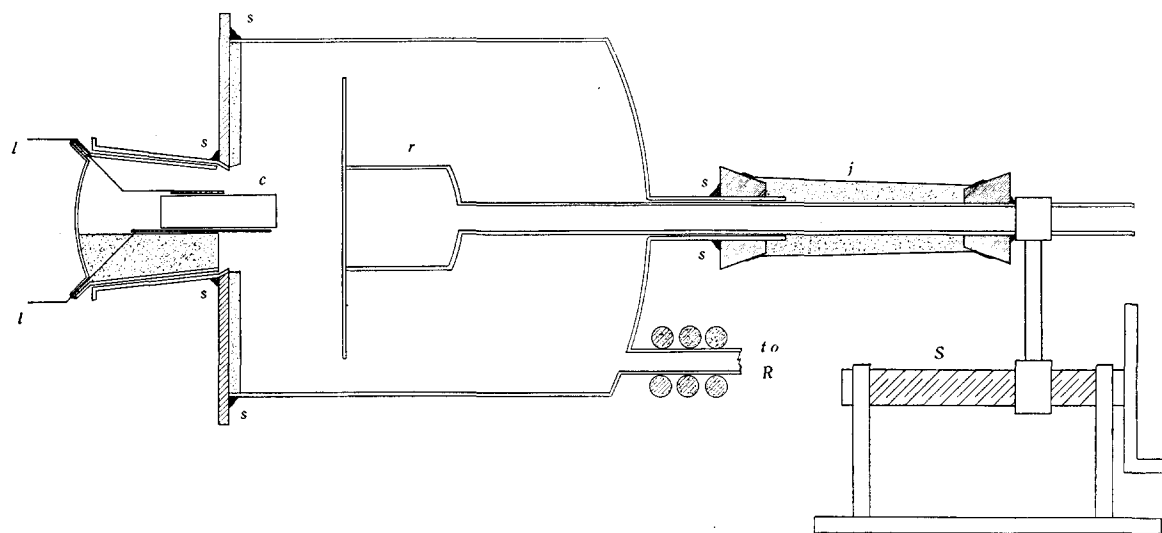


FIG. 1. Apparatus for measuring velocity of high-frequency sound in nitrogen tetroxide. Early form.

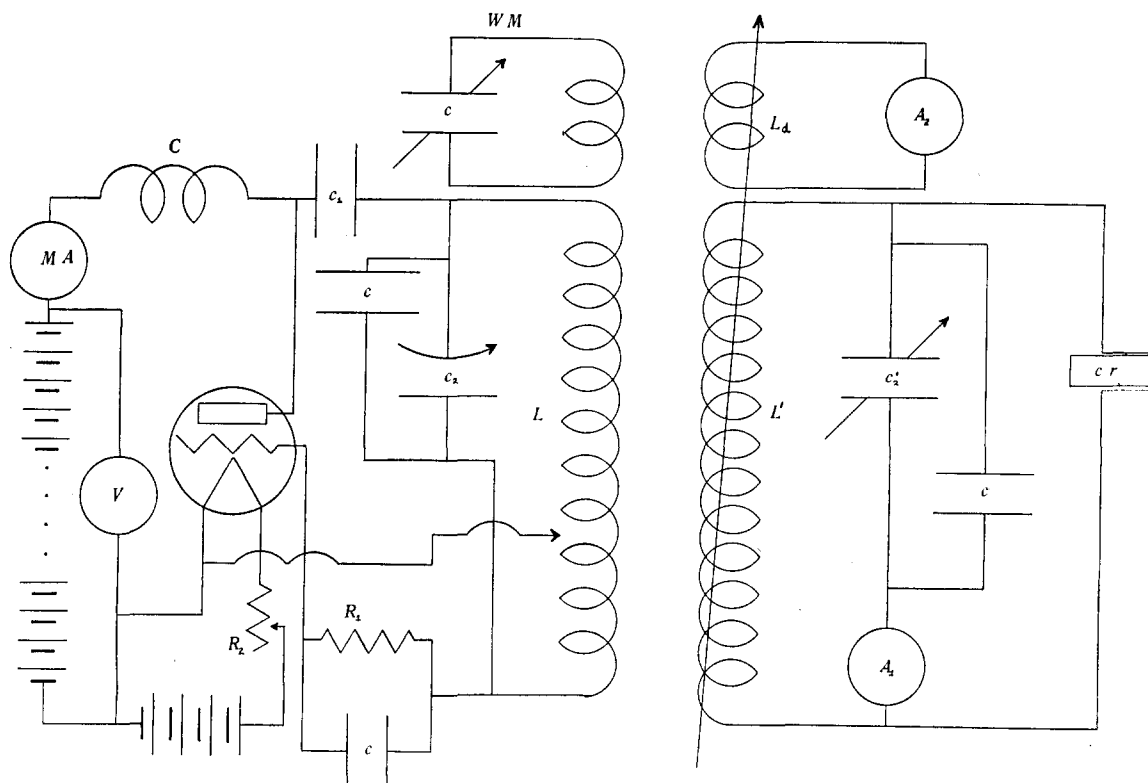


FIG. 2. Oscillating and resonance circuits for forcing vibration of quartz crystal.

reservoir of liquid nitrogen tetroxide at a definite temperature.

The quartz crystals were cut as suggested by Pierce. No success was had in inducing oscillation by means of his circuit, hence the power oscillator of Wood, Loomis and Hubbard¹⁷ was employed. To the left of Fig. 2 is an ordinary Hartley oscillator and to the right a resonant circuit containing the crystal (*cr*). The inductances *L*, capacities *c*, choke *C* and resistances *R* have values determined by the tube and the crystal employed. In operation the Hartley oscillator was set to the frequency of the crystal with the aid of the standard wave meter, *WM*, the circuit *L'**c'*₂ tuned to resonance with *Lc*₂ as indicated by the thermomilliammeter *A*₁, and the two circuits varied simultaneously until the crystal broke into oscillation.

¹⁷ (a) Wood and Loomis, *Phil. Mag.* (VII) 4, 417 (1927).

(b) Hubbard and Loomis, *Nature* 120, 189 (1927).

(c) Hubbard and Loomis, *Phil. Mag.* (VII) 5, 1177 (1928).

(d) Hubbard and Loomis, *J. Opt. Soc. Amer.* 17, 295 (1928).

Moving the reflector had no effect on the plate meter of the Hartley oscillator (*MA*), but caused a regular rise and fall in the current indicated by the thermomilliammeter *A*₂ coupled to the resonance circuit through a small coil *L*_{*d*}. Other methods of detection were tried but none was completely satisfactory. The frequency was measured to about 0.2 percent by the standard wave meter. To check the apparatus the velocity of sound in air was measured. Erratic results were obtained very near the crystal, as was noted above, but at distances greater than three or four half wave-lengths the velocity was 332 m/sec. at 0° in close agreement with the accepted value. This figure was the mean of four series, comprising seventeen measurements in all.

The nitrogen tetroxide was prepared by heating a mixture of sand and lead nitrate previously dried at 120°. A strong current of oxygen—dry and free from CO₂—was passed through the combustion tube to minimize decomposition. The product was first collected in a trap cooled with solid CO₂-alcohol, then distilled through a column

of P_2O_5 , and finally collected in a bulb half filled with P_2O_5 and cooled in liquid air or CO_2 -alcohol. The product obtained from distillation was pure white as a solid, and reddish brown as a liquid at the boiling point. Permanent gases were removed after the bulb had been sealed onto the main apparatus, first by pumping on the solid N_2O_4 with a mercury diffusion pump, and then by boiling off two liters of the gas into an evacuated flask with the temperature of the liquid about 0° . The residue was analyzed for air by sealing off a 50–100 cc bulb and noting the amount of undissolved gas after breaking the point of the bulb under KOH solution.

The reaction on the reflector fell off rapidly with distance from the crystal and only a few half wave-lengths could be measured. In the single successful series of measurements, the value 192.6 was obtained for the velocity of sound of frequency 51.7 kc in N_2O_4 at 25° and 565 mm. From this a rough value of the rate constant, $k_1 = 5600$ was calculated. Analyses showed 0.1 percent of air.

One of the chief criticisms of the early apparatus was the use of large surfaces of paraffin and vaseline. It was later shown that N_2O_4 exerts a slight but definite oxidizing action on these substances, NO and N_2O_3 being formed. This would tend to increase the velocity of sound. Another desirable modification was an increase of the sensitivity to permit measurements of a greater number of half wave-lengths and also greater distances from the crystal. It was also necessary to decrease the size of the reflector since at low frequencies large reflectors introduce periodic errors.

Final experiments

With all this in mind a new apparatus was built (see Fig. 3). The reflector was cut to $1\frac{1}{2}$ inches square. A new crystal holder was constructed of nichrome IV. Brass parts were triple gold plated and burnished. A groove was cut in the end plate, and the bottom of the Pyrex tube ground and polished to fit in this. The joint was made vacuum tight by filling the outside of the groove with a beeswax-rosin-ferric oxide mixture (at s, s). For the movable joint a metal stuffing box was used, sealed to the upper end of the chamber (s, s). A rod of nichrome IV supporting

the plane glass reflector at one end passed through a well fitting nichrome bearing into the stuffing box. This was of steel, silver brazed to the bearing (at a, a), and contained a disk of talc turned and polished to a close fit, surmounted by a second disk of ceresin wax, and a third disk of Bakelite. Pressure was applied to the topmost disk by the threaded top which was also tubulated to act as a guide for the rod. Even under vacuum it was possible to advance or withdraw the rod without any leak. The rod was moved by a standardized screw (not shown).

The electrical circuit is shown in Fig. 4. The ordinary type of crystal controlled oscillator was employed. Values of L , C_1 and C_2 varied with the crystal used. To observe the change in the plate current as the reflector was moved, the bulk of the current was balanced out by the dry cell and the resistances R_3 and R_4 . Only a small fraction of the current flowed through the Ayrton shunt AS to the galvanometer G . The latter had fifty divisions, each corresponding to 1.1 micro-ampere. Although the amplitude of the sound must have been much less with this oscillator the reaction on the reflector in air was sufficient to produce full scale deflection of the galvanometer between nodes and antinodes.

No change was made in the method of making nitrogen tetroxide, as that was deemed satisfactory. The last experiment however was made with gas prepared by distilling C.P. red fuming nitric acid in a current of oxygen through a column of P_2O_5 and glass pearls and then through the apparatus previously used. It was found that practically all of the nitrogen tetroxide could be distilled off with the volatilization of only a small amount of nitric acid, and most of this was left in the first receiver. Further distillations under vacuum removed the remainder.

After distilling the nitrogen tetroxide into the main apparatus it was purified even more carefully than before. It was repeatedly distilled, frozen, left over P_2O_5 , and pumped free of more volatile gases. After each experiment it was re-purified, and before use analyzed for permanent gases and examined for N_2O_3 by condensation. A trace of the latter gas was sufficient to show a slight blue color against the pure white nitrogen tetroxide, especially as the trioxide condensed first.

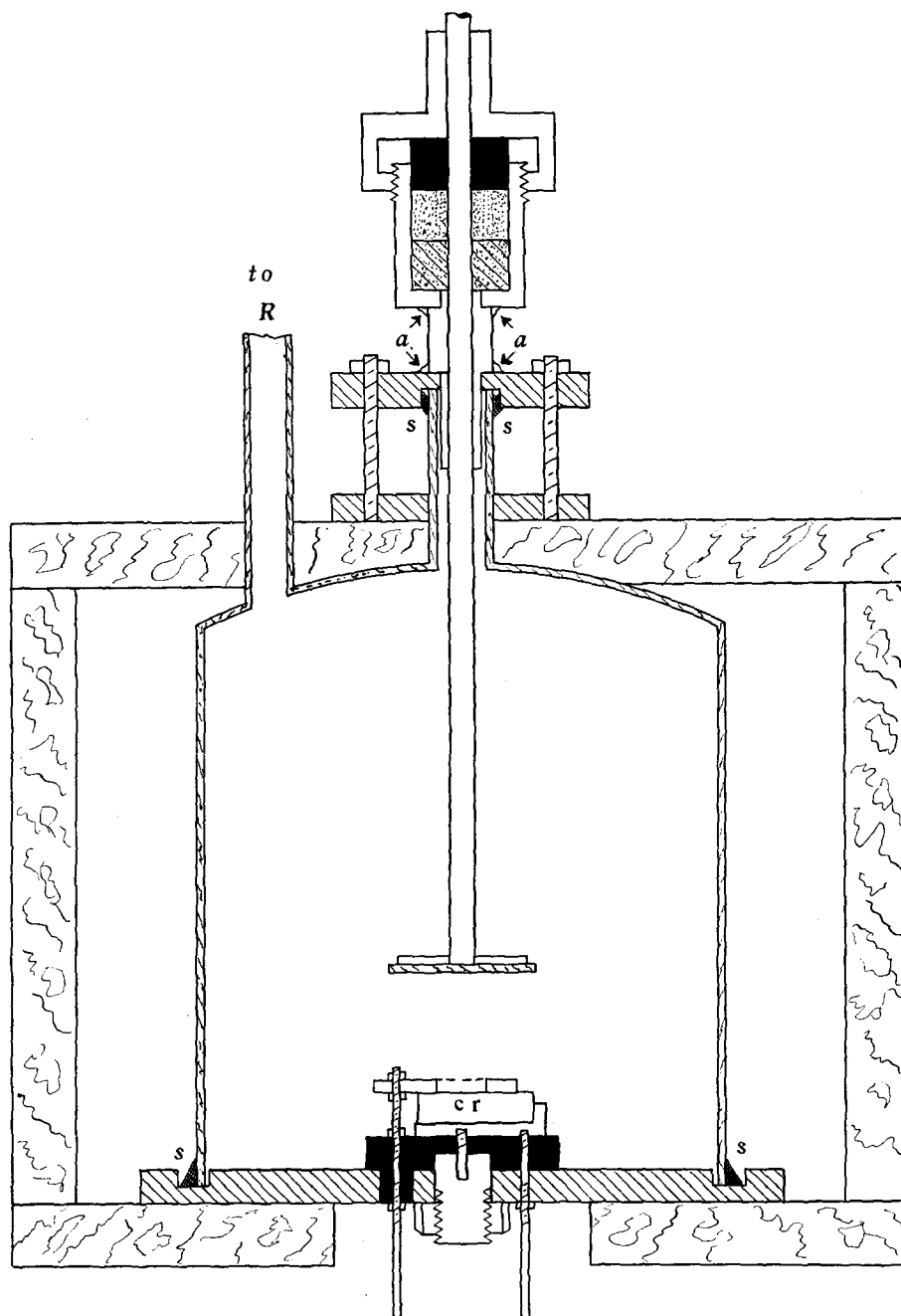


FIG. 3. Apparatus for measuring velocity of high-frequency sound in nitrogen tetroxide. Final form.

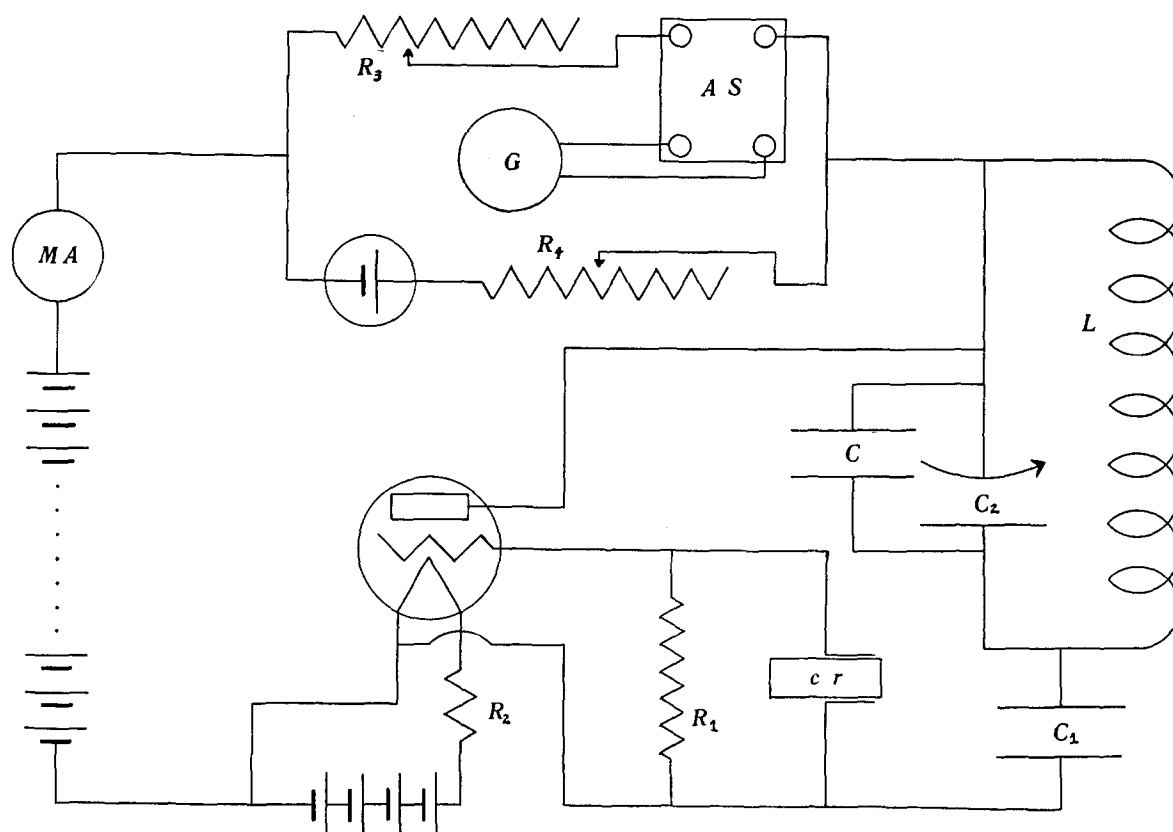


FIG. 4. Circuit of piezoelectric oscillator used in final experiments.

Three crystals were employed, approximate frequencies (to 0.2 percent) 53.8, 100.6, and 860 kc. These values were obtained by heterodyning the crystal oscillator with a second oscillator and measuring the frequency of the latter with a standard wave meter. More accurate measurements could easily have been made but were not deemed worth while. It should be noted that the frequency of a quartz crystal varies slightly with the temperature, and also changes with the mounting unless this is invariable.

The apparatus was checked by measurements in air at the two lower frequencies. At 53.8 kc and atmospheric pressure the velocity of sound, corrected to 0° , was found to be 333.0 m/sec. as the mean of 296 determinations of the half wavelength, $\lambda/2$. At 100.6 kc and atmospheric pressure the mean of 411 determinations gave 332.0 m/sec. for the velocity. Pierce obtained 332.4 m/sec. at 50 kc and 331.8 m/sec. at 100 kc. Reid found values for the velocity of sound which

decreased with increasing distance from the source. At a mean distance of 15 cm the velocity was 332.7 m/sec. at 50 kc. At 30 cm it was 332.1 m/sec. and at 45 cm it was 331.8 m/sec. The mean distance in our experiment was about 10 cm so the high result is not surprising.

The results for nitrogen tetroxide are given in Tables I, II and III. The roman numerals represent different fillings of the chamber (new samples of nitrogen tetroxide); the Arabic numerals represent series of measurements on the same sample. In all the experiments except VI, Table I, from 3 to 5 stopcocks were in contact with the apparatus. All were lubricated with an "acid-proof" grease. In addition to these a mercury manometer was used intermittently to check the constancy of the pressure. This was disconnected whenever a reading was not being made. The actual pressure in the chamber, however, was determined from the vapor pressure curve of nitrogen tetroxide, which seems to be fairly well

known.¹⁸ The amount of volatile decomposition product which reached the chamber during a run from these reactive parts of the apparatus must have been very small, as the amount of N_2O_3 produced on standing overnight was barely detectable. In the experiments reported the percentage of permanent gases was always below 0.3 percent, and no blue color of N_2O_3 could be observed on condensation. The stopcocks and manometer were used simply as a convenience and to save time. If positive results had been obtained no possible precautions would have been spared. As conclusive evidence that the presence of the stopcocks and manometer did not affect the velocity of sound, Experiment VI, (Table I) was made with a redesigned apparatus eliminating these reactive parts. The chamber and reservoir were separated by a thin glass partition which could be broken when desired. Provision was made for evacuating, filling and sealing off the reservoir, and for evacuating and sealing off the chamber separately. The wave-length found checked very well with the results of the other experiments, and the average velocity of sound obtained from all the measurements with the 53.8 kc crystal agreed with the low-frequency measurements of Grüneisen and Goens.⁹

In Experiment IV with the 53.8 kc crystal a rough determination of the absorption was made. It will be recalled that in air the reaction on the reflector caused a change of fifty scale divisions on the galvanometer between node and antinode, even at some distance from the crystal. In nitrogen tetroxide at a distance of less than $\frac{1}{4}$ inch from the crystal or only one $\lambda/2$ a change of less than fifteen divisions was observed. This fell off rapidly as the reflector was withdrawn from the crystal as shown in Table IV. In the space of some 6 inches or 45λ the reaction fell practically to zero.

At the higher frequencies no evidence of transmission could be obtained even very close to the crystal and although a range of pressures was ex-

plored. A reaction on the reflector of 0.5 scale divisions, or $1/100$ of the effect in air, could easily have been detected. A confirmation that the absorption in N_2O_4 at 53.8 kc was much greater than that in air, the absorption at 100.6 greater than at 53.8 kc, and that at 860 kc greater than at 100.6 kc was the fact that at decreasing pressure limits for increasing frequencies enough

TABLE I. *Wave-length and velocity of sound in nitrogen tetroxide at 53.8 kc, 550 mm pressure, and 25°.*

Expt.	No. of check series	No. $\lambda/2$ measured	Av. $\lambda/2$ (scale divs.)
I	6	93	1.348
II	11	393	1.361
III	7	303	1.359
IV	5	317	1.364
V	3	114	1.354
VI	8	353	1.357
Total		1220	Av. 1.360
Velocity of sound 186.9 m/sec.			

TABLE II. *Attempts to measure wave-length and velocity of sound in nitrogen tetroxide at 100.6 kc and various temperatures and pressures.*

Expt.	Temp. liquid	Press. (mm)	Temp. gas	Observations
Series I				
I 1	-10.09	150	21.4	No transmission; crystal oscillated strongly.
2	- 3.65	216	21.5	
3	+ 0.07	265	21.2	
4	+ 5.01	343	21.2	
Series II				
II 1	+ 4.71	338	19.8	No transmission; crystal oscillated strongly.
2	10.52	453	20.7	
3	15.03	565	20.3	No transmission; crystal oscillated feebly.
4	19.93	714	19.9	

At pressures greater than about 450 mm the crystal could not be made to oscillate strongly.

TABLE III. *Attempts to measure wave-length and velocity of sound in nitrogen tetroxide at 860 kc and various temperatures and pressures.*

Expt.	Press. (mm)	Temp. gas	Observations
Series I			
I	97	25.0	No transmission; crystal oscillated strongly.
II	131	25.5	
Series II			
III	123	25.0	No transmission; crystal oscillated strongly.
IV	78	25.0	

At pressures greater than about 140 mm the crystal could not be made to oscillate.

¹⁸ (a) Scheffer and Treub, *Zeits. f. physik. Chemie* **81**, 308 (1912).

(b) Baume and Robert, *Comptes Rendus* **168**, 1199, 1201 (1919).

(c) Macisevskii, *J. Russ. Phys. Chem. Soc. (Chemical Part)* **48**, 1917 (1916).

(d) Mittasch, Kuss, and Schlueter, *Zeits. f. anorg. Chemie* **159**, 1 (1926).

TABLE IV. Readings of screw, half wave-lengths, and change in galvanometer deflection in nitrogen tetroxide at 53.8 kc, 550 mm and 25.0°.

Screw reading	Difference	No. $\lambda/2$	$\lambda/2$	Av. galv. defl. div.
Series I				
28.95	13.20	10	1.32	14.8
42.15	16.51	12	1.37	13
58.66	12.59	9	1.40	10
71.25	10.53	8	1.32	7
81.78	9.47	7	1.35	5
91.25	11.50	8	1.44	3
102.75	10.56	8	1.32	2
113.31	12.04	9	1.34	1.5
125.35	19.74	15	1.32	0.5
145.09				
Series II				
31.26	15.94	12	1.33	14
47.20	13.44	10	1.34	11
60.64	12.24	9	1.36	8
72.88	12.57	9	1.39	6.5
85.45	11.74	9	1.31	4
97.19	12.37	9	1.37	2.6
109.56	13.77	10	1.38	1.6
123.33	9.75	7	1.39	0.5
133.08	11.41	8	1.42	0.6
144.49				

energy was absorbed to stop or greatly diminish the oscillation of the crystal. These limits were 575 mm for the 53.8 kc crystal, 450 mm for the 100.6 kc crystal and about 140 mm for the 860 kc crystal. Of course it might have been possible to increase the sensitivity of detection or the amplitude of the sound waves, and hence force some of the sound through the gas. But with the present apparatus it seems to be clearly demonstrated that the absorption is too great to be neglected. Since greatly increasing absorption accompanies dispersion, as shown by the theory of Luck and the experiments of Kneser, it may be assumed that we are entering a dispersive region, but no clue is afforded as to the cause of the dispersion.

III. DISCUSSION

Kistiakowsky and Richards calculated theoretical values of V_0 and V_∞ to check against their experimental points. Unfortunately in making use of Einstein's equations for this calculation they failed to check his algebra and hence missed the slip in sign in the equation for V_0 . Hence a new calculation was desirable. This is made in Table V for 25° and various pressures, and the

TABLE V. Observed velocities of sound in nitrogen tetroxide at 25° and various pressures.

p (mm)	u obs.(m/sec.)	p (mm)	u obs.(m/sec.)
Kistiakowsky and Richards		Natanson	
9.9 kc		617	187.2*
776	183.0	492	189.9*
761	183.8	231	197.3*
364	192.4	102	208.1*
270	197.0†	43.6	220.2*
41.6 kc		Nernst and Keutel	
760	183.6†	606	188.7
491	188.8	308	196.6*
275	195.5†	221	199.8*
146	203.0†	106	210.4*
80.3 kc		Argo	
760	183.5†	685	189.0*
486	189.4†	Grüneisen and Goens	
333	193.5	760	184.1
304	195.3	565	187.0
Teeter		440	189.6
53.8 kc		265	194.5*
550	186.9		
Richards and Reid			
9 kc		92 kc	
668	185.2	185.3	
260	195.1†	195.4	
162	202.0	202.5	

* Extrapolated over 1°–5°, using temperature coefficient of 0.95 m/sec./degree.

† Average values.

curves are plotted in Fig. 5. On this diagram are given all recorded points obtained at or near this temperature at all frequencies. In making the calculation, the new data of Verhoek and Daniels¹² were used. These authors give $D = 13,960$ cal./mole at constant volume¹⁹ (not 14,600 as used by Richards and Reid) and they use the values $C_v''(\text{N}_2\text{O}_4) = 12.75$ and $C_v'(\text{NO}_2) = 6.8$. These are not very accurate but do not greatly affect the results. Verhoek and Daniels' data do not permit the ready calculation of either K or α at a given pressure. They give instead equations involving $C_{\text{N}_2\text{O}_4}^\circ = g/mv$, the

¹⁹ F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. 53, 1186 (1931).

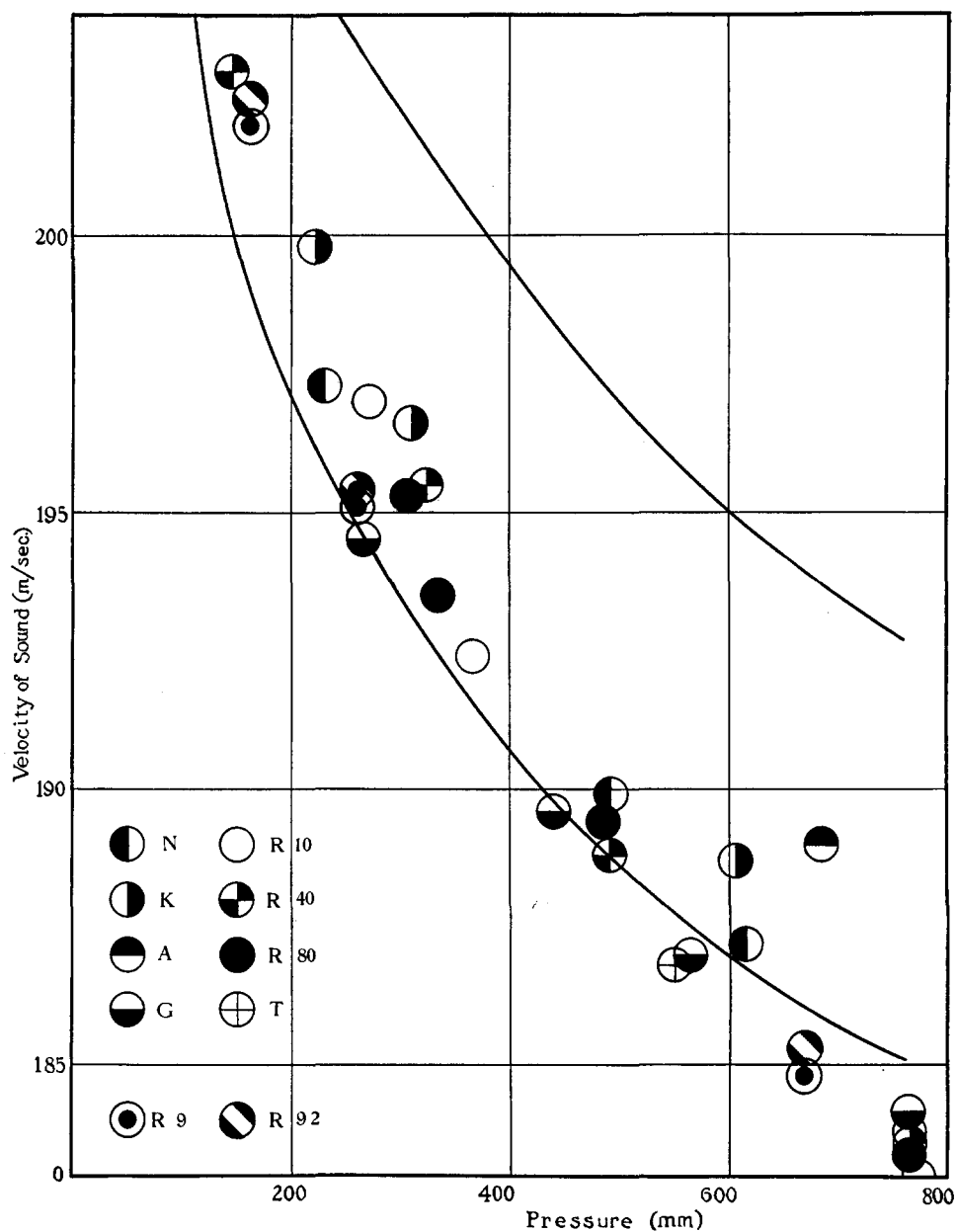


FIG. 5. Experimental and theoretical velocities of sound in nitrogen tetroxide at 20° and various pressures. Upper curve, values of u_{∞} , lower curve values of u_0 , both calculated from Einstein's theory, by using Verhoek and Daniels' dissociation data. *N*, data of Natanson; *K*, Nernst and Keutel; *A*, Argo; *G*, Grüneisen and Goens; *R*10, *R*40, *R*80, data of Kistiakowsky and Richards at 10 kc, 40 kc, and 80 kc, respectively; *T*, Teeter, *R*9, *R*92 data of Richards and Reid at 9 kc, and 92 kc, respectively.

"concentration" of the gas, assumed all N_2O_4 , in moles per liter. This may be expressed in terms of P , the total pressure in atmospheres, and α by the relation $\alpha = (P - p_{N_2O_4}^0) / p_{N_2O_4}^0$, where $p_{N_2O_4}^0$ is the pressure which would be exerted by undissociated N_2O_4 , which Verhoek and Daniels set equal to gRT/Mv . Here again we have the use of the ideal gas laws for N_2O_4 , so that the resulting values for α will still be somewhat in error. However, assuming ideal conditions to apply, $C_{N_2O_4}^0 = p_{N_2O_4}^0 / RT = P / RT(1 + \alpha)$. This gives two equations for K , $K = 4\alpha^2 P / (1 - \alpha^2)$, and $K = a - bP / RT(1 + \alpha)$, where a and b are empirical constants found from the experimental curves. Equating the two values of K and solving for α ,

$$\alpha = \frac{bP/RT + [(bP/RT)^2 + 4(a + 4P)(a - bP/RT)]^{1/2}}{2(a + 4P)}.$$

The values of α thus calculated are always slightly lower than the corresponding values from previous calculations.

It should be noted that the points obtained by the authors, Grüneisen and Goens, and Richards and Reid, define a fairly smooth curve which crosses the experimental curve for u_0 , deviations being negative at atmospheric pressure and becoming positive below 260 mm. Some of Kistiakowsky and Richards' points come fairly close to this experimental curve, but others as well as most of the early values lie above it. Exactly the same type of divergence between theory and experiment is seen in Richards and Reid's paper, Table V, where at constant pressure negative deviations of experiment from theory are found at 1° , and positive deviations at 30° . This type of behavior might be expected of an equilibrium mixture of two gases, one of which (N_2O_4) deviates much more from the ideal gas laws than the other.

This brings us to the paper of Richards and Reid. Are these authors really justified in neglecting absorption, deviation from the gas laws, and time lag? Are their values for the velocity constant really significant? Their arguments are complicated and not at all clear. Furthermore the confusion is increased by a number of errors throughout the paper. The algebraic mistake in their final equation has already been noted. In

addition Tables III and IV giving the experimental values of the velocity of sound seem to be somewhat confused. All of the velocities are said to be "fully corrected," yet in the last three lines of Table III and all of Table IV it is not possible to obtain the sixth column ($V_w - V_0$) by subtracting the third column (V_0) from the fifth column (V_w). If the sixth column be assumed correct (and if it is incorrect their whole argument falls) then a number of the values of V_0 have not been corrected. It also seems that values of $V_{451} - V_{94}$ have been labeled ($V_w - V_0$) and so used in the calculation whereas it is more logical to use values of ($V_{451} - V_0$) for the dispersion. The heat of dissociation at constant pressure was also used instead of that at constant volume.

Let us examine their arguments in order. To show that θ is negligible they first compare rate constants calculated from Eqs. (8) and (9). It is not clear just how Eq. (8) is used in this calculation, since this equation includes the effect of absorption as well as time lag. The magnitude of the former is entirely unknown and no mention is made of any assumption concerning it. From their calculations they conclude that if the constant k_1 calculated from experimental dispersions by (9) does not vary with frequency at frequencies greater than or equal to its own order of magnitude, the time lag can be completely neglected. They state, rather arbitrarily, that any dispersion as large as 1 m/sec. may be attributed at least in part to the dissociation. In order to establish further that θ may be neglected, they state the necessity of obtaining concordant values of k_1 at low frequency (and dispersion) and at higher frequency (and dispersion). The dispersion at the higher frequency must be "significantly greater than the maximum which can be produced by heat capacity change." What is this maximum? The maximum for CO_2 is about 9 m/sec. while the greatest dispersion observed by Richards and Reid for N_2O_4 was 5 m/sec. Furthermore a dispersion as great as 1 m/sec. is observed at 92 kc only at low temperatures (1°). The conclusion would seem to be that where absorption can be neglected, θ cannot be and *vice versa*. Richards and Reid next attempt to show that even small dispersions can be interpreted as wholly due to dissociation. Their argument is here particularly complicated and unconvincing,

but finally reduces to the agreement of values of k_1 at high and low frequency.

The apparatus used does not differ very greatly from that used by Kistiakowsky and Richards. An important exception is the use of 9 and 92 kc magnetostriction oscillators and dual reflectors in the same tube. This eliminates the difficulty of comparing different samples which accompanies the older method. At higher frequencies (94 and 451 kc) however separate tubes were used, and these were made still smaller. This brings us to the highly uncertain "tube correction." This was determined by measuring the difference for various gases between the 9 and 92 kc magnetostriction oscillators in 1 inch tubes and the 451 and 94 kc oscillators in 1 cm tubes. There is some question as to how the corrections of 0.4 and 0.8 m/sec. for the different tubes were calculated, and as to the justification of the assumption that no correction need be applied to the 92 kc oscillator in the 1 inch tube, and that -0.2 m/sec. is applied to the 451 kc oscillator in the 1 cm tube. The former is somewhat explained by the measured value of the velocity of sound in argon at 30° and 760 mm, 324.0 m/sec. "according well" with the value "324.2 calculated from data in *International Critical Tables*." The difference, however, is of the order of magnitude of the tube corrections (and of some of the dispersions observed). It should also be noted that in NO_2 the value of V_{94} in the 1 cm tube is about 0.6 m/sec. less than that of V_{92} in the 1 inch tube even after the corrections have been applied. Besides this there is the question, raised previously, of the increased tube correction in the dispersion region. This correction seems especially important for the calculation of the rate constants at 30° at 92 and 451 kc, for it is upon their equality that the whole argument depends. Different corrections at the two frequencies would throw the constants apart. The same applies to the correction for absorption which would increase as the absorption maximum is approached. A very rough calculation shows that the absorption maximum comes somewhere near 700 kc. Furthermore if the measured dispersion at 92 kc (0.2 m/sec.) is only 0.1 m/sec. too high (and all the velocities are accurate only to ± 0.1 m/sec. at best) the rate constant will be increased by nearly 50 percent.

The final argument for neglecting all the deviations from the simple theory is a comparison of observed velocities with those "calculated from (8) when absorption and time lag are negligible" and $\omega = 0$. This means the simple Einstein equations must have been used, although this is not pointed out. How good is the agreement? At higher pressures than 260 mm it is "unsatisfactory" and no data are given. At 260 mm and 30° , the only temperature for which data at 451 kc are available, the observed velocity of sound is about 2 m/sec. greater than the theoretical. At 1°C where dissociation is much less the observed velocity is about 1.1 m/sec. less than the theoretical. This latter value should be particularly noted as later Richards and Reid state that at 1°C , V_0 calculated from (9) agrees with the observed velocity at low frequencies within 0.1 m/sec. We have found (9) to be in error, but since this equation does not give directly a value of V_0 , they may have used some intermediate equation, making a direct check on their statement difficult. However the values calculated from (8) in Table V seem to be free from error (cf. the value at 25° , 194.4, with that of u_0 in Fig. 5 of the present paper). In making the calculations Richards and Reid used interpolated experimental data of Verhoek and Daniels for the highest temperatures, but the figure at 1°C involves a long extrapolation of the dissociation constant and the use of the ideal gas laws. Richards and Reid consider the agreement between theory and experiment— $+2$ to -1.1 m/sec.—"sufficiently good" to base conclusions on dispersions of 0.2 to 1.8 m/sec. In view of the large discrepancies it seems rather questionable to use the measured rather than the calculated values of V_0 in Einstein's equations, or as a matter of fact to use these equations at all.

If Kneser's equations are solved for β^{-1} we obtain

$$\beta^{-1} = (2\pi\nu C_a/C)[(V_\infty^2 - V_v^2)/(V_v^2 - V_0^2)]^{\frac{1}{2}}.$$

Since C_a is wholly unknown it is not possible to carry out this calculation accurately. Making a rough guess at C_a and using Richards and Reid's dispersion data, β comes out about 5×10^{-5} at 92 and at 451 kc (Kneser found 1×10^{-5} for CO_2). It seems therefore that an intelligible re-

sult might be obtained by treating the dispersion as wholly due to time lag.

Another point which may be raised is the disagreement between the original results of Kistiakowsky and Richards over practically the same frequency range and the results of Richards and Reid. In the former no definite frequency trend in the region 10–80 kc was observed. At about 260 mm the velocity at 10 kc was nearly 2 m/sec. greater than that at 80 kc and that at 40 kc lay in between. Similar divergences were noted at other pressures. There is little difference apparent in the technique of the two series of measurements, but in the new series the tube correction of 0.4 m/sec. is applied. Application of this correction to the old results would not establish a definite frequency trend. It is difficult to see why the new

measurements are so much better than the old, and Richards and Reid offer no explanation.

To sum up it seems that the interpretation of the measurements of the velocity of sound is not nearly as easy as at one time supposed. It seems hazardous to neglect any of the three disturbing factors—absorption, deviation from the ideal gas laws, and time lag in equilibrium between the degrees of freedom. Not only does it seem that the time lag should not be neglected but it also seems possible that it can account for all the results obtained so far by Kistiakowsky and Richards, Richards and Reid and the present author: all the velocity increases being anomalous dispersion due to the time lag and the high absorption that accompany the dispersion.