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Further Observations Concerning the Propagation of Sound in Nitrogen Tetroxide

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The absorption of sound in nitrogen tetroxide is discussed, and it is pointed out that absorption measurements should be capable of distinguishing whether a given absorptive region is due to failure of the dissociation reaction or of the heat capacity to follow the adiabatic cycle of the sound wave. Appropriate expressions for the absorption are derived from Einstein's theory, and are briefly discussed. An experimental method of determining the absorption maximum is described in which the temperature is varied at constant pressure and frequency. Under these conditions the acoustical variables are maintained very nearly constant. An attempt to detect the absorption maximum at 450.1 kc and 260 mm in nitrogen tetroxide was unsuccessful because of the inaccuracy of the absorption measurements. It is concluded that dispersion measurements provide at present an easier and more accurate method of investigating the acoustical properties of rapidly dissociating gases than measurements of the absorption coefficient. Occasion is taken to discuss the tube corrections applied to the previous dispersion measurements at greater length than was before considered necessary. Several corrections to the previous work are also appended.

INTRODUCTION

A RECENT communication from this laboratory[1] described measurements on the dispersion of sound in nitrogen tetroxide, and discussed in considerable detail an argument by which it was believed legitimate to interpret them as due to failure of the dissociation reaction to attain equilibrium in the sound wave. The chief purpose of this note is to extend the argument to acoustical absorption.

Our report has been followed by an article by Teeter[2] in which he devotes much space to unfavorable criticism of our work. We shall take this opportunity to answer such parts of Teeter's attack as appear to us to require discussion. The bulk of his criticism is, however, based on arguments which we consider that we have already adequately refuted, and it would serve no useful purpose to labor them further.

PART I. A DISCUSSION OF THE ABSORPTION OF SOUND IN DISSOCIATING GASES

The interpretation of absorption measurements in terms of dissociation rates

It has already been demonstrated[1] that suitable measurements of the dispersion of sound in a dissociating gas are capable of showing whether (a) the dissociation reaction, (b) the heat capacity, or (c) both the dissociation reaction and the heat capacity concomitantly are failing to attain equilibrium in the adiabatic cycle. This demonstration is not wholly free from objection, since it is based on a somewhat oversimplified picture of the conditions in the path of the sound-wave.[3] However, since it appears to represent the most satisfactory description of the phenomenon which is at present available, it is perhaps worth while to extend the treatment to absorption. In order to do this with as little complication as possible it is proposed to treat quantitatively only cases (a) and (b), leaving the somewhat more doubtful case (c) for later qualitative discussion. In developing the argument it will be convenient to review that previously given for cases (a) and (b) in connection with the dispersion.

Calling π and Δ the complex pressure and

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* At present Fellow of the John Simon Guggenheim Memorial Foundation.

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

[2] Teeter, J. Chem. Phys. 1, 251 (1933).

[3] The assignment of a single characteristic time to the rate of adjustment of the heat capacity of a gas in which several quantum states are excited is at present without theoretical justification. See Bourgin, Phys. Rev. 42, 721 (1933). It seems, nevertheless, to be a reasonable experimental expedient. See Richards and Reid, Nature 130, 739 (1932). A more completely deduced description of the concomittant failure of dissociation reaction and heat capacity may, for the present, be expected to yield results of substantially the same form as that given here and in the previous communication.

density variations of the sound wave, the theory of Einstein[4] gives for a dispersive gas

$$\frac{\pi}{\Delta}=\frac{P}{\rho}\left[1+\frac{A_0+ifA_\infty}{B_0+ifB_\infty}\right] \tag{1}$$

where P and ρ are the equilibrium pressure and density, respectively, and

$$f\equiv\omega/\zeta \tag{2}$$

if ω is the frequency of the sound wave in radians, and ζ is the characteristic frequency of the process which produces the dispersion. In the case of a unimolecular reaction $\zeta\equiv k_1$, the rate constant. For a lag in heat capacity ζ is proportional to the number and effectiveness of the collisions which excite an active state of the molecule.[5] The quantities $1+A_0/B_0$ and $1+A_\infty/B_\infty$ represent the ratio of the isothermal to the adiabatic compressibilities when f sensibly vanishes and when f becomes sensibly infinite, respectively. The subscripts 0 and ∞ will be used in this sense throughout.

Since, as will later become apparent, the absorption due to the process characterized by ζ becomes negligible at very low and at very high frequencies, the real part (r.p.) of π/Δ becomes equal to the square of the phase velocity V. Thus from (1) the result is obtained that

$$V_\infty{}^2/V_0{}^2=B_0(B_\infty+A_\infty)/B_\infty(B_0+A_0)=Q^2 \tag{3}$$

and the useful abbreviation Q, which is intimately connected both with dispersion and absorption, is defined. The relationship (3) is alone sufficient to determine whether (a) or (b) has produced a given dispersive region, since the maximum change in velocity will be quite different for the two unless the dissociation heat is small. In the case of nitrogen tetroxide at 25°C and 260 mm, for example, the degree of dissociation α is about 0.3, and

Case (*a*)

$$\begin{cases} A_0=\left(\dfrac{2D}{T}-\bar{C}_0\right)\dfrac{1-\alpha}{1+\alpha}+R\left(\dfrac{2-\alpha}{\alpha}\right)\cong 56.4\text{ cal.}\\ A_\infty=A_D=R\cong 2\text{ cal.}\\ B_0=\dfrac{D^2}{RT^2}\dfrac{1-\alpha}{1+\alpha}+\bar{C}_0\left(\dfrac{2-\alpha}{\alpha}\right)\cong 651\text{ cal.}\\ B_\infty=B_D=\bar{C}_0\cong 10\text{ cal.}\end{cases}$$

according to the result of Einstein. This is on the assumption that the heat capacity continues to follow the wave without lag, as in case (a). For case (a) then, $Q^2\equiv Q_D{}^2=1.105$. In case (b) A_0 and B_0 remain unchanged, but the heat capacity alone drops out at high frequencies. To describe this it is sufficiently definite to write $\bar{C}_0=\bar{C}+\bar{C}_\omega$ where $\bar{C}_0$ represents the average heat capacity of the $N_2O_4-NO_2$ mixture at equilibrium and at constant volume, and $\bar{C}$ and $\bar{C}_\omega$ are its frequency-independent and -dependent parts, respectively. $\bar{C}_0$ is probably about 10 calories·mole^{-1}, and the utmost change of the heat capacity in regions of frequency which are at present accessible may be expected to be a drop to half this value. Thus $\bar{C}$ will be taken as 5 calories·mole^{-1}, and A_∞ and B_∞ become

Case (*b*)

$$\begin{cases} A_0\cong 56.4\text{ cal.}\\ A_\infty=A_c=\left(\dfrac{2D}{T}-\bar{C}\right)\dfrac{1-\alpha}{1+\alpha}+R\left(\dfrac{2-\alpha}{\alpha}\right)\cong 59.1\text{ cal.}\\ B_0\cong 651\text{ cal.}\\ B_\infty=B_c=\dfrac{D^2}{RT^2}\dfrac{1-\alpha}{1+\alpha}+\bar{C}\left(\dfrac{2-\alpha}{\alpha}\right)\cong 623\text{ cal.}\end{cases}$$

and for case (b) $Q^2\equiv Q_c{}^2\cong 1.008$.

Thus it is seen that approximately ten times as much change in velocity results from case (a) as from case (b). A change of velocity greater than 0.4 percent, $((Q_c-1)\times 100)$, must, therefore, involve a partial failure of the dissociation reaction. It was an extension of this argument to case (c) by means of a simplified model for the heat capacity which made possible the calculation of rate constants from the measurements reported previously.[1]

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

[5] Kneser, Ann. d. Physik **11**, 761 (1931), introduced the rate constant which we employed in the previous work, and shall continue to use here. Because the notation of Einstein has been retained wherever possible Kneser's β has been replaced by θ, both meaning identically the average lifetime of the excited molecule. Thus $\zeta\theta\equiv 1$ in our notation. In Kneser's, $\zeta\beta\equiv 1$.

In order to evaluate the corresponding maxima of the absorption coefficient it will be necessary to examine the structure of the complex pressure and condensation variations, π and Δ. For these Einstein[4] has written

$$\pi = \pi_0 e^{i\varphi} e^{i\omega(t-ax)} \qquad (4)$$

$$\Delta = \Delta_0 e^{i\omega(t-ax)} \qquad (5)$$

where the amplitudes are $\pi_0 e^{i\varphi}$ (complex) and Δ_0 (real), t is the time, x the distance in the direction of propagation, and a a complex quantity involving both velocity and absorption. It is apparent that the imaginary part of a becomes the only real part of the two exponents, and hence is a damping coefficient. If the symbol β denotes the absorption coefficient for the amplitude expressed as a reciprocal length, then a becomes

$$a = (1/V - i\beta/\omega) \qquad (6)$$

where $2\pi V = \omega\lambda$ and $i = (-1)^{\frac{1}{2}}$. The familiar relationships, in which u denotes displacement in the direction of the wave normal,

$$\partial\pi/\partial x = -\rho\partial^2 u/\partial t^2 \quad \text{and} \quad \Delta = -\rho\partial u/\partial x \qquad (7)$$

yield a wave equation of the usual form in which π/Δ is the square of a complex plane wave velocity, and has the value

$$\pi/\Delta = 1/a^2 = [V/(1 - i\beta V/\omega)]^2. \qquad (8)$$

Eq. (1) is that from which the velocity and absorption of sound are to be determined in terms of the physical properties of the gas. It may readily be seen that the real part of π/Δ is more easy to obtain, from (1), than the real part of a (the real part of $(\Delta/\pi)^{\frac{1}{2}}$). Thus the convenient solution for the velocity is

$$\text{r.p.}\ \frac{\pi}{\Delta} = V^2\left\{\frac{1-\beta^2V^2/\omega^2}{(1+\beta^2V^2/\omega^2)^2}\right\}. \qquad (9)$$

Similarly the imaginary part (i.p.) of Δ/π gives conveniently the absorption coefficient, as is apparent from (1), (6) and (8). Thus

$$\text{i.p.}\ \Delta/\pi = -i2\beta/\omega V. \qquad (10)$$

Up to this point nothing has been added to the argument of Einstein.

If, now, the absorption coefficient for the intensity expressed as a reciprocal number of wave-lengths is introduced according to the usual definition

$$I_x = I_0 e^{-2\beta x} = I_0 e^{-hx/\lambda}$$

(10) becomes

$$h = -(2\pi V^2/i)(\text{i.p.}\ \Delta/\pi). \qquad (11)$$

The imaginary part of the reciprocal of (1) gives

$$h = 2\pi V^2 \frac{\rho}{P}\left\{\frac{B_0(A_\infty + B_\infty)f - B_\infty(A_0 + B_0)f}{(A_\infty + B_\infty)^2 f^2 + (A_0 + B_0)^2}\right\}. \qquad (12)$$

For the sake of convenience the rôle of absorption in the real part of Δ/π will be neglected, and it will be taken that

$$\text{r.p.}\ \Delta/\pi \cong 1/V^2$$

and, consequently, from the reciprocal of (1), that

$$V^2 \cong \frac{P}{\rho}\left\{\frac{(A_\infty + B_\infty)^2 f^2 + (A_0 + B_0)^2}{B_0(A_0 + B_0) + B_\infty(A_\infty + B_\infty)f^2}\right\}. \qquad (13)$$

The approximation so introduced amounts to neglecting terms in h^2, or, practically, to setting

$$(\text{r.p.}\ \pi/\Delta)(\text{r.p.}\ \Delta/\pi) \cong 1, \quad 2Q^2 \cong Q^4 + 1$$

which, in the present condition of interferometric absorption measurements, will be without influence.[6] Substituting (13) into (12) gives finally

$$h \cong 2\pi y\{(Q^2 - 1)/(1 + Q^2 y^2)\} \qquad (14)$$

where y, which has been suggestively called the "relative frequency" by Luck,[6] is defined as

$$y \equiv fB_\infty/B_0 \equiv \omega B_\infty/\zeta B_0. \qquad (14a)$$

Herzfeld and Rice,[7] Bourgin,[8] Henry[9] and

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[6] Luck, Phys. Rev. **40**, 440 (1932) has carried through the solution for a dissociating gas without a heat capacity lag (case (a)) without making this approximation. Our (14) and (20) for this case are a slightly less accurate version of his

$$h_D = 4\pi\left[1 + \frac{(1 + Q_D^2 y_D^2)^2}{(Q_D^2 - 1)^2 y_D^2}\right]^{\frac{1}{2}} - \frac{1 + Q_D^2 y_D^2}{(Q_D^2 - 1) y_D^2}.$$

The approximation does not enter (15), and (16) has been given in both the approximate and the exact forms.

[7] Herzfeld and Rice, Phys. Rev. **31**, 691 (1928).

[8] Bourgin, Phil. Mag. (vii) **7**, 821 (1929).

[9] Henry, Proc. Camb. Phil. Soc. **28**, 249 (1932).

Kneser[10] have given similar equations for nondissociating gases with variable heat capacity. The exposition used above was clearly implied by Einstein,[4] and has been here repeated only in order to give it somewhat more general significance.

The maximum of the absorption coefficient h may of course be found by setting $dh/d\omega=0$. It occurs at a frequency

$$\omega_{\max}=\zeta B_0/QB_\infty \tag{15}$$

and has the value

$$h_{\max}=4\pi[(Q-1)/(Q+1)]\cong\pi(Q-1/Q) \tag{16}$$

as Luck,[6] Henry[9] and Kneser[10] have pointed out in appropriate cases.

If (1) is written without regard for terms in h^2

$$\omega\cong(\zeta B_0/B_\infty)\{(V_\omega{}^2-V_0{}^2)/(V_\infty{}^2-V_\omega{}^2)\}^{\frac{1}{2}} \tag{17}$$

and $\omega_{\max}$ from (15) is substituted therein, there is obtained for the velocity at the point of maximum absorption

$$V_{\omega(\max)}{}^2=(V_\infty{}^2+V_0{}^2Q^2)/(Q^2+1)$$

which Luck,[6] Henry[9] and Kneser[5] have also reported.

Remembering that at 260 mm and 25°C in nitrogen tetroxide for case (a) $Q=Q_D=1.051$ and for case (b) $Q=Q_c=1.004$, the maximum absorption coefficient for the dissociation reaction $h_{D(\max)}$ is seen to be about 0.312 when the heat capacity remains fully active[11] and the maximum absorption coefficient for the heat capacity $h_{c(\max)}$ is approximately 0.030 if the dissociation reaction continues to follow the wave without lag. Here again case (a) gives about ten times the effect of case (b), and an experimental distinction between the two should easily be possible.

Turning now to case (c) where both heat capacity and dissociation contribute simultaneously to the absorption we shall make use of the same approximate model as was previously employed for the dispersion. It will be supposed that a single time constant θ is sufficient to describe the dispersive behavior of the heat capacity, and that the frequency dependence of the heat capacity conforms to the expression first suggested by Kneser[5] where $\bar{C}_v$

$$\bar{C}_v=\bar{C}+\bar{C}_\omega(1/(1+i\omega\theta))$$

is the contribution of the heat capacity to the complex velocity of sound at a frequency ω. Substituting this in the equation of Einstein in the usual way gives the complex velocity of sound as in Eq. (6) of the previous communication. For the present purpose the reciprocal of this may be written

$$\frac{\Delta}{\pi}=\frac{\rho}{P}\left\{\frac{k_1B_0-\omega^2\theta\bar{C}+i[k_1\omega\theta B_c+\omega\bar{C}_0]}{k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})+i[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]}\right\} \tag{18}$$

where A_0, B_0, A_c, and B_c have the values given above. The absorption coefficient in case (c) is then given by the expression

$$h_{DC}\cong2\pi\left\{\frac{(k_1B_0-\omega^2\theta\bar{C})[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]-(k_1\omega\theta B_c+\omega\bar{C}_0)[k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})]}{(k_1B_0-\omega^2\theta\bar{C})[k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})]+(k_1\omega\theta B_c+\omega\bar{C}_0)[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]}\right\}. \tag{19}$$

This is not only unsightly, but has the disadvantage that it does not readily yield expressions of the type of (15) and (16). Nevertheless it must be briefly discussed in view of the experimental work which follows.

In case (a), when the heat capacity is without lag,

$[\theta=0;\ y_D=(\omega/k_1)\cdot(\bar{C}_0/B_0)]$, (19) reduces to

$$h_D\cong2\pi y_D\{(Q_D{}^2-1)/(1+Q_D{}^2y_D{}^2)\} \tag{20}$$

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[10] Kneser, Ann. d. Physik **16**, 337 (1933). Kneser has given (14) for the case $B_0=C_i+C_a$ and $B_\infty=C_a$ in his notation. He has obtained (14) from the tangent of the phase angle φ by the approximation $2\pi\tan\varphi\cong h$. This may be seen to be identical with the approximation here introduced if $\tan\varphi$ is obtained from Eqs. (1) and (2) of our previous communication by neglecting terms in β^2.

[11] Luck (reference 6) was the first to point this out.

and in case (b) when the dissociation reaction is without lag,

$(k_1 \gg \omega,\ \theta^{-1};\ y_c = \omega\theta B_c/B_0)$, (19) reduces to

$$h_c \cong 2\pi y_c\{(Q_c^2-1)/(1+Q_c^2 y_c^2)\}. \qquad (21)$$

If the dissociation is so slow that it plays no part in the compressibility ratio $(k_1=0,\ f=\omega\theta)$, (19) gives Kneser's expression[10] applied to a gaseous mixture of very particular properties:

$$h \cong 2\pi f \frac{\bar{C}}{\bar{C}_0}\left\{\frac{Q^2-1}{1+Q^2(\bar{C}f/\bar{C}_0)^2}\right\}. \qquad (22)$$

This case is without interest at present, since frequencies so high that the dissociation reaction has been wholly eliminated have not yet been employed to study nitrogen tetroxide. The magnitudes of the absorption maxima corresponding to (20) and (21) have already been discussed.

It appears best at present to limit the treatment of intermediate cases to a qualitative paragraph. In general, as might be expected, two absorption maxima, corresponding to two separate dispersive regions, appear when k_1 and θ^{-1} are different by more than two or three orders of magnitude. The two maxima are then roughly independent of each other. If k_1 is small compared to θ^{-1} the two separate peaks are of about the same height, corresponding to the two appropriate forms of (16). If, on the other hand, the heat capacity lag occurs at a lower frequency than that of the dissociation reaction, i.e., θ^{-1} is small compared to k_1, the absorption from the former is small, but that due to the latter considerably greater than (20) indicates, since the situation will then approximately be

$$h \cong 2\pi \frac{\omega}{k_1}\frac{\bar{C}}{B_c}\left\{\frac{Q^2-1}{1+Q^2\omega\bar{C}/k_1B_c}\right\}$$

where Q has a value greater than Q_D by an amount nearly proportional to the ratio $(\bar{C}_0/\bar{C})^{\frac{1}{2}}$. As k_1 and θ^{-1} approach each other the two absorption peaks merge into one which is conspicuously higher than either alone. It appears reasonable to suppose that in the limiting case where both dissociation and heat capacity fail at an identical frequency of sound the maximum of the absorption coefficient will be given by

$$h_{DC(\max)} \cong \pi(Q-1/Q), \quad \text{where} \quad Q=\left\{\frac{B_0(R+\bar{C})}{\bar{C}(A_0+B_0)}\right\}^{\frac{1}{2}}$$

If this is true, $h_{DC(\max)}$ will rise to 0.8 in nitrogen tetroxide at 25°C and 260 mm provided that $\bar{C}$ is reduced to 5 calories. In case the heat capacity fails at lower frequencies than the dissociation reaction or at the same frequency, $\omega_{D(\max)}$ will shift to higher frequencies in rough conformity to (15). An indirect consequence of this has already been illustrated by the dip in the curves of Fig. 1 of the previous communication.

An attempt to determine the absorption maximum by experiment

Since it appears from the previous discussion that the magnitude and position of the absorption maximum is influenced by heat capacity effects, it becomes reasonable to inquire whether absorption measurements may not conveniently supplement the information already gained from dispersion. Two publications have already reported observations concerning the absorption of sound in nitrogen tetroxide, but they do not, unfortunately, permit even qualitative conclusions.

Kistiakowsky and Richards[12] quote measurements of the logarithmic decrement coefficient of the d.c. plate current of the amplifier coupled to the magnetostriction oscillator as a function of pressure and frequency. This has been shown to be unreliable as a measure of absorption unless the conditions are very carefully controlled.[13] Their results will none the less be reproduced in Table I as the best at present available. It

TABLE I. *Decrement coefficient of the electrical reaction expressed as a reciprocal number of wave-lengths.*

Reprinted from Kistiakowsky and Richards.[12]

Frequency (kc)	P in mm 760	400	150
10	—	0.12	0.48
42	0.04	0.12	—
80	0.06	0.10	0.40

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[12] Kistiakowsky and Richards, J. Am. Chem. Soc. **52**, 4661 (1930).

[13] Klein and Hershberger, Phys. Rev. **36**, 1262 (1930). Hubbard, ibid. **41**, 523 (1932).

is apparent that these coefficients can have little relation to h as defined above, since both at 10 kc and 80 kc and 150 mm they exceed the theoretical value of $h_{D(\max)}$. It appears rather that they represent some result of the mass reaction of the gas on the oscillator, and that, therefore, the amplitude of the oscillator is not independent of the position of the reflector. It must be pointed out that the 10 kc and 42 kc measurements are further invalidated by a damping coefficient which corresponds in magnitude to the tube-dispersion.[14] It seems, therefore, unwise to attempt to form any conclusions from them.

The observations of Teeter[2] are even less worthy of confidence. His electrical decrement coefficient at 25°C, 550 mm, and 54 kc is 0.82, which is some eight times as large as that reported by Kistiakowsky and Richards[12] at higher frequency and lower pressure (Table I above, 80 kc, 400 mm) and can, therefore, hardly bear any useful relation to the absorption coefficient. Teeter's failure to obtain evidence of transmission of sound above 54 kc is strikingly in contradiction both with the prediction of theory and with the observations of previous experimenters.[12, 1]

It is apparent that in both these investigations the comparison of measurements is made precarious by discontinuous changes in acoustical conditions as the pressure and frequency are changed. Each different oscillator introduces a new set of acoustical conditions, and each pressure change involves a significant alteration of the mass-reaction of the gas on the oscillator. A method of locating the absorption maximum by means free from these objections was, therefore, devised. By using the same oscillator and reflector for all measurements, and by holding the pressure constant, large changes of the type indicated above are eliminated. The gas may then be taken through its absorption maximum by varying the temperature, since the dissociation rate constant of nitrogen tetroxide varies with temperature in proportion to a factor $\exp -14{,}000/RT$. The density of the gas will, of course, vary inversely with the degree of dissociation, but over a small temperature range it seems reasonable to suppose this influence negligible.

If the rate constant of 4.8×10^4 sec.$^{-1}$ for nitrogen tetroxide at 25°C and 260 mm is accepted from the dispersion measurements, and the constants A_0, B_0, $\bar{C}_0$ are taken as being those given in the previous section, $\omega_{D(\max)}$ will be about 470 kc at this temperature and pressure. This frequency must not be considered a prediction, since it is of course extremely sensitive to $\bar{C}_0$, and $\bar{C}_0$ has been arbitrarily given the value of 10 cal. It suffices, however, to show that the 450.1 kc oscillator already described (Fig. 4 and corresponding text of the work on dispersion, reference 1) is suitable to explore the absorption maximum at 260 mm in the neighborhood of 25°C. At 30°C the rate constant is about 6.7×10^4 and at 15°C about 2.6×10^4 at this pressure so that variation of the temperature between these limits should be sufficient to carry the gas through the absorption maximum provided that no heat capacity lag is present. The change in the absorption to be expected in this range is not, however, great, and it is difficult to predict whether measurements of the logarithmic decrement coefficient of the electrical reaction may be made with sufficient accuracy to detect it.

Table II summarizes a series of measurements at 451 kc and 260 mm, using this method. The first column, which is headed x/λ, is the distance from the reflector to the oscillator measured in wave-lengths. Thus the face of the oscillator corresponds to $x/\lambda=0$, and the first, third, fifth, etc., points of maximum electrical reaction, which do not correspond to an integral number of wave-lengths, are not reported. The relative electrical reaction is expressed as the ratio between the microammeter deflection at a point $x/\lambda=n$ divided by that at the point $x/\lambda=1$. Only 15 wave-lengths are recorded, although by suitable amplification nearly twice that number could be detected.

In argon, at a density approximating that of N_2O_4 at 25°C and 260 mm, the electrical reaction of the 451 kc oscillator decreased to 62 percent of its initial value after 15 wave-lengths.

That this attempt to locate the absorption maximum has been unsuccessful may be seen by looking horizontally across the table (for example at $x/\lambda=5$, 10 and 15). No significant diminution of the relative electrical reaction is noticeable at any temperature, and it is apparent that an

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[14] See Lamb, *The Dynamical Theory of Sound*, 2nd Ed., p. 196 (published by Arnold).

TABLE II. *Relative electrical reaction at various distances from the oscillator in nitrogen tetroxide at 260 mm, 451 kc, and various temperatures.*

x/λ	17.0°	18.3°	19.2°	20.0°	21.0°	22.0°	23.0°	24.1°	25.1°	26.1°	27.0°	29.0°
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.64	0.61	0.66	0.72	0.76	0.64	0.60	0.59	0.68	0.73	0.64	0.63
3	.46	.46	.49	.48	.52	.45	.41	.46	.46	.49	.42	.48
4	.32	.31	.40	.37	.37	.30	.33	.28	.33	.36	.32	.33
5	.27	.23	.28	.27	.27	.23	.29	.21	.24	.24	.20	.25
6	.18	.18	.20	.21	.19	.16	.17	.17	.16	.18	.15	.18
7	.15	.11	.15	.16	.15	.11	.13	.12	.13	.12	.12	.13
8	.12	.08	.11	.12	.11	.08	.10	.08	.11	.11	.09	.10
9	.09	.06	.09	.10	.08	.07	.09	.07	.07	.09	.07	.07
10	.08	.05	.08	.08	.07	.05	.08	.06	.05	.06	.07	.06
11	.06	.03	.07	.06	.05	.03	.07	.05	.04	.05	.05	.05
12	.04	.02	.06	.05	.04	.03	.06	.04	.03	.04	.04	.04
13	.03	.01	.05	.04	.04	.03	.04	.03	.03	.03	.04	.04
14	.03	.01	.04	.03	.03	.02	.03	.03	.01	.03	.03	.02
15	.02	.01	.02	.03	.02	.01	.03	.02	.01	.02	.02	.02

accuracy which is greater by at least one order of magnitude is necessary to secure the desired information. The measurements have nevertheless been reported, since such scant conclusions as they permit are considered distinctly favorable to the interpretation of the dispersion which has previously been given.

It will be noticed that the intensity of the electrical reaction drops with fair uniformity to 2 percent of its initial value after 14 wave-lengths. This is in quantitative agreement with the prediction of Luck based on the supposition that the dissociation reaction alone is failing to follow the sound wave. Although the electrical decrement coefficient[15] and the acoustical absorption coefficient may be considered identical only under experimental conditions far more circumspectly controlled than those here described, this agreement is considered encouraging. A diminution to 2 percent after 14 wave-lengths is conspicuously less than that to be expected in case (c), if the dissociation reaction and all of the vibrational heat capacity are simultaneously failing in the sound wave, and $Q \equiv Q_{DC} = 1.14$. The possibility of case (b) has been conclusively eliminated by the dispersion measurements, and need not be discussed. Table II appears to indicate, therefore, that case (a), where the dissociation reaction alone is producing the absorption, is that which approximately obtains in nitrogen tetroxide at 25°C and 450 kc. Furthermore, the fact that decrement of the electrical reaction is not greater may be taken as support for the already well grounded conclusion that the tube correction in this apparatus is small. Such tentative conclusions as are permissible from Table II are, therefore, in full accord with those previously based on the far more quantitative dispersion measurements.

At present the heat capacity lag constants θ_{NO_2} and $\theta_{N_2O_4}$ must, therefore, be considered unknown.[16]

In closing the section which deals with absorption the situation may perhaps be summarized. It appears that at present measurements of the dispersion of sound are both easier to perform and more trustworthy in their implications than measurements of the absorption. It is, in fact, useless to attempt to

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[15] A single decrement coefficient is not quantitatively satisfactory for describing the results in Table II.

[16] Teeter (reference 2) has stated that the dispersion which we have observed in nitrogen tetroxide may intelligibly be interpreted as wholly due to a heat capacity effect, and justifies this by a calculation in which a mean lifetime θ of 5×10^{-5} sec. is assigned to the $NO_2-N_2O_4$ mixture in rough analogy to Kneser's results on carbon dioxide. The calculation is made on the basis of an equation which is the dispersive analogue of (22) above, and is, therefore, applicable only when the dissociation reaction has been wholly eliminated from the adiabatic cycle. Since this cannot be the case under the conditions of our measurements, we disagree with his conclusion. Furthermore, if $\theta = 5 \times 10^{-5}$ as Teeter supposes possible the corresponding absorption maximum would be at about 3 kc at 30°C and 260 mm from Eq. (15) above. This is not consistent with his own conclusion that the absorption maximum "comes somewhere near 700 kc." The basis for his conclusion is not given, and since neither temperature nor pressure are specified it cannot be compared with any deductions which are here supported.

obtain quantitative information concerning the absorption with the apparatus at our disposal in this laboratory. Nevertheless, it is to be hoped that some investigator experienced in absorption measurements, who has at his disposal a large number of calibrated quartz crystals, will ultimately bring this research to a positive conclusion. The position and magnitude of the absorption maximum can provide information of great theoretical interest concerning heat capacity effects in dissociating gases. This information is more difficult to obtain from dispersion measurements, for the reason that the position and magnitude of the absorption maximum indicate the value of V_∞, whereas dispersion measurements can obtain V_∞ only at much higher frequencies by direct measurement. If the dispersive region is compounded of two or more concomittant types of time lag the terminal velocity at high frequencies corresponding to each separate process may be clearly deducible from the absorption maximum although wholly inaccessible to direct measurement.

PART II. SUPPLEMENTARY DATA CONCERNING THE DISPERSION MEASUREMENTS PREVIOUSLY REPORTED

Further discussion of the tube-correction

The application of a tube-correction determined by experiment considerably increased the accuracy of the measurements of dispersion which were previously reported. We feel that the method by which this correction was obtained has already been sufficiently discussed, but that the account of its application is too brief to be immediately intelligible. Further, parts of Table III and all of Table IV were inadvertently printed with the measurements uncorrected, in direct contradiction to what was stated in the text. This has caused an obscurity concerning the tube correction which is wholly unnecessary[17] and we welcome an opportunity to dispel it. It must, however, be emphasized that nothing will be written in this section which was not previously considered in calculating the rate constants.

TABLE III.

T°C	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	ΔV (m·sec.$^{-1}$)
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	92.06	177.2	0.8
8.0	—	—	92.06	178.3	0.8
8.1	9.340	177.5	—	—	
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	202.1	450.7	205.6	3.4
	94.00	202.0	450.7	205.5	
	94.00	202.2	450.7	205.4	

TABLE IV.

P (mm)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	ΔV (m·sec.$^{-1}$)
			30°C		
342	94.00	198.4	450.7	200.7	2.3
260	94.00	202.1	450.7	205.4*	3.4
235	94.00	203.4	450.7	207.9	4.5
			25°C		
668	9.301	185.2	91.89	185.3	0.1
260	9.301	195.1	91.89	195.4	0.3
162	9.301	202.0	91.89	202.5	0.5
			1.0°C		
260	9.340	171.1	92.10	172.9	1.8
156	9.340	175.4	92.10	179.1	3.7
132	9.340	176.7	92.10	181.0	4.3

* This number is the average of the three corresponding measurements in Table III and should evidently be printed 205.5. It has not been corrected in order to facilitate comparison with the previous printing.

In order to be consistent with the text of the previous work, Tables III and IV should have been printed as they are here given. A careful comparison with the previous printing will show that the tube-corrections have been applied in the manner stated to all measurements in which the difference between the two velocities quoted did not accord with the sixth column and that, with the exception of a single misprint, the agreement is now complete and the sixth column unaltered. One further change has been made in reprinting the tables in that the sixth column

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[17] Teeter (reference 2) has pointed out the inconsistencies in Tables III and IV, and has correctly estimated their origin.

has been headed ΔV to show that it represents the difference in velocities at the two appropriate frequencies instead of $V_\omega - V_0$ as previously. These quantities may, of course, be quite different, but in the tables happen to be the same within experimental error.

Before describing in further detail the calculation of the rate constants from these measurements it should be emphasized that at 1°C and 132 mm (Table IV) ΔV is 4.3 m·sec.$^{-1}$, and the velocity at 9 kc, 176.7 m·sec.$^{-1}$. At 7°C and 260 mm (Table III), on the other hand, the velocity is almost identical at 9 kc and ΔV is only 0.8 m·sec.$^{-1}$. These two measurements alone are considered sufficient refutation of any fundamental objections to our conclusions based on the tube-correction, or a possible major effect due to heat-capacity dispersion. It was not previously considered necessary to emphasize this point.

The calculation of rate-constants from these measurements will now be considered in greater detail. It has already been stated that the chief cause for numerical disagreement between the measured velocity of sound and that calculated from Einstein's theory lies in uncertainty concerning the density of the gaseous mixture. A method of calculation was, therefore, employed in which the pressure and density were wholly eliminated by the use of the velocity of sound at very low frequency. This was effected by writing, in the notation of this paper,

$$k_1 = (\omega\bar{C}_0/B_0)\{(V_\infty{}^2 - v_\omega{}^2)/(v_\omega{}^2 - v_0{}^2)\}^{\frac{1}{2}}$$

where the symbol v now refers to an experimentally determined phase velocity. $V_\infty{}^2$ was calculated from the experimental velocity by means of the relation

$$V_\infty{}^2 = v_0{}^2\{B_0(\bar{C}_0 + R)/C_0(A_0 + B_0)\}.$$

This procedure is applicable quite generally to measurements on the dispersion of sound. Not only does it very largely remove systematic errors because of imperfections of the gas, incorrect determination of its thermodynamic constants, etc., but it makes possible the calculation of reasonably accurate time lag and dissociation rate constants when the measured values of the velocity accord relatively, but are greatly different from their values calculated from theoretical considerations alone.

For this reason no great concern was felt when the measured and calculated velocities differed by as much as 2 m·sec.$^{-1}$. The tube corrections were applied merely to make ΔV obtained from $V_{92} - V_9$ a self-consistent quantity, and similarly to make comparable the quantity $V_{451} - V_{94}$. The method of calculation made it unnecessary that V_{94} and V_{92} should be comparable, or that either should agree with the calculated velocity to anything like the precision claimed for ΔV. It will be remarked, for instance, that at 30°C and 260 mm V_{92} is 202.6 m·sec.$^{-1}$, and V_{94}, 202.1 m·sec.$^{-1}$. A difference of this kind is to be expected, for no effort has been made to apply a tube-correction which will make the two comparable. It is further a matter of indifference which of the two is accepted provided that the calculation of the rate constant is consistently made. There are two reasonable methods of making the calculation, (A) to add 0.5 m·sec.$^{-1}$ to V_{94} and to V_{451} to make them comparable to V_9 and V_{92}, or (B) to subtract 0.2 m·sec.$^{-1}$ from V_{94} to account for the dispersion and to use this for V_0. The result obtained is the same within experimental error

$$\text{(A)} \quad k_1 = \frac{\omega\bar{C}_0}{B_0}\left\{\frac{(211.5)^2 - (206.0)^2}{(206.0)^2 - (202.4)^2}\right\}^{\frac{1}{2}} = 1.249\,\frac{\omega\bar{C}_0}{B_0}$$

$$\text{(B)} \quad k_1 = \frac{\omega\bar{C}_0}{B_0}\left\{\frac{(211.0)^2 - (205.5)^2}{(205.5)^2 - (201.9)^2}\right\}^{\frac{1}{2}} = 1.250\,\frac{\omega\bar{C}_0}{B_0}.$$

Nevertheless an attempt was made to ascertain whether V_{92} or V_{94} was the more worthy of confidence by measuring the velocity of sound in argon, a quantity which can be calculated with some precision since $C_P/C_v = 1.667$ on theoretical grounds. On this basis V_{92} appeared the more accurate, as already reported.

One further aspect of this argument which appears to have caused confusion is the determination of the difference $V_9 - V_0$, because of the entry of the gas into the dispersive region. This was shown negligible in all cases by a calculation at 1°C and 260 mm. Here $V_\infty \leqq 177.9$, $V_{92} = 172.9$, $V_9 = 171.1$ m·sec.$^{-1}$. k_1 is, therefore, approximately

$$k_1 \cong \frac{2\pi(9.2\times 10^4)\bar{C}_0}{B_0}\left\{\frac{(177.9)^2-(172.9)^2}{(172.9)^2-(171.1)^2}\right\}^{\frac{1}{2}} \cong 7.0\times 10^3.$$

In order to find if V_9 is appreciably different from V_0 the calculation is then made

$$7.0\times 10^3 = \frac{2\pi(9.3\times 10^3)\bar{C}_0}{B_0}\left\{\frac{(177.9)^2-(171.1)^2}{(171.1)^2-V_0^2}\right\}^{\frac{1}{2}}$$

and it is found that $V_9 - V_0 = 0.03$ m·sec.$^{-1}$ and therefore inconsiderable. It was on this basis that we have written, "The accuracy of the rate constants in Table VI must now be considered. It may be shown from these by (9)" [the equation used above] "that the velocity of sound at very low frequency at 1°C is less than 0.1 m·sec.$^{-1}$ below that quoted at 9 kc. Error from this cause is, therefore, eliminated."

One further point concerning the tube-correction requires more extended discussion. We have suggested that the tube-correction may undergo a change in the dispersive region of frequency, since a literal application of the Helmholtz-Kirchhoff expression for the damping of plane waves in small tubes appears to indicate a certain increase in damping as the compressibility ratio of the gas is increased. We were content to show that this effect, if it occurred, would be negligible. Teeter has, however, based a criticism of our work on this subject, and the argument must, therefore, be more fully stated.

For this purpose it will be sufficient to use a very approximate statement of the Helmholtz-Kirchhoff relation. The tube correction for a particular diameter of tube, a particular gas, and a particular frequency will be called τ_ω when $V_\omega - V_0 \doteq 0$. If the conditions in the gas are changed so that $V_\omega - V_0$ becomes appreciable (for example by lowering the temperature or pressure) the Helmholtz-Kirchhoff expression leads to the expectation that a larger tube-correction τ_ω' would be found.[18] A much simplified approximation

$$\tau_\omega'/\tau_\omega \cong V_\omega^2/V_0^2$$

reproduces the numerical implications of the Helmholtz-Kirchhoff expression with quite sufficient accuracy for the present purpose. Since V_ω^2/V_0^2 might change from 1.00 to 1.25 from the beginning to the end of the dispersive region an increase of 0.5 m·sec.$^{-1}$ might occur in a tube-correction of 2.0 m·sec.$^{-1}$. Since $V_\infty - V_0$ is about 10 m·sec.$^{-1}$ this represents a 5 percent change in the differences in velocity due to the tube-correction. With a tube-correction of 2 m·sec.$^{-1}$, then, the tube-correction will be approximately $\tau_\omega + 1.05(V_\omega - V_0)$, and will equal τ_ω for small values of $V_\omega - V_0$.

This estimate of the error may easily be shown, however, to be unnecessarily generous when applied to our measurements. In the tubes which we used the tube-correction was always less than 2 m·sec.$^{-1}$ at high frequencies, and only at high frequencies did $V_\omega - V_0$ become of important magnitude. At lower frequencies the tube-correction was great, but $V_\omega - V_0$ small enough to be negligible. An estimate of the error possibly introduced by change in the tube-correction is appended in Table V. V_ω^2/V_0^2 from appropriate measurements gives the column headed τ_ω'/τ_ω. The column headed $2\tau_\omega$ is the most probable value of the tube-correction when $V_\omega - V_0 = 0$ multiplied by two for good measure. The last column shows twice the error probably introduced by neglecting the possible change in the tube-correction in the dispersive region, and has been called the maximum error.

TABLE V. *Estimate of error introduced into previous measurements on dispersion by a possible change in the tube-correction.*

Conditions	$\tau_\omega'\cdot\tau_\omega$	$2\tau_\omega$ m·sec.$^{-1}$	Maximum error $2(\tau_\omega'-\tau_\omega)$ m·sec.$^{-1}$
9 kc 1°C 260 mm	1.001	0.8	0.001
92 kc 1°C 260 mm	1.002	2.0	0.004
94 kc 30°C 260 mm	1.010	0.4	0.004
451 kc 30°C 260 mm	1.050	0.6	0.030

It is perhaps sufficient comment on this table to repeat that our claimed error was never less than 0.2 m·sec.$^{-1}$. We can therefore only reiterate our previous statement that the error introduced by neglecting the tube-correction change "is

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[18] Since it is desired only to find the maximum error due to this change the legitimacy of such a literal interpretation of the expression for the tube-dispersion need not be discussed.

believed to be considerably inferior to that due to other causes." We do not understand on what grounds Teeter has disregarded this statement without attempting to refute it.

In concluding this section it should be noted that nothing which has been said above must be considered as *a fortiori* justification of our previous work, for it is an amplification of an argument already indicated. Neither must it be considered a defense, for our previous position has not been attacked, but wholly disregarded. We must express our regret that it has been necessary to discuss in such intimate detail matters of very small scientific interest.

The effect of deviations from ideal gas laws and of absorption on rate constants computed from dispersion measurements

We had previously supposed that the approximate agreement of V_0 and of dV_0/dP at 260 mm with the values obtained from Einstein's equation[19] combined with the method we have used in calculating the rate constants, removed any serious error due to non-ideality of the mixed gas. Teeter's demonstration, from the argument given by Luck, that this is not necessarily the case, is therefore welcome. His estimate of the error introduced at the absorption maximum is, however, conclusive only if Q $(=V_\infty/V_0)$ is a measured quantity. When, as in the case we have discussed, V_∞ is calculated, k_1 at the absorption maximum becomes from (3) and (15)

$$k_1=\omega\{\bar{C}_0(\bar{C}_0+R)/B_0(A_0+B_0)\}^{\frac{1}{2}}$$

and A_0 is also involved. Luck has already pointed out that the coefficients involved in the calculation of A_0 from his development of the theory cannot at present be estimated. It might, of course, be argued that the experimental agreement of V_0 with the result calculated when using ideal gases indicates that A_0 and B_0 are affected equally by departures from ideal behavior. This would introduce, at the absorption maximum, about the error which Teeter has estimated, but would involve as a corollary our original assumption that rate constants calculated from small values of $V_\omega-V_0$ are without error due to this cause. It appears impossible, at present, to give this question a more satisfactory answer. This is especially the case because experimental determinations of the density are lacking below 25°C and, even above this temperature, do not define the value of P/ρ with accuracy sufficient for acoustical purposes.

Teeter has pointed out that errors in rate constants due to departure from ideal behavior are of opposite sign to those due to the neglect of the effect of absorption on the velocity. He has estimated the latter effect variously as 20 percent and as 4 percent.[20] We agree with the latter of these two estimates. In the only case of quantitative importance for our argument, that at 30°C, 451 kc and 260 mm, this effect may readily be calculated. Here Q, when using the average value from the "maximum" and "minimum" heat capacity, is about 1.048, $\bar{C}_0$ is 9.83 and B_0 (using $\alpha=0.359$, $D=14.0$ kg cal$\cdot$mole^{-1}) is 661. This gives $h=0.267$ from (14). Then

$$\frac{v_\omega}{V_\omega}=\left\{\frac{1-(h/4\pi)^2}{[1+(h/4\pi)^2]^2}\right\}^{\frac{1}{2}}=0.99933$$

where v_ω is the measured velocity of sound $(2\pi v_\omega=\omega\lambda)$ and V_ω is the square root of the real part of π/Δ. This equation is of course derived from (9), and was first suggested by Luck.[5] The measured velocity of sound is, therefore, about 0.14 m$\cdot$sec.$^{-1}$ below that given by r.p. π/Δ under these conditions. The relation of the true rate constant k_1 to that calculated neglecting the absorption k_R is then

$$\frac{k_1}{k_R}=\left\{\frac{V_\infty^2-V_\omega^2}{V_\omega^2-V_0^2}\right\}^{\frac{1}{2}}\left\{\frac{v_\omega^2-V_0^2}{V_\infty^2-v_\omega^2}\right\}^{\frac{1}{2}}=1.04$$

which agrees with Teeter's estimate. This is well within the experimental error which we have allowed, and is probably overbalanced by the error due to the departure of the gas from ideal behavior.

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[19] This is well illustrated at 25°C by Teeter's Fig. 5. It should perhaps be pointed out that our measurement at 9 kc and 668 mm has been incorrectly plotted in this figure, although it is correctly quoted in the corresponding table. The error is minor, but it gives an unmerited appearance of incoherence to our work.

[20] Teeter, reference 2 and J. Am. Chem. Soc. **54**, 4111 (1932).

There appears to be no reason at present for revision of the rate constants which we have given previously from either of the causes discussed in this section.

Corrections of the previous communication

Unfortunately, a number of misprints and one actual error appear in the previous work.

The following corrections should be noted. The argument was developed throughout by using the correct and not the incorrect statements.

Page 115. Lines 13 and 14, left-hand column. The real part of the two exponents should be $-\beta x$ and not $-\beta$.

Page 116. Lines under Eq. (8) should read "γ is the ratio of the isothermal to the adiabatic compressibilities."[21]

Page 117. Eq. (9) should read[22]

$$k_1=\omega\left\{\frac{\bar{C}_0RT^2\alpha[2+\alpha(1-\alpha)]}{(2-\alpha)\{\bar{C}_0RT^2[2+\alpha(1-\alpha)]+D^2\alpha(1-\alpha)\}}\right\}\left\{\frac{V_\infty{}^2-V_\omega{}^2}{V_\omega{}^2-V_0{}^2}\right\}^{\frac{1}{2}}.$$

The calculations of the rate constants were made using the convenient grouping of constants printed by Gruneisen and Goens,[23] after a comparison with a properly reduced version of our (8). It may easily be verified that the rate constants we have given are free from the error involved in (9) as originally printed.

Page 117. Fig. 2 should have as abscissae $\infty\ \bar{4}\ \bar{5}\ \bar{6}\ \bar{7}\ 0$ making the point of inflection of the $\omega=10^5$ curve nearly at $\theta=\bar{5}$.

Page 119, 22nd line from top, right-hand column, should read "pure plane sinusoidal wave."

Page 123. Tables III and IV should read as printed above.

Page 123, lines 17–15 from bottom, right-hand column. The statement "The second equation of (3) neglects the influence of temperature and pressure on the degree of dissociation" is nonsense, and should be deleted.

Page 125, line 10, right-hand column, should read

$$V_\infty=(V_0{}^2\gamma_\infty/\gamma_0)^{\frac{1}{2}}$$

and it should be emphasized that V_0 refers to the experimental velocity.

Page 127. The formula for $1/\Lambda$ should omit M_2 from the denominator of the last term on the right.

The only systematic error which Teeter has pointed out must now be discussed. We have incorrectly used 14.6 kg·cal. as the heat of dissociation at constant volume derived from the measurements of Verhoek and Daniels[24] instead of the correct value of 14.0 kg·cal. The effect of this error is to make the rate constants previously reported uniformly about 9 percent too low. It is not surprising that this figure falls within the estimated experimental error of 10 percent because uncertainty concerning the dissociation heat was of course included in the estimate. Evidently it is necessary to consider that the dispersion measurements indicate a reaction rate constant of 5.3×10^4 sec.$^{-1}$ at 260 mm and 25°C, and similarly to raise by 9 percent all the rate constants quoted. The exact absolute values of these constants have, however, little contemporary importance. It is more significant that the activation energy which was previously given (13.9 ± 0.9 kg·cal.) is unchanged, and is now so near to the most probable value of the dissociation heat (14.0 kg·cal.) that the agreement between the two must be considered in part fortuitous.

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[21] Teeter has pointed out this slip. By stating that we have the ratio inverted he is apparently, however, referring to (8) which is correctly printed. His statements that $\gamma=C_P/C_v$ and that it is a complex have no relation to anything we have said. It is necessary to call attention to this since, as he has not reprinted γ, the impression is distinctly misleading. The relation between Einstein's β and Luck's l is of course $\beta l\equiv1$.

[22] We are indebted to Teeter for calling attention to this error.

[23] Gruneisen and Goens, Ann. d. Physik **72**, 193 (1923).

[24] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).