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UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 102 : THE RATE OF DISSOCIATION OF NITROGEN PEROXIDE, BY W. L. ARGO

THE RATE OF DISSOCIATION OF NITROGEN PER-OXIDE

BY W. L. ARGO

The relation between the pressure, temperature and density of nitrogen peroxide is satisfactorily expressed by the statement that there is equilibrium between two gases with formulae N_2O_4 and NO_2.[1] Up to the present, no experiments have been made with the object of ascertaining whether any appreciable time is require for establishing equilibrium between these two gases, after an alteration of pressure. The purpose of the present paper is to determine whether in very rapid changes of pressure there is any evidence of "lag" in the reaction.

In his experiments on the rates of reaction of gases, van't Hoff[2] found that in many cases the walls of the vessel hastened the reaction. To eliminate this factor, and at the same time to obtain the necessary rapidity in the pressure changes, the oscillations of stationary sound waves have been made use of in this research.

If the change of dissociation is very rapid there will be equilibrium between the nitrogen tetroxide and dioxide, according to the equation $N_2O_4 \rightleftarrows 2NO_2$, at every instant during the oscillations of the sound waves, and the local density of the gas at each moment will correspond to what would be found by ordinary density measurements for the local pressure and temperature.

If, on the other hand, the rate of reaction is so small that no appreciable changes in dissociation occur, the density at every moment will be that calculated by the gas law $pV = nRT$, when n is constant.

If the velocity of sound in nitrogen peroxide can be calculated with sufficient accuracy for each of these limiting assumptions, it will be possible, by measurement of sound velocity

[1] Gibbs: Trans. Conn. Acad., 3, 240 (1878).

[2] Van't Hoff-Cohen: Studien zur chemischen Dynamik, p. 45 (1896).

in the gas, to decide whether the rate of dissociation corresponds to either one of these limiting cases or has some intermediate value.

Calculation of $d\rho/dp$

Symbols used:

T = absolute temperature.

p = pressure of nitrogen peroxide in mm mercury.

p_1 = pressure of air in mm mercury.

V = volume in cc of 92.08 grams nitrogen peroxide at p.

V_1 = volume in cc of 28.97 grams air at p_1.

d = density of nitrogen peroxide compared with air, at T and p.

$\rho = \dfrac{92.08}{V}$ (density of nitrogen peroxide, in grams per cc).

$\rho_1 = \dfrac{28.97}{V_1}$ (density of air in grams per cc).

R = 62340.

α = 92.08/28.97d — 1 ("degree of dissociation").

c'_r = sp. heat per formula weight, at constant volume, of NO_2.

c'' = sp. heat per formula weight, at constant volume, of N_2O_4.

$c_v = \dfrac{(1 - \alpha)c''_r + 2\alpha c_v}{1 + \alpha}$

κ_1 = 1.405 (Ratio of specific heats at constant pressure and constant volume for air).

K = dissociation constant of nitrogen peroxide, defined by

$\dfrac{4\alpha^2}{V(1 - \alpha)} = K.$

h = heat given out, in cal., when N_2O_4 changes to $2NO_2$ at constant volume.

λ = wave length in cm of stationary sound waves in nitrogen peroxide.

λ_1 = wave lengths in cm of stationary sound waves in air.

ν = no. of vibrations per second of rod forming sound waves.

Calculation of $\dfrac{d\rho}{dp}$ *from wave lengths.* From the formulae for the velocity of sound.[1]

$$\frac{d\rho}{dp} = \frac{\text{const.}}{\lambda^2 \nu^2}; \quad \frac{d\rho_1}{dp_1} = \frac{\text{const.}}{\lambda_1^2 \nu^2},$$

$$\frac{d\rho}{dp} = \frac{\lambda_1^2 \rho_1}{\lambda_1^2 p \kappa_1}. \tag{1}$$

This gives an experimental method for determining $\dfrac{d\rho}{dp}$

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[1] Clausius: Mech. Wärmetheorie, p. 52 (1876).

for nitrogen peroxide from measurements of wave length in it and in air, for the same note.

Calculation of hypothetical $\frac{d\rho}{dp}$. The value of $\frac{d\rho}{dp}$ may be calculated under the two assumptions made above:

Assumption A.—That the dissociation is so rapid that chemical equilibrium exists at every moment.

Assumption B.—That the dissociation is so slow that no chemical reaction takes place during the changes due to the sound waves.

The values under Assumptions A and B will be indicated by $\left(\dfrac{d\rho}{dp}\right)_A$ and $\left(\dfrac{d\rho}{dp}\right)_B$, respectively. These will be compared with the experimental value $\left(\dfrac{d\rho}{dp}\right)_{exp.}$ given by equation (1).

For a small adiabatic change of the nitrogen peroxide

$$0 = -h\left(\frac{\partial\alpha}{\partial V}\right)_T dV + \frac{1.359}{42660}pdV - h\left(\frac{\partial\alpha}{\partial T}\right)_v dT + (1-\alpha)c_v'' dT + 2\alpha c_v' dT$$

$$\therefore \frac{dV}{dT} = \frac{h\left(\dfrac{\partial\alpha}{\partial T}\right)_v - (1-\alpha)c_v'' - 2\alpha c_v'}{\dfrac{1.359}{42660}p - h\left(\dfrac{\partial\alpha}{\partial V}\right)_T}. \tag{2}$$

Also

$$(1+\alpha)RT = pV. \tag{3}$$

From (2) and (3), and noting that $\dfrac{d\rho}{dp} = -\dfrac{\rho}{V}\dfrac{dV}{dp}$

$$\frac{d\rho}{dp} = -\frac{\rho}{\dfrac{R\left\{T\left(\dfrac{\partial\alpha}{\partial T}\right)_v + 1 + \alpha\right\}\left\{\dfrac{1.359}{42660}p - h\left(\dfrac{\partial\alpha}{\partial V}\right)_T\right\}}{h\left(\dfrac{\partial\alpha}{\partial T}\right)_v - (1-\alpha)c_v'' - 2\alpha c'} + RT\left(\dfrac{\partial\alpha}{\partial V}\right)_T - p}. \tag{4}$$

Under *Assumption A*, since $K = \dfrac{4\alpha^2}{V(1-\alpha)}$,

$$\left(\frac{\partial\alpha}{\partial V}\right)_T = \frac{K(1-\alpha)^2}{4(2-\alpha)} = \frac{\alpha^2(1-\alpha)p}{(2-\alpha)RT}.$$

And since from van't Hoff's equation, $\dfrac{d\ln K}{dT} = \dfrac{h}{1.985T^2}$,

$$\left(\frac{\partial\alpha}{\partial T}\right)_v = -\frac{h\alpha(1-\alpha)}{1.985T^2(2-\alpha)}.$$

Equation (4) now becomes by substitution

$$\left(\frac{d\rho}{dp}\right)_A = \cfrac{\dfrac{\rho}{p}}{\left\{-\dfrac{hM}{1.985T} + (1+\alpha)\right\}\left\{1.985 - \dfrac{h\alpha M}{T}\right\} - \alpha M +}{\dfrac{h^2M}{1.985T^2}} \quad (5)$$

$$\dfrac{h^2M}{1.985T^2}\quad (1-\alpha)c_v'' + 2\alpha c_v'$$

in which $M = \dfrac{\alpha(1-\alpha)}{2-\alpha}$ and α has the value calculated from ordinary density measurements.

Under *Assumption B* $\left(\dfrac{\partial\alpha}{\partial V}\right)_T = 0$ and $\left(\dfrac{\partial\alpha}{\partial T}\right)_V = 0$, and equation (4) becomes

$$\left(\frac{d\rho}{dp}\right)_B = -\cfrac{\rho}{\dfrac{R(1+\alpha)1.359p}{-(1-\alpha)c_v'' - 2\alpha c_v'} - p} = \frac{c_v}{c_v + 1.985}\cdot\frac{\rho}{p} \quad (6)$$

corresponding to Laplace's formula for an ordinary gas.

Data Used.—For h the value —12900 cal., calculated by van't Hoff,[1] has been used. The values of α were calculated from the density ρ, by equation (3); ρ and p were found directly by E. and U. Natanson in their determinations of sound wave length. In my experiments the weight, volume and temperature were determined and the pressure was found by Gibbs' equation[2]

$$\log_{10}\frac{(3.178-d)^2P}{2(d-1.589)} = 9.47056 - \frac{3118.6}{T}$$

in which P is the pressure in atmospheres.

The only data about which there is much uncertainty are the values of c_v' and c_v''. From Berthelot and Ogier's[3]

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[1] Van't Hoff-Cohen: Studien zur chem. Dynamik, p. 158 (1896).

[2] Gibbs: Trans. Conn. Acad., **3**, 239 (1878).

[3] Ann. Chim. Phys., [5] **30**, 382 (1883).

determinations of the total heat given out on cooling nitrogen peroxide through various intervals of temperature, and taking the heat of dissociation as $-(13132 + 2T)$ cal., Schreber[1] has calculated the values of c_v' and c_v'' on the assumption that $c_v'' = 2c_v'$. He gives the values 12.85 and 6.43. His calculation, however, contains the erroneous assumption that the heat required to raise the temperature of 92.08 grams of nitrogen peroxide through 1° at constant volume (C_v) is equal to the corresponding value for constant pressure 14.85 cal., (C_p), less 1.985 (instead of $(1 + \alpha)1.985$). Moreover, Schreber's number 14.85 was obtained by averaging the values found for various intervals of temperature ranging from about $290° - 28°$ to $150° - 28°$ on the wrong assumption that C_p is independent of the temperature. The specific heat at constant pressure for 92.08 grams must increase with increasing dissociation according to the equation $C_p = C_v + 1.985(1 + \alpha)$. Unfortunately the experimental data on which these values are based are not sufficiently concordant to warrant a strict recalculation. A rough estimate, however, was made as follows:

By taking intervals of temperature θ (about 25° each) from 290° to 28°, and calculating the values of $\theta\{(1 - \alpha)c_p'' + 2\alpha c_p'\}$ for the averages of the value of α at the upper and lower ends of each interval, and summing these values over intervals corresponding to Berthelot and Ogier's experiments, a set of numbers is obtained whose average is 14.85 when c_p'' is taken as 13.4 and c_p' as 7.7.[2] This gives $c_v'' = 11.4$ and $c_v' = 5.7$.

The value $c_v' = 5.7$ is low compared with those of other gases of similar formulae, as shown by the following table:

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[1] Zeit. phys. Chem., **24**, 651 (1897).

[2] These values were found after a few approximations. c_v'' is assumed equal to $2c_v'$. This assumption is justified to a certain extent by the fact that the relation between density of nitrogen peroxide and temperature is closely represented by an equation of Gibbs' in which this assumption is implied. (See Trans. Conn. Acad., **3**, 244 (1878).)

$$CO_2 \quad 7.55$$
$$N_2O \quad 7.95$$
$$H_2O \quad 6.65$$
$$SO_2 \quad 7.88$$
$$H_2S \quad 6.27$$
$$CS_2 \quad 9.93$$

Average, 7.70

If in these calculations the value —12900 cal., calculated by van't Hoff from Deville and Troost's measurements is used for the heat of dissociation instead of —13132 cal., calculated by Schreber from Natanson's experiments, the values for c_v'' and c_v' would come out about 12 percent greater, say 12.8 and 6.4. Van't Hoff[1] mentions the value 16.86 for 92 grams of nitrogen peroxide "at high temperatures where decomposition can be neglected," but does not say how he obtained it. This would give $16.86/2 - 1.985 = 6.45$ for c_v''. Because of this agreement with van't Hoff's value, and the higher values for other gases, the values

$$c_v'' = 12.8 \text{ and } c_v' = 6.4$$

have been used in the calculations. Fortunately the effect of errors in the specific heats on the values $\left(\dfrac{d\rho}{dp}\right)_A$ and $\left(\dfrac{d\rho}{dp}\right)_B$ are relatively small. (See p. 444.)

Comparison of Calculated and Observed Values of $\left(\dfrac{d\rho}{dp}\right)$

The following table shows the calculated values of $\left(\dfrac{d\rho}{dp}\right)_A$, and $\left(\dfrac{d\rho}{dp}\right)_B$, and the values of $\left(\dfrac{d\rho}{dp}\right)_{exp.}$ obtained from four sets of the sound wave measurements of E. and U. Natanson:[2]

t	p mm	d (measured)	λ_1 mm	λ mm	$\left(\dfrac{d\rho}{dp}\right)_A \times 10^8$	$\left(\dfrac{d\rho}{dp}\right)_B \times 10^8$	$\left(\dfrac{d\rho}{dp}\right)_{exp.} \times 10^8$
21.72° C	230.59	2.486	42.09	23.64	3.659	3.275	3.558
21.25	367.08	2.599	42.05	23.08	3.833	3.452	3.733
21.81	617.63	2.709	41.80	22.27	3.987	3.619	3.953
19.96	640.76	2.762	41.98	22.19	4.092	3.718	4.042

[1] Van't Hoff-Cohen: Studien zur chem. Dynamik, p. 158 (1896).

[2] Wied Ann., **24**, 454 (1885).

The experimental values $\left(\dfrac{d\rho}{dp}\right)_{\text{exp.}}$ agree very closely with those for $\left(\dfrac{d\rho}{dp}\right)_{\text{A}}$, the greatest deviation being 2.8 percent and the least 0.9 percent. On the other hand, the experimental values differ from $\left(\dfrac{d\rho}{dp}\right)_{\text{B}}$ by from 8.5 percent to 7.5 percent.

The Effect of Errors in Data

The following table shows the percent effect on the values at the heads of the columns caused by a one percent increase in the data shown in the first column:

	$\left(\dfrac{d\rho}{dp}\right)_{\text{A}}$	$\left(\dfrac{d\rho}{dp}\right)_{\text{B}}$	$\left(\dfrac{d\rho}{dp}\right)_{\text{exp.}}$
λ_1	o	o	+2
λ	o	o	—2
α	+1.04 to +0.96	+1.15 to +1.17	o
c_v	+0.013 to +0.010	+0.15 to +0.17	o
—h	+0.05 to +0.09	o	o

Thus, to bring the values $\left(\dfrac{d\rho}{dp}\right)_{\text{exp.}}$ down to the values $\left(\dfrac{d\rho}{dp}\right)_{\text{B}}$ there would have to be consistent errors of about +4 percent in λ, or —4 percent in λ_1 (or +2 percent in λ *and* —2 percent in λ_1). Chance errors in the measurement of wave length are much less than this (see values, page 449), and it is quite improbable that methodical errors would have opposite signs in λ and λ_1.

To bring the values $\left(\dfrac{d\rho}{dp}\right)_{\text{B}}$ up to the value $\left(\dfrac{d\rho}{dp}\right)_{\text{exp.}}$ an error of about +7 percent would be necessary in d, or an error of about +50 percent in c_v. Errors of these magnitudes are practically impossible in d, and very unlikely even in the case of the doubtful c_v.

The results of the above comparison may be taken therefore as conclusive evidence that *Assumption B* is not in accordance with the facts.

It may be noted in connection with this conclusion that it is clearly impracticable to use sound velocity as a means of measuring the ratio $\frac{c_p}{c_v}$ for nitrogen peroxide.

New Experiments

Natanson's determinations involved the use of a mercury manometer and stop-cocks. The stop-cock lubricant is readily attacked by the nitrogen peroxide, and as a result water vapor in slight traces may have reached the gas and catalysed the reaction. In order to check the above conclusion with a carefully dried gas and, at the same time, to investigate the effect of water vapor, added in known quantity, the following experiments were carried out.

The apparatus finally designed had neither stop-cocks nor manometer. The stop-cocks were eliminated because it was found that even metaphosphoric acid used as lubricant allowed leaks. As the use of a manometer would require stop-cocks to protect the mercury from the peroxide, the pressure of the gas was calculated from measurements of its volume and weight by the use of the Gibbs' equation (see page 441).

The sound-producing apparatus was somewhat different from the Natanson type. The sounding tube AB, 120 cm long and 1.0 cm cross section, with a flattened bulb at each
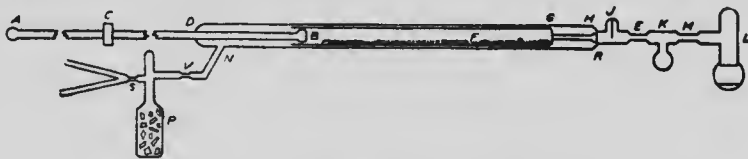

Fig. 1

end, is clamped at its middle, C. It is sealed into the gas chamber DF at D, so that DB is 20 cm long. As this is equivalent to a second clamp at D the sounding tube is damped at

$1/2$ and $1/4$ its length. The gas chamber in this way is theoretically stationary, whereas in the Natanson type it formed part of the vibrating system. The apparatus is thus less fragile and the dust heaps are less irregular than when they are formed on a vibrating surface. The adjustment of length of the gas column is made by means of an inner tube F, supported by platinum loops sealed into its walls. It can be adjusted by tapping the end of the gas chamber. The loops fitted tightly enough to prevent the tube from sliding when the apparatus was held vertically. The powder for forming the dust heaps, precipitated silica, was placed in this inner tube.

At G a glass rod GH was sealed into the flat end of the inner tube. Its length was such that when the tube was moved back sufficiently, a capillary tube, sealed in at J, was broken. This capillary contained about 0.001 gram of water. The bulb K, of about 6 cc capacity, in which the nitrogen peroxide was to be finally condensed by liquid air, opened into the nitrogen peroxide reservoir L and the gas chamber through constrictions E and M. The side tube N opened into a glass bulb P containing cocoanut charcoal which was in communication with an air pump and a McLeod gauge.

The nitrogen peroxide was prepared from pulverized lead nitrate dried for an hour at about 120° C. This was mixed with dry sand to prevent caking, and was decomposed in a combustion tube through which passed a strong current of dry oxygen. The nitrogen peroxide was condensed in the reservoir L, of about 15 cc capacity, containing phosphorus pentoxide. The reservoir was then sealed off until ready for use. The nitrogen peroxide remained in contact with the phosphorus pentoxide for one week before it was used in the experiment.

The preparatory operations were as follows: The apparatus from D to K was enclosed in a heating oven. The nitrogen peroxide reservoir was immersed in liquid air, opened, and sealed to the apparatus at M. (The blowing was done through a phosphorus pentoxide tube to prevent access of moisture.) When the air-pump was started, the nitrogen

peroxide was heated to its melting point and then re-frozen slowly to prevent the lodging of air bubbles in the interstices of the frozen mass. The bulb was then kept immersed in liquid air.

The apparatus from D to R was heated to $195°$ C to remove the adsorbed water from the powder and from the walls of the vessel. As previous experiments had shown that at this temperature the water in the capillary etched and cracked the glass the part RM was heated only to $150°$ C. The bulb P was also heated to $200°$ C. When, after about three hours, the system had been exhausted to a pressure of 0.02 mm, the gauge and pump were sealed off at S. The bulb P was then immersed in liquid air to produce as complete a vacuum as possible. After six hours the bulb was sealed off at V and the reservoir L was removed from the liquid air. After allowing the apparatus to reach room temperature, about $20°$ C, and making certain that no nitrogen peroxide had condensed in the gas chamber, the reservoir L was sealed off at M.

In the adjustment of the apparatus to form stationary sound waves, the sounding tube, clamped at D, was rubbed between C and D with ether-moistened cotton wool. The length of the gas column in the inner tube BG was then altered by gentle tapping until well-defined heaps were formed.

After this preliminary adjustment the gas cylinder was placed in a thermostat at $22°$ C. For easy removal of the apparatus this consisted of a water tank, kept at $22°$ C $\pm$ 0.05, through which a cylinder about 8 cm in diameter ran longitudinally. When the apparatus had been supported by brass clips in this cylinder the openings were closed with loosely packed cotton wool. The temperature of the air-bath so formed reached that of the water tank about an hour after the apparatus had been inserted, and remained at $22°$ C $\pm$ 0.1 throughout an experiment.

To secure the necessary rigidity the clamp for damping the sounding tube at the point C was imbedded in a heavy concrete block. A layer of cork fastened to the glass with

adhesive tape and fish glue prevented the tube from slipping through the clamp.

When the temperature of the air-bath had become $33°$ C the sounding tube was clamped at C and set into vibration as before. Then the apparatus was removed from the thermostat and the dust-heaps were measured to 0.5 mm. The readings were averaged by the method proposed by Kundt.[1] Repetitions of this procedure gave a series of readings as checks on the measurement.

The wave length in air, λ_1, was obtained at the same time by inserting the end A of the sounding tube into a glass tube about 3 cm diameter and 50 cm long, containing precipitated silica. The temperature of the air was determined by two thermometers at either end of the tube and the dust heaps were measured as in the gas cylinder.

When a sufficient number of readings had been made, the capillary containing the water was broken. To insure distribution of the moisture throughout the nitrogen peroxide the gas cylinder was heated and cooled several times and the inner tube BG moved backwards and forwards. The gas cylinder was then left in the thermostat for twenty-four hours. With the nitrogen peroxide now definitely known to contain water vapor another wave-length measurement was made.

To determine the weight of nitrogen peroxide in the gas cylinder, the bulb K was immersed in liquid air until no color could be distinguished by looking longitudinally through RD. After the bulb was sealed off at E and dried, it was placed in a desiccator for half an hour and was then weighed. Both the bulb and a standardized solution of potassium permanganate were cooled in ice and then the top of the bulb was broken and held under the solution. In this way all the nitrogen peroxide was absorbed by the potassium permanganate. (No odor of the gas was distinguishable above the solution.) The permanganate reduced by the nitrous acid was determined by titrating with freshly standardized ferrous sulphate solution.

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[1] Pogg. Ann., **127,** 497 (1866).

The weight of nitrogen peroxide in the bulb was thus determined.

The weight was also determined directly by weighing the dried bulb and broken tip. A satisfactory check between the two methods served to establish the purity of the nitrogen peroxide.

Finally the volume of the gas cylinder was determined by weighing it empty and filled with water.

The complete results of the experiments are given below.

Length of waves in nitrogen peroxide at 22°C			Length of waves in air at 19.0°C	
Expt. No.	Dry or moist	In cms.	Exp. No.	In cms.
E4	Dry	1.440	E1	2.659
E9	Dry	1.440	E2	2.669
E10	Dry	1.436		
E12	Dry	1.455		Average, 2.664
E13	Dry	1.442		
E15	Dry	1.436		
		Average, 1.441		
E16	Moist	1.442[1]		

Weight of Nitrogen Peroxide in Bulb.

(a) By titration:

No. cc pot. permang. ($0.2874N$) = 202.75 cc.
No. cc ferrous sulphate ($0.1686N$) = 137.60 cc.
Net pot. permang. = 122.01 cc.
Weight nit. peroxide = 1.6129 gm.

(b) By direct weighing:

Wt. of bulb + nit. peroxide + 0.0012 gm. water = 7.4318 gm.
Wt. of opened bulb + pieces (empty) = 5.7976 gm.
Wt. of water = 0.0012 gm.
Wt. of nit. peroxide = 1.6330 gm.

The average value 1.623 grams was used in the calculation.

---

[1] The sounding tube was accidentally broken while another "moist" measurement was in progress. As the dust heaps in E16 were well defined it was thought unnecessary to make further experiments.

Volume of Gas Chamber.

Wt. of tube + bulb empty = 480.5 gm.
Wt. of tube + bulb full of water at 19.5° C = 1036.0 gm.
Volume = 556.5 cc.

The values $\left(\dfrac{d\rho}{dp}\right)_A$, $\left(\dfrac{d\rho}{dp}\right)_B$ and $\left(\dfrac{d\rho}{dp}\right)_{exp.}$ were cal-

culated as already explained.

t	d	p	$\left(\dfrac{d\rho}{dp}\right)_A \times 10^6$	$\left(\dfrac{d\rho}{dp}\right)_B \times 10^6$	$\left(\dfrac{d\rho}{dp}\right)_{exp.} \times 10^6$
22.0° C	2.722	679.9 mm	4.002	3.629	3.873

It is seen that the experimental value agrees with $\left(\dfrac{d\rho}{dp}\right)_A$ within 3 percent. This is probably within the limits of the experimental errors. On the other hand, it differs by more than 6 percent from the value $\left(\dfrac{d\rho}{dp}\right)_B$. This is in accord with the results calculated from Natanson's measurements. It can be concluded, therefore, that the rate of reaction even in the dry gas does not correspond to *Assumption B.*

Summary of Conclusions

1. The rate of reaction between nitrogen tetroxide and nitrogen dioxide is so great that there is no appreciable lag in the reaction during the rapid changes of pressure caused by stationary sound waves in nitrogen peroxide.

2. Conclusion 1 holds both for nitrogen peroxide dried over phosphorus pentoxide and for the gas containing 0.32 volume percent of water vapor

3. It is impracticable to use measurements of sound velocity for determining $\dfrac{c_p}{c_v}$ for nitrogen peroxide.

This research was carried out at the suggestion and under the direction of Dr. F. B. Kenrick. The experimental work was completed at the University of California.

University of Toronto
University of California
January, 1914