lead chloride is given by 4.947 − 0.00164 (t − 500), that of zinc chloride by 2.424 − 0.00046 (t − 500).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

AN ATTEMPT TO MEASURE THE VELOCITY OF DISSOCIATION OF NITROGEN TETROXIDE BY THE METHOD OF SOUND WAVES

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For some years it has been apparent that sound waves offer an opportunity to investigate the velocity of dissociation of rapidly dissociating gases. The argument was at first[1] purely qualitative, it being supposed that when the compressions and rarefactions in the sound waves succeeded each other with sufficient rapidity the dissociating gas would no longer be able to attain equilibrium. An increased velocity of sound with increasing frequency was therefore to be expected when a certain critical region of frequency had been reached. Einstein gave this conception greater precision in a well-known paper[2] relating the velocity constant of the reaction to the increase in velocity of sound with increasing frequency. Since the velocity constants of rapid reactions are of the utmost importance for the kinetic interpretation of reaction velocities, Einstein's theory was soon tested, first by Selle[3] and later by Grüneisen and Goens.[4] Nitrogen tetroxide, which dissociates considerably in a convenient temperature range, was the object of study of both of these investigations. The work of Grüneisen and Goens was of an extremely scholarly character, the velocity of sound being measured by the resonance tube method to frequencies of 15,600 cycles per second from 10 to 35° and from 760 to 265 mm. pressure. The velocity being independent of frequency to a few tenths of a per cent. over this range, these authors estimated that the velocity constant of the reaction must exceed 10,000, a conclusion with which this communication is in entire accord. More recently Olson and Teeter[5] in a brief note, report an increase of velocity at 50 kilocycles. Their results have not been confirmed by this investigation. Their published data are limited, and no critique of their conclusion can be attempted here. It seems possible that they have underestimated their systematic error, a point of unusual importance in the calculation of the velocity constant.

[1] Keutel, "Inaug. Disser.," Berlin, 1910.

[2] A. Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

[3] H. Selle, *Z. physik. Chem.*, **104**, 1 (1923).

[4] E. Grüneisen and E. Goens, *Ann. Physik.*, **72**, 193 (1923).

[5] A. R. Olson and C. E. Teeter, *Nature*, **125**, 150 (1930).

The discovery by Pierce[6] of the magneto-striction oscillator made easily available a far wider range of conditions, and suggested a reëxamination of nitrogen tetroxide. The negative result obtained from this study was not to be expected, and leads to certain theoretical conclusions.

Experimental Procedure

The apparatus employed was necessarily rather complex, and in the interests of space conservation no attempt will be made to describe it completely. It naturally falls into two main divisions, the electrical circuit, which generated the sound waves, detected their nodal points in the gas-filled tube, and measured their frequencies, and the glass apparatus which generated and purified nitrogen tetroxide, maintained its temperature, and measured its pressure during the progress of the experiment. It will be convenient to describe the two separately.

The magneto-striction oscillators employed followed closely the design of Pierce[6] and drove one of three one-inch nichrome rods. The frequencies of these were approximately 10, 41.5 and 80 k. c. respectively. At the termination of an experiment with a given frequency the rod which had been used was heterodyned against another rod and the resulting beat note analyzed on a bridge closely resembling that recommended by Pierce. The variable inductance and capacity in this bridge were Leeds and Northrup calibrated precision instruments and gave the frequency of the heterodyne note to better than twenty cycles. Appropriate corrections for the temperature of the rods were, of course, applied. The rods were finally compared, by means of an intermediate heterodyne nichrome rod of about 45 k. c., with a calibrated quartz crystal of 47.45 k. c. (temperature coefficient 0.47 cycle per degree centigrade). The frequencies of the nichrome rods used during the experiments were therefore known with an estimated error of 20 cycles, or, respectively, 0.2, 0.05 and 0.03% for the 10, 41.5 and 80 k. c. rods. The greatest error in this determination was in the calibration of the capacities and inductance of the frequency bridge, and was largely eliminated by making many readings with a wide range of capacities and inductance and averaging. A characteristic series of such measurements follows.

TABLE I

TYPICAL FREQUENCY DIFFERENCES AS READ FROM CAPACITY BRIDGE

Difference in frequency in cycles per second between fourth harmonic of 10 k. c. rod (at 25°) and 41.5 k. c. rod at 20.7°.

1987, 2021, 1978, 1987, 1984, 1953, Av. = 1985
Corr. to 25° = 1969

Of the glass apparatus only one piece, the observation tube, merits a detailed description. Since nitrogen tetroxide is a highly corrosive gas it was necessary that this tube be constructed as far as possible of materials exceedingly resistant to oxidizing action. Glass and nichrome satisfy this condition and, as a glance at Fig. 1 will show, no other materials were found necessary with the exception of a single small and well-protected cement joint. In Fig. 1, A represents the one-inch nichrome rod balanced on a

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[6] G. W. Pierce, *Proc. Am. Acad. Sci.*. **63**, 1 (1928). Mr. W. J. Cahill, whose work under Professor Pierce demonstrated the precision of measurements made with 2.54-cm. magnetostriction rods in 2.54-cm. tubes, acted as advisor in the very early stages of this investigation.

small asbestos support B, and fitting as tightly as possible without cramping its oscillations the long straight uniform glass tube which constituted the observation chamber. The driving coils for this rod were slipped over the outside of the tube, and were interchangeable with a magnetizing coil which made it possible to polarize the rod and change its position without opening the sealed tube at C. At the conclusion of any experiment the tube was blown open at C, another rod substituted for A, and the tube resealed, thus making a removable joint with possible leakage, oxidizable grease, etc., entirely unnecessary. The gas space through which sound waves were transmitted is represented by the region D. E is a piston of glass tubing which fitted snugly the main tube, and had a polished reflecting face carefully adjusted normal to the walls of the latter. Scrupulous plane-parallelism between this reflecting surface and the end of the nichrome rod is, of course, necessary to secure accurate measurements of the half-wave length of sound. The piston was sealed at F to two lengths of glass rod which extended parallel through the distance of motion of the piston, and terminated in a nichrome nut G which was sealed to them by glass-covered tungsten wires. A loop of glass-supported nichrome rod H shaped to receive the parallel glass rods served to prevent irregularities in the orientation of the polished piston face E by providing a rigid guide for the motion of the parallel glass rods. Motion of the piston was obtained by means of a nichrome screw which passed through G, and out of the tube through the asbestos–graphite packing I. A knurled handle, J, was rigidly attached to the screw. The side-tube K, which served to introduce the gas to be observed, is shown sealed as during the progress of an experiment. At L was a quartz spiral manometer which was attached to the apparatus throughout the experiments, and served to measure the pressures of gas in the tube to ±1 mm.

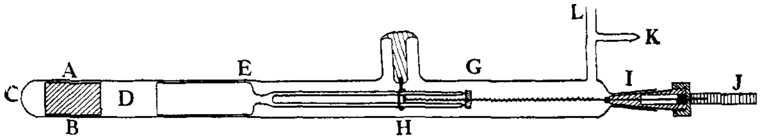

Fig. 1.—Glass chamber for measuring the velocity of sound in a corrosive gas.

Nitrogen tetroxide was prepared in the usual manner by heating lead nitrate in a stream of oxygen. The gas was repeatedly dried by passing through phosphoric anhydride tubes, and finally subjected to a vacuum distillation, being condensed at the temperature of solid carbon dioxide to rid it of any adsorbed or included permanent gases. It was then allowed to evaporate into the already evacuated apparatus and the purification, pumping, etc., systems were sealed off, leaving the apparatus essentially as illustrated in Fig. 1.

During an experiment the apparatus, with the exception of the quartz manometer, was covered with an air thermostat which maintained 25.0 ± 0.1°. The position of the piston was ascertained through a plate glass window by a cathetometer mounted scrupulously parallel to the axis of the piston. This gave complete independence of irregularities in the construction of the screw, and defined the position of the piston to 0.1 mm. The pressure and temperature of the gas were read at the start and finish of the experiments, and at such intermediate points as seemed advisable. Experiments with air were made with dry, carbon dioxide-free air. Experiments with nitrogen tetroxide were begun at atmospheric pressure, and the pressure progressively diminished by condensing out portions of the gas in small tubes at K (Fig. 1), which were then sealed off. This served the further useful purpose of indicating the presence of nitric oxide by the bluish color of the condensate, and of permanent gases by the slowness of the process of condensation. If either was found present in appreciable quantity the experiment was discontinued and the result discarded.

The half wave length of sound was determined as the difference between the position of the piston at two resonance points. The resonance points were determined by a milliammeter in the plate circuit of the amplifier of the oscillating circuit, the reflection of sound from the piston at the resonance point greatly increasing the plate current. By suitable adjustment almost any desired magnitude of deflection could be obtained. The resonance points were uniformly sharp and evenly spaced over the entire range of the piston stroke (some 200 mm.) at pressures down to 300 mm. At 140 mm. the enormous increase of absorption made it impossible to examine more than some twenty or thirty half wave lengths. Since the regularity of spacing of the resonance peaks is a matter of some importance for the interpretation of the results, one series of typical measurements on nitrogen tetroxide is given in Table II.

TABLE II

CATHETOMETER READINGS AND HALF WAVE LENGTH VALUES IN N_2O_4

41,633 cycles per second, 277 mm., and 25.0°. Cathetometer readings made every 10 half wave lengths.

Mm.	670.1	646.6	623.3	599.9	576.5	553.1	529.6	506.1	482.6
Difference	23.5	23.3	23.4	23.4	23.4	23.5	23.5	23.5	

After condensing a portion of gas and re-evaporating, the last reading, 80 half wave lengths from first, was 482.7 mm. Velocity of sound $= 4.163 \times 10^4 (670.1 - 482.7) (2/80) = 195.2$ meters per sec.

Experimental Results

The results of all measurements may be summarized in a series of almost self-explanatory tables.

TABLE III

VELOCITY OF SOUND IN AIR AT 25.0° AND VARIOUS FREQUENCIES AND PRESSURES

Frequency	Pressure	Number of nodes	Velocity
9,916	730	8	345.6
41,633	758	40	346.5
41,633	152	40	346.5
80,350	760	110	345.5
80,350	147	20	346.1

In Table III, as in all subsequent tables, frequency is quoted in cycles per second, pressure in mm. of mercury, and velocity in meters per second. The number of nodes, or half-wave lengths, measured is also quoted, since this plays an obviously important part in estimating the relative accuracy of each particular measurement. The average value obtained from these figures is 346.0 meters per second and when reduced[7] to 0° becomes 331.2 meters per second, a satisfactory agreement with the most probable absolute value of 331.6 meters per second.

Tables IV, V and VI give similar data for nitrogen tetroxide at different frequencies, and, in addition, an arbitrary number which designates the sample of gas which filled the tube in each particular determination. The temperature coefficient, used for covering temperature variations of 0.1°,

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[7] The method of reduction and the next to most recent velocity of sound in dry air may be found in G. W. Pierce, *Proc. Am. Acad. Arts Sci.*, 60, 281 (1925).

was taken from Grüneisen and Goens as 1.0 meter increase in velocity per degree centigrade at all pressures.

TABLE IV

VELOCITY OF SOUND IN N_2O_4 AT 9916 CYCLES PER SECOND, 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
1	776	21	183.0
2	761	18	183.8
2	364	17	192.4
2	273	17	197.0
3	269	19	196.8

TABLE V

VELOCITY OF SOUND IN N_2O_4 AT 41,633 CYCLES PER SECOND, 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
4	763	87	183.6
5	762	89	183.7
5	762	89	183.7
6	751	80	183.5
6	491	80	188.8
5	277	80	195.2
4	274	72	195.5
6	272	79	195.8
4	146	20	203.6
6	146	22	202.3

TABLE VI

VELOCITY OF SOUND IN N_2O_5 AT 80,350 CYCLES PER SECOND, 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
7	765	110	183.6
8	764	150	182.8
7	759	140	184.2
9	759	55	184.0
10	754	150	184.1
11	752	100	184.0
11	752	160	183.9
7	487	110	189.4
7	485	109	189.4
12	333	128	193.5
7	304	193	195.3

The results given in Tables IV to VI have been represented as points in Fig. 2. The solid curve drawn through them defines the velocity of sound at all pressures considered to better than 0.5%, since the largest single deviation does not exceed this value. The figure demonstrates conclusively that, within this limit, there is no systematic change of velocity with frequency between 10 and 80 k. c., since the distribution of points about the solid curve appears perfectly random. It also should be noted that points measured by Grüneisen and Goens show satisfactory agreement with the solid curve, especially since the pressure determinations for these points with the exception of the 760 mm. value depend on the vapor pressure data of nitrogen tetroxide[8] and hence may be considerably in error.

Several details call for brief comment. In the first place, it was most unfortunate that measurements could not be obtained at 140 mm. with the 80 k. c. oscillator, since this would have doubled the significance of the negative result reported. This was, of course, repeatedly attempted but, because of the difficulty of supporting adequately the very short rod for

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[8] F. E. C. Scheffer and J. P. Treub, *Z. physik. Chem.*, **81**, 308 (1912).

optimum oscillation conditions, because at such low pressures exceedingly little energy enters the gas from the vibrating metal, and because absorption was most pronounced, every attempt to measure velocities at this frequency below 300 mm. met with failure.

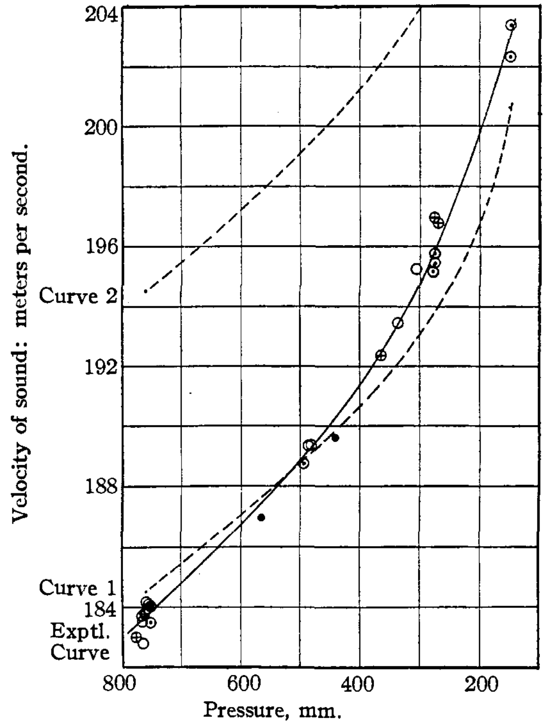

Fig. 2.—The velocity of sound in nitrogen tetroxide at 25° and various pressures: ⊕ represents 10 k. c. observations; ⊙, 41.5 k. c. observations; ○, 80 k. c. observations, and ● the summarized observations of Grüneisen and Goens; Curve 1 represents the theoretical velocity according to Einstein for $\omega = 0$, Curve 2 for $\omega = \infty$.

Again, although the accuracy of any determination could have been increased by measuring a larger number of half-wave lengths, it was found unnecessary to do so. An examination of a relatively small number of nodes was sufficient to fix the velocity of sound in any particular determination to about 0.05% and errors in other parts of the procedure produced greater deviations than this. Each determination was carried out by running the piston along the tube from a position as near as possible to the vibrating rod to the end of its stroke, the spacing and number of the peaks being noted. A considerable quantity of the gas was then condensed out at K

(Fig. 1) and reëvaporated, and the peak nearest the end stroke of the piston redetermined. It was always found to check the previous value within 0.2 mm., which was the accuracy of determining a single resonance peak.

The greatest source of error was evidently small, almost undetectable traces of permament gases and nitric oxide, since variations of as much as 0.5% were observed between velocities measured with different fillings of the apparatus. No method of purification or evacuation was found completely to obviate these.

Theoretical Discussion

The Einstein theory permits the calculation of the velocity of sound in a dissociating gas at zero frequency, at infinite frequency and at intermediate frequency provided the absorption coefficient is sufficiently small. For zero frequency the expression is

$$V_{\omega=0} = \sqrt{\frac{P}{\rho}\left(1+\frac{A}{B}\right)} \qquad (1)$$

for infinite frequency

$$V_{\omega=\infty} = \sqrt{\frac{P}{\rho}\left(1+\frac{R}{\bar{c}_v}\right)} \qquad (2)$$

and for intermediate frequencies

$$V_{\text{intermed.}} = \sqrt{\frac{P}{\rho}\left(1+\frac{K^2AB+R\bar{c}_v\omega^2}{K^2B^2+\bar{c}_v^2\omega^2}\right)} \qquad (3)$$

where V represents the velocity of sound, ω the circular frequency, P the pressure, ρ the density, R the molecular gas constant, $\bar{c}_v$ the averaged specific heat at constant volume, K the velocity constant of dissociation, and A and B are abbreviation constants defined by

$$A = \left(2\frac{D}{T}-\bar{c}_v\right)\frac{n_1}{n_1+n_2}+R\left(1-4\frac{n_1}{n_2}\right)$$

$$B = \frac{D^2}{RT^2}\frac{n_1}{n_1+n_2}+\bar{c}_v\left(1-4\frac{n_1}{n_2}\right)$$

D being the heat of dissociation, T the temperature and n_1, n_2 the molecular numbers of nitrogen tetroxide and nitrogen dioxide, respectively.

For this calculation, therefore, a knowledge of the equilibrium constant of nitrogen tetroxide and its heat of dissociation, and of the specific heats of nitrogen dioxide and nitrogen tetroxide is necessary. The first two quantities were obtained from the work of Bodenstein,[9] the value of K being 0.1455 and of D 12,940 cal. at 25°. The specific heats of the gases have not been measured, and must be calculated on the basis of certain assumptions. It has therefore been assumed that c_v of nitrogen dioxide equals that of carbon dioxide, nitrous oxide, etc., namely, 6.8 cal., whereas that of nitrogen tetroxide is larger by 6/2 R calories, and hence becomes 12.75 cal. While no strong arguments for these values may be advanced,

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[9] M. Bodenstein, *Z. physik. Chem.*, 100, 68 (1922).

they are reasonable approximations, and even if considerably in error the validity of the calculation would be little affected.

Using these values the pressure–velocity curves indicated by dotted lines 1 and 2 in Fig. 2 are obtained for Equations 1 and 2, respectively. It will be noted that dotted curve 2, which indicates the maximum effect possible, lies far above the observed values. Dotted curve 1 agrees better with the experiments here reported, but does not coincide within the limit of experimental error. This is not surprising, since the calculated velocity is highly sensitive to the values chosen for the dissociation data, as is strikingly illustrated by the fact that Grüneisen and Goens, using less accurate values for these quantities, obtain a calculated value for the velocity at 760 mm. which is almost 2% higher than that given on dotted curve 1.

Grüneisen and Goens, using Equation 3, and taking into account their probable experimental error, have estimated that at 25° the reaction velocity constant must be larger than 10^4. On the basis of the present communication this lower limit must be raised. It may safely be assumed that the probable error of the sound velocity measurements here reported does not exceed the maximum deviation, 0.5%, and hence the minimum velocity constants compatible with the 41.5 k. c. and 80 k. c. measurements are 2.6×10^4 and 5×10^4, respectively, since at these two frequencies agreement is obtained within the allowed error with determinations at lower frequencies.

It is of some interest to compare the lower limit of the velocity constant thus determined with the upper limit of the reaction velocity as deduced, on some assumption concerning the reaction mechanism, from the kinetic theory. It is most plausible to assume that the dissociation process belongs to the so-called "quasi-unimolecular" reaction type,[10] that, in other words, the activation of a nitrogen tetroxide molecule on collision is followed either by its decomposition or by its deactivation on another collision. Since, for the present purpose, only the upper limit of the reaction velocity is of interest, only the case need be considered where the mean life of the activated nitrogen tetroxide molecules is short compared with the time between inelastic collisions, and hence the rate of decomposition is essentially equal to the rate of activation. It will further be expedient to assign to the heat of activation its lowest possible value, the heat of reaction. Unfortunately, the cross sections of the nitrogen dioxide and nitrogen tetroxide molecules, which must be used to calculate the total number of kinetic collisions Z, are unknown and experimentally inaccessible. It is, therefore, necessary to assume cross sections for these molecules, and the values of $d_{\mathrm{NO}_2} = d_{\mathrm{CO}_2} = 4.2 \times 10^{-8}$ cm. and $d_{\mathrm{N}_2\mathrm{O}_4} = \sqrt[3]{2d^3_{\mathrm{NO}_2}} = 5.3 \times 10^{-8}$ have been chosen as being least likely to be in error.

Granting these assumptions which, although not wholly defensible, can

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[10] Lindemann, *Trans. Faraday Soc.*, 17, 598 (1922).

hardly yield too low a value for the maximum dissociation velocity which is kinetically possible, the computation is easily made. The data employed may be either the measurements made at 150 mm. and 41.5 k. c. or 250 mm. and 80 k. c. since the result obtained will be approximately the same for the two. It follows from ordinary kinetic considerations that, if only two degrees of freedom of the molecule participate, the velocity of decomposition at 150 mm. and 25° will be

$$-\frac{dn_1}{dt} = Ze^{-D/RT} = 2.6 \times 10^{27} \times 2.7 \times 10^{-10} = 7 \times 10^{17} \text{ molecules per cc. per sec.}$$

t referring, of course, to time, and the other symbols having the significance defined above. From the minimum value of the velocity constant K determined by experiment at 41.5 k. c. and 150 mm. (2.6×10^4), it is evident that the rate of decomposition must be greater than $Kn_1 = 5.5 \times 10^{22}$ molecules per cc. per second, a number far greater than that calculated above. It is necessary, therefore, to assume, as has been done by Polanyi, Hinshelwood, and others for several reactions, that more than two degrees of freedom participate in the activation process. Since the total number of internal degrees of freedom of the nitrogen tetroxide molecule is twelve, the maximum possible rate of activation and reaction is given[11] approximately by

$$-\frac{dn_1}{dt} = Ze^{-D/RT}\frac{(D/RT)^{11}}{11!} = 1.1 \times 10^{25} \text{ moles per cc. per sec.}$$

this value is not greatly in excess of the experimental value, which indicates that the activation of nitrogen tetroxide must involve a large number of degrees of freedom, and hence be very similar in character to the decomposition of nitrogen pentoxide.

A comparison may also be made between the rate of association of nitrogen dioxide molecules—which, in the case under consideration, must be larger than 1.1×10^{23} molecules per cc. per sec.—and the number of triple collisions. The second quantity is easily estimated, using the approximation that the number of triple collisions is related to the number of all collisions as the molecular diameter to the mean free path, and may thus be assigned the value 2×10^{24}.

As a result of this calculation it may be stated with some confidence that the maximum theoretical velocity of decomposition and the number of triple collisions have values close to that calculated from the minimum velocity constant defined experimentally. The discrepancy between the two is sufficiently small to suggest at first sight the desirability of performing further measurements at higher frequencies and lower pressures in an attempt to discover whether or not the kinetic theory of reaction velocity may be applied to the process with ordinary molecular dimensions, or

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[11] K. F. Herzfeld "Kinetische Theorie der Wärme" Braunschweig, 1925.

whether larger effective cross sections must be postulated. More critically examined, such an extension of these measurements appears much less promising, owing to the greatly increased absorption of sound in nitrogen tetroxide at low pressures.

A few rough determinations of the absorption of sound were made in the course of the experimental work described above by noting the magnitude of change in plate current at succeeding nodal points. It cannot, of course, be claimed that this is a method of precision, but since no data of the kind have been published for nitrogen tetroxide, and since an assumption concerning absorption appears in the theory of Einstein, a brief summary of these observations will be set down here. Figure 3 represents a typical series of measurements, in this case those corresponding to the determination reported in detail in Table II. A line drawn through these points has a clearly exponential form, which may be expressed approximately by the empirical equation

$$I = I_0 e^{-hN}$$

where I and I_0 represent intensities, h an absorption coefficient and N the number of half wave lengths between I_0 and I. The values for h best fitting the curves at various pressures are given in Table VII.

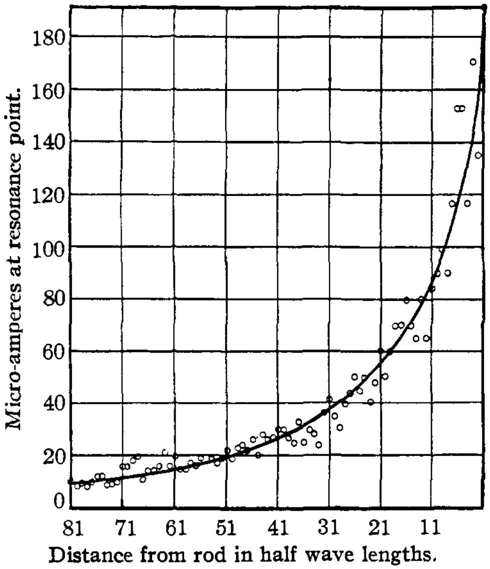

Fig. 3.—Absorption of sound in nitrogen tetroxide as illustrated by diminution in plate current at resonance points with increasing distance of reflector from vibrating rod. 41.5 k. c., 25.0°, 277 mm.

TABLE VII

ABSORPTION COEFFICIENTS IN NITROGEN TETROXIDE AT VARIOUS PRESSURES AND FREQUENCIES

Mm. pressure	760	400	150
10 k. c.	...	0.06	0.24
41.5 k. c.	0.02	.06	...
80 k. c.	.03	.05	0.20

It appears, therefore, that in nitrogen tetroxide the absorption of sound increases extremely rapidly below 400 mm. pressure, although, as is to be expected if the dissociation is far more rapid than the frequency, it is not noticeably dependent on frequency. Similar measurements with air showed no significant change in *h* with pressure. The bearing of Table VII on further experiment is immediately apparent. Not only does the increased absorption at lower pressures very greatly diminish the accuracy of experiments by decreasing the number of half wave lengths which may be examined, but below 140 mm. the absorption becomes so great that it is likely that Einstein's reasoning would no longer apply. At increased frequencies it seems highly probable that absorption would set in at higher pressures, since Pierce[6] observed at 200 k. c. in carbon dioxide, a similar but non-dissociating gas, an absorption about a hundred times as great as that in air.

Measurements of this character are nevertheless being undertaken by one of us. It seems further advisable to investigate other dissociating gases and vapors in less accessible regions of temperature, for it is by no means certain that the behavior of nitrogen tetroxide is typical of all such dissociation processes.

Summary

1. The velocity of sound at 25° in nitrogen tetroxide has been investigated from 10 to 80 k. c., and from 760 to 140 mm., and has been found to be independent of frequency.

2. It has been calculated that the minimum velocity constant defined by these experiments is not far from the maximum possible velocity constant deduced from the kinetic theory of gases.

3. The bearing of this conclusion on the kinetic theory of reaction velocity is discussed.

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PARAMAGNETISM INDEPENDENT OF THE TEMPERATURE AND THE EXISTENCE OF ELECTRONIC ISOMERS IN POLYATOMIC IONS

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It has been almost universally believed that the phenomenon of paramagnetism owes its origin to the motion of the unbalanced electrons in the stationary states of molecules. Employing the model of such molecular magnets Langevin[1] was very successful in accounting for the magnetic behavior of many substances, not only in the gaseous state where interaction between the molecules is slight, but also in the crystalline state and in solution. He was led to Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. Many substances, however, display a somewhat more com-

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[1] Langevin, *Ann. chim. phys.*, [8] 5, 70 (1905).