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EXPERIMENTS ON THE RATE OF DISSOCIATION OF NITROGEN TETROXIDE

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1. **Previous Work.**—The dissociation of the colorless gas nitrogen tetroxide to form the highly colored red nitrogen dioxide has long been of interest to chemists. The equilibrium between the two gases provided one of the earliest examples for the application of thermodynamics to the calculation of the effect of temperature on chemical equilibrium;¹ and the very high rate of attainment of the equilibrium has been the subject of much speculation and experiment.

Previous to the quite different mode of attack to be described in the present article, a number of attempts have been made to determine the rate of the dissociation and recombination by measuring the velocity of sound through an equilibrium mixture of the two gases. Using high enough frequencies, one should obtain the velocity corresponding to the passage of the sound wave through the mixture of the two gases without reaction, but at low enough frequencies one should expect the equilibrium to adjust itself by reaction to the periodic compression and rarefaction, and hence should expect a decrease in the velocity of sound, which amounts theoretically to about 3.8% with gas at 25° and atmospheric pressure.² At intermediate frequencies one should expect a "critical region" with intermediate velocities. A theory of the effect of frequency on the velocity

¹ Gibbs, *Trans. Connecticut Acad.*, 3, 108, 343 (1875-6-7-8); *Am. J. Sci.*, Ser. 3, 18 (1879).

² See Table VII in article by Grüneisen and Goens.⁸ Their calculation was made in accordance with the theory of Einstein,³ correcting for an obvious slip as to sign in Einstein's work. Kistiakowsky and Richards,¹⁰ apparently not correcting for the wrong sign, give a larger theoretical lowering of about 5.1%.

of sound in such a gas, assuming that the absorption coefficient is sufficiently small, has been developed by Einstein.³

Using frequencies in the audible range, measurements of the velocity of sound through the mixture have been made by E. and L. Natanson,⁴ Keutel,⁵ Argo,⁶ Selle⁷ and Grüneisen and Goens.⁸ E. and L. Natanson measured the velocity for only a single frequency, and hence could make no estimate as to the position of the critical range of frequencies where the velocity would be affected by the reaction. Keutel and also Selle came to the conclusion that the critical range lay within the audible. However, the experiments of Argo and the very thorough and careful investigation of Grüneisen and Goens make it appear certain that the critical range lies above the audible range of frequency, say 15,000 cycles per second, and that the specific reaction rate for the dissociation of nitrogen tetroxide at 760 mm. pressure and 25°, assuming first order decomposition, is at least as high as 10^4 seconds⁻¹.

Using frequencies in the ultrasonic range, measurements have been made by Olson and Teeter⁹ and by Kistiakowsky and Richards.¹⁰ Olson and Teeter concluded that the critical range had actually been passed at a frequency of 51,570 cycles per second in gas at 565 mm. pressure and 25°. The more extensive work of Kistiakowsky and Richards, however, now makes it appear reasonably certain that the critical range lies above 80,000 cycles per second at pressures from 300 to 760 mm. at 25°, and that the specific rate for the reaction is at least as high as 5×10^4 seconds⁻¹.

2. Criticism of the Acoustic Method.—There are a number of serious difficulties inherent in the acoustic method, owing primarily to the very small change in velocity that would be expected theoretically under the two assumptions of no reaction and a complete adjustment of the equilibrium to the periodic changes in pressure.

The apparatus for making the measurements is complicated, and the possible effect of the walls of the tube containing the gas must be allowed for. Small traces of impurities are known to have a large effect on the velocity; thus with the most careful purification Kistiakowsky and Richards were not able to duplicate results with successive fillings to better than about one-half a per cent.

A particularly serious difficulty also lies in the fact that the velocity of sound appears to vary with the frequency, when this is pushed high

³ Einstein, *Berlin. Ber.*, 380 (1920).

⁴ E. and L. Natanson, *Wied. Ann.*, **24**, 454 (1885); **27**, 606 (1886).

⁵ F. Keutel, *Inaug.-Diss.*, Berlin, 1910.

⁶ W. L. Argo, *J. Phys. Chem.*, **18**, 438 (1914).

⁷ H. Selle, *Z. physik. Chem.*, **104**, 1 (1923).

⁸ E. Grüneisen and E. Goens, *Ann. Physik*, **72**, 193 (1923).

⁹ A. R. Olson and C. E. Teeter, Jr., *Nature*, **124**, 444 (1929).

¹⁰ G. B. Kistiakowsky and W. T. Richards, *THIS JOURNAL*, **52**, 4661 (1930).

enough, even in a pure non-reacting gas,¹¹ although much work must still be done in this field.

The absorption of sound by the gas, which increases greatly with decreased pressure,¹² and would probably increase with frequency at high enough frequencies,¹³ is also serious, since it would otherwise be advantageous to work at lower pressures and temperatures in order to slow down the rate of the reaction, and at higher frequencies in order to get up into the critical region. With increased absorption the accuracy of the measurements is decreased, and the validity of the Einstein theory brought into question.

Finally it may be remarked that the method is in any case an indirect one, and that, up to the present time at least, no actual reaction velocity has ever been measured by this method, nor indeed any effect of reaction on the velocity of sound experimentally demonstrated.

3. General Nature of the Present Experiments.—The above well-known difficulties with the acoustic method make it desirable to investigate the possibility of other methods. In the present article we shall describe an entirely different mode of attack which, in spite of its own serious difficulties and uncertainties, nevertheless appears to give some idea as to the rate of dissociation of nitrogen tetroxide.

The general nature of the method was to cause an equilibrium mixture of the two gases to flow with a sudden drop in pressure through a perforated diaphragm, and take measurements of the temperature of the gas both before passage through the diaphragm and at successive positions in the path of flow beyond. The sudden drop in pressure and concentration on passage through the diaphragm should be followed by an increase in the degree of dissociation of the tetroxide and, since the reaction is endothermic, this should be accompanied by a drop in the temperature of the gas. Hence, knowing the velocity of flow and the temperature at different distances beyond the diaphragm, it was hoped that conclusions as to the rate of dissociation could be drawn.

The interpretation of the results obtained by the method is affected by two serious sources of uncertainty which must now be mentioned. They will be considered in more detail later.

The first uncertainty arises because of lack of knowledge as to the behavior of the jets which issue from the fine holes in the diaphragm. We purposely used a large number of fine holes set close together to try to break up the persistence of any jet structure, and we shall make our calculations on the assumption that we had a flow of homogeneous gas. We cannot be certain, however, how well this was actually achieved.

¹¹ G. W. Pierce, *Proc. Am. Acad.*, **60**, 271 (1925); C. D. Reid, *Phys. Rev.*, **35**, 814 (1930).

¹² See Ref. 10, Table VII.

¹³ See Ref. 11, first article, section 26.

The second uncertainty arises because of difficulties in determining the temperature of the flowing gas. The measurements were made with the help of copper-constantan thermocouples inserted in the path of the gas flow, as will be described later in detail. The exact interpretation of the readings is made difficult, (a) because the metal of the thermocouples might exert a catalytic influence on the dissociation, (b) because the actual readings obtained presumably correspond to a combined effect partly coming from the walls and only partly from the gas, and (c) because the rapidly flowing stream of gas in impinging on the thermocouples will tend to heat up by friction and compression. With regard to the possibility of catalytic influence, we have no evidence. With regard to the second difficulty of conduction of heat from the walls to the thermocouple junctions, however, it should be noted that the walls tend to some extent to drop to the same temperature as the adjacent gas, and that the difference in temperature between successive thermocouples, which is the thing of prime interest, is presumably more correctly given by the readings than the absolute temperatures. With regard to the possible heating of the thermocouples by the friction and compression of the impinging gas, it may be noted that this would also tend to some extent to balance out in the case of the temperature differences between successive couples, and in addition it may be remarked that the kinetic energy of the gas would not be high enough to produce an important effect of this kind, if the conditions of homogeneous flow assumed for our calculations are really correct. Finally, considerable insight into the significance of the observed temperature readings was obtained by carrying out *blank runs* with a non-dissociating gas, ethyl chloride, and comparing the readings with those obtained in the *regular runs* with the nitrogen tetroxide.

In spite of the above uncertainties the results obtained with the method are of considerable interest, especially in view of the negative results obtained with the acoustic method, and we may now proceed to a detailed description of the apparatus.

4. Description of the Apparatus.—The apparatus consisted essentially of a boiler B, containing liquid tetroxide and delivering gas through the diaphragm D, which then passed down the flow tube T and was finally condensed at C with the help of liquid air in a Dewar tube, as shown in Fig. 1.

The boiler B, which was about 9 cm. in diameter and 22 cm. in length, was made of Pyrex glass and arranged to accommodate the electrical heater H as shown in the figure. This was found to assure smooth boiling. The side tube M_1 led to a manometer for measuring the high pressure before passage through the diaphragm, and also provided connection for filling the apparatus, pumping, and attaching phosphorus pentoxide tubes when desired.

The boiler was connected with a barrel, ground to receive a plug carrying the diaphragm, as shown in detail in Fig. 2. The plug P was made of lead glass in order that the platinum diaphragm could be sealed to it. It was provided with a thermocouple T for measuring the temperature of the gas before passage through the diaphragm.

The diaphragm D was a platinum disk 0.127 mm. thick with a turned-over lip which fitted inside the plug for sealing. It was provided with 96 holes so distributed that equal areas of the disk contained approximately equal numbers of holes. They were made by forcing the point of a needle a set distance through the disk in the direction opposite to that of the flow, and had a diameter varying from 0.08 to 0.12 mm. with an average of 0.10 mm.

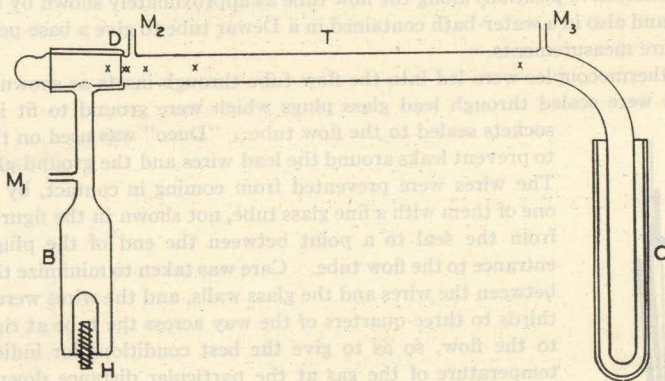


Fig. 1.—General view of apparatus. Crosses indicate position of thermocouples.

The barrel B was connected to the flow tube by a square shoulder, arranged so that the holes in the diaphragm were approximately uniformly distributed over the open area provided. The ground glass joint between the plug and barrel was made tight by painting on the outside with "Duco."

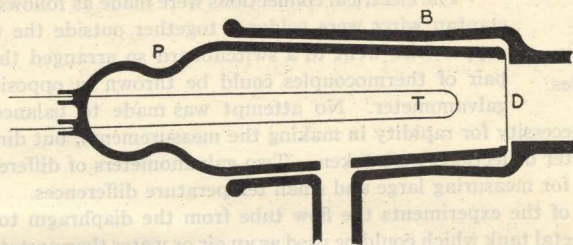


Fig. 2.—Detail of plug and diaphragm.

The flow tube was made from a uniform piece of Pyrex tubing having an inside diameter of about 4 cm. and a total length of 120 cm., with a smooth right-angle bend 75 cm. from the diaphragm. It was provided with manometer connections at M_2 as close as possible to the diaphragm and at M_3 60 cm. further down the tube. The tube was also provided with thermocouples as will be described below. There were three manometers: manometer no. 1, for measuring the high pressure before passage through the diaphragm, was an ordinary U-tube filled with mercury open at one end to the atmosphere, and connected at the other end either directly to the boiler at M_1 in the case of the blank runs, or through another U-tube filled with concentrated sulfuric acid for protection against the nitrogen oxides in the case of regular runs. Even with this protection the mercury was attacked in a short time and the tube had to be cleaned frequently. Manometer No. 2, for measuring the pressure drop in the flow tube, was

merely a U-tube filled with mercury in the case of the blank runs and sulfuric acid in the case of the regular runs, and connected between M_2 and M_3 . Manometer No. 3, for measuring the absolute value of the pressure on the low side of the diaphragm, was similar to No. 1 in the blank runs, and consisted of a closed-end U filled with sulfuric acid in the case of the regular runs. It was connected to the tube at M_3 .

Thermocouples were placed, in the high pressure gas as already shown in Figs. 1 and 2, at successive positions along the flow tube as approximately shown by the crosses in Fig. 1, and also in a water-bath contained in a Dewar tube to give a base-point for the temperature measurements.

The thermocouples were led into the flow tube through insets as shown in Fig. 3. The leads were sealed through lead glass plugs which were ground to fit into Pyrex sockets sealed to the flow tube. "Duco" was used on the outside

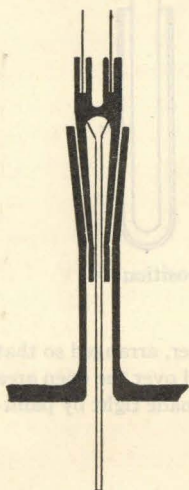


Fig. 3.—Detail of thermocouples.

to prevent leaks around the lead wires and the ground-glass joints. The wires were prevented from coming in contact, by insulating one of them with a fine glass tube, not shown in the figure, running from the seal to a point between the end of the plug and the entrance to the flow tube. Care was taken to minimize the contact between the wires and the glass walls, and the wires were run two-thirds to three-quarters of the way across the tube at right angles to the flow, so as to give the best conditions for indicating the temperature of the gas at the particular distance down the flow tube involved.

The thermocouples were constructed of copper and constantan joined together with soft solder. They were attacked only slowly by the nitrogen oxides, were inexpensive, had high sensitivity, and since one of the metals was copper made it possible to have no junctions between unlike metals except at the points whose temperature difference was desired.

The electrical connections were made as follows. All the constantan wires were soldered together outside the tube, and each copper wire went to a switchboard so arranged that any desired pair of thermocouples could be thrown in opposition on to the galvanometer. No attempt was made to balance the e. m. f., owing to the necessity for rapidity in making the measurements, but direct readings of the galvanometer deflections were taken. Two galvanometers of different sensitivities were provided for measuring large and small temperature differences.

For some of the experiments the flow tube from the diaphragm to the bend was enclosed in a metal tank which could be used as an air or water thermostat for controlling the external temperature.

5. Experimental Method.—The nitrogen tetroxide used in the regular runs was either prepared by heating lead nitrate or taken from a cylinder furnished through the courtesy of the Fixed Nitrogen Research Laboratory. The latter material contained some nitric oxide which was removed by treating with oxygen. It should be especially noted that material of extreme purity is not necessary for these experiments as in the case of the acoustic method. The material used was always dried by standing over phosphorus pentoxide and in some cases a drying tube was sealed on to the apparatus in which the material was condensed when not in use. No special correlation between the results and the extent of drying was apparent.

The ethyl chloride used in the blank runs was of U.S. P. grade as sold to physicians for local anesthesia. It was chosen as a comparison substance since its boiling point (12.5°) is nearer to that of nitrogen tetroxide (21.6°) than any other common, non-poisonous, stable liquid.

The apparatus was filled by condensing the desired material at C, Fig. 1, with the help of liquid air, and was then pumped off, the residual air being flushed out by warming up the tetroxide. It was necessary to remove the residual air thoroughly in order to obtain low pressures in the flow tube when running.

Four operators were needed to carry out a run. One man adjusted the heating of the boiler to maintain a prearranged pressure of gas on the high side of the diaphragm, and took readings of the three manometers at thirty-second intervals and thermostat temperatures when the bath surrounding the flow tube was used. A second man maintained the liquid air level in the Dewar so as to obtain the maximum rate of condensation. A third man took galvanometer readings corresponding to different pairs of thermocouples in a prearranged order. These readings were taken at ten-second intervals. The fourth man called the time for the readings and recorded results. The total time for a run was from 450 to 900 seconds according to conditions.

6. Experimental Results.—Using the apparatus and method described above, eighteen regular runs were made using nitrogen tetroxide and nineteen blank runs using ethyl chloride. In nine of the regular runs the flow tube was either in the open air at room temperature or surrounded by an air thermostat at room temperature, and in the remaining nine the flow tube was surrounded by water at room temperature. In seven of the blank runs the flow tube was surrounded by air at approximately room temperature, in four runs by air at an elevated temperature, and in eight runs by water at an elevated temperature.

The nine regular runs in which the flow tube was surrounded by water gave very irreproducible results, and the eight blank runs in which the flow tube was surrounded by water at an elevated temperature showed that the thermocouple readings were much more affected by the temperature of the surroundings with water in the thermostat than with air. Owing to this irreproducibility and to the fact that our interest lies in the temperatures which would be obtained under adiabatic conditions, we shall consider in detail only the data obtained when the flow tube was surrounded by air.

These results are summarized in Tables I, II and III, arranged according to the material used and the approximate temperature ranges for the air surrounding the flow tube. The first column of the tables gives the number of the run in chronological order. The second and third columns give the pressures of the gas before and after passage through the diaphragm. The remaining columns give the calculated temperature intervals between successive thermocouples in the line of flow.

The nature of the results is also shown in Fig. 4, where the calculated temperatures of the thermocouples are plotted against position for runs 1 and 2, illustrating the behavior of nitrogen tetroxide expanded into the flow tube surrounded by air at room temperature, and for runs 9 and 15, illustrating the behavior of ethyl chloride expanded from about the same pressure, in one case into the flow tube surrounded by air at room temperature, and in the other case into the flow tube surrounded by air at

tained on the high side of the diaphragm. Approximately steady conditions were obtained only in the middle of a run, and the data given in the tables are average values corresponding to readings taken from three minutes after the run started until one minute before all the material had passed over, or until the end of fifteen minutes in the case of very long runs.

The manometer readings for determining the pressures given in the second and third columns of the tables were taken every thirty seconds, but owing to difficulties with the manometers, which included the action of the oxides on the mercury even though it was protected by sulfuric acid, and the diffusion of the oxides through the sulfuric acid into the upper end of the closed manometer No. 3, the pressures recorded cannot be regarded as accurate. The pressures attained on the low side appeared to be very dependent on small amounts of residual permanent gas, which may have had a cushioning effect at the end of the flow tube where condensation took place. The actual rate of flow appeared mainly dependent on the pressure on the high side.

Galvanometer readings were taken every ten seconds, in general two successive readings on a given thermocouple in the case of the less sensitive galvanometer, and three to allow the more sensitive galvanometer to reach its final deflection. Only the final readings were used in making the averages, and this together with the large number of combinations read makes the number of readings included in the average for a given thermocouple small, varying from one to five. The temperature intervals given in the tables are calculated from the galvanometer readings from calibrations of copper-constantan couples.

Thermocouple No. 1 was located in the gas just before its passage through the diaphragm. The remaining thermocouples Nos. 2 to 6 were located at the approximate distances from the diaphragm of 4.5, 9.5, 35.5, 90 and 593 mm. in Runs Nos. 1 to 13, and 2, 7, 22, 30, 89 and 587 mm. in Runs Nos. 14 to 20. In these latter runs the thermocouples were made with heavier constantan wire than in the earlier and this was doubled to give additional stiffness.

7. The Qualitative Nature of the Results.—The general nature of the results is evident from the figures given in the tables.

From the similarity in the results obtained under similar conditions and the progressive changes with changed conditions, it is evident that the experimental findings show sufficient reproducibility to warrant consideration. The run showing the least satisfactory agreement with the others is No. 14 in Table I, which is the only one in that table obtained with the second set of heavier thermocouples. This may mean that these thermocouples were irregularly affected to a greater extent by external conditions than the finer ones. (The very irreproducible runs made with

the flow tube immersed in water mentioned above were also made with these thermocouples.)

The regular runs made with nitrogen tetroxide as shown in Table I are characterized by a large drop in the computed temperature on passing through the diaphragm, followed by a small continued drop in the first few centimeters of the flow tube, and a gradual rise further down the tube. The initial drop is presumably to be correlated partly with an ordinary Joule-Thomson effect but mainly with the heat used up by the dissociation of tetroxide, the small continued drop to be correlated with a continuation of the dissociation toward completion, and the final small rise with the heating effect of the walls of the tube. The runs show a smaller temperature drop the lower the initial pressure, and this is perhaps to be explained partly by the decreased change in degree of dissociation, and partly by the increased effect of the walls when a smaller amount of gas is flowing through the apparatus.

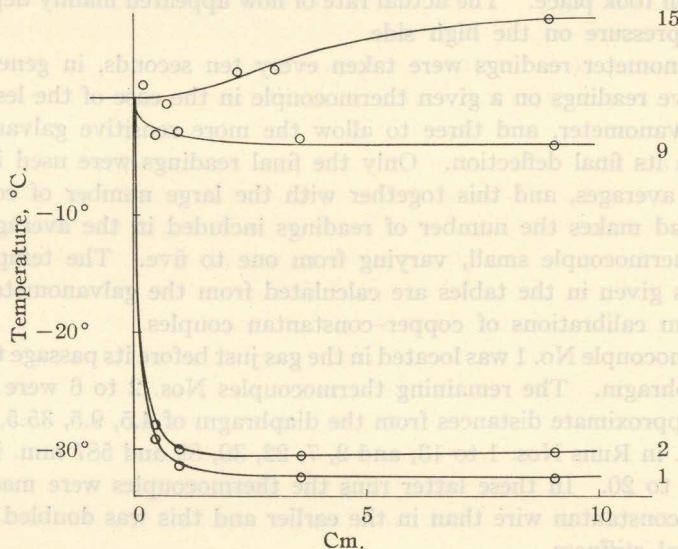


Fig. 4.—Plot of typical runs.

The blank runs made with ethyl chloride with the flow tube surrounded by air at nearly the same temperature as the ethyl chloride show a small initial drop in temperature in passing through the diaphragm, followed by small oscillations which have been neglected in drawing the curve in Fig. 4, and may be due to spurious causes. The small initial drop is perhaps to be correlated with the Joule-Thomson effect which amounts¹⁴ to -4.51° per atmosphere drop in pressure at 20° . The initial drop is smaller the lower the initial pressure, and this is perhaps to be explained partly

¹⁴ "International Critical Tables," Vol. V, p. 146.

by the decreased Joule-Thomson effect and partly by the increased effect of the walls when a smaller amount of gas is flowing through the apparatus.

The blank runs made with ethyl chloride with the flow tube surrounded by air at an elevated temperature show the effect of the walls in leading to higher temperature readings, with a gradual rise in passing down the tube and only the highest pressure run showing the initial drop which we have correlated above with the Joule-Thomson effect. The small oscillations in the readings may be due to spurious causes and have again been neglected in drawing the curve in Fig. 4.

The combined effect obtained by comparing the results obtained in the two kinds of blank runs with those obtained in the regular runs reinforces the impression that the temperature drops experienced by the nitrogen tetroxide in passing through the diaphragm and flowing down the tube are mainly to be correlated with the dissociation of the tetroxide which results from the decrease in its concentration.

8. Quantitative Discussion of the Results.—Although the results obtained are certainly not very accurate, and their interpretation is not unambiguous, nevertheless it seems desirable to use them for a preliminary calculation of the rate of dissociation of nitrogen tetroxide, since a knowledge of this very fast rate would be of importance for the theory of chemical kinetics, and the elaborate acoustic method has so far furnished no figure at all. The result which we calculate must, however, be regarded as subject to very great uncertainty, perhaps even as to order of magnitude.

(a) **Data for the Calculation.**—As data for the calculation we shall take the average of the results obtained in runs 1 and 2, which appeared to be typical and reasonably clean cut runs, made under nearly the same conditions and both of them taking the same total time for the material to pass over. The averaged data for the two runs are summarized in Table IV.

TABLE IV
AVERAGED DATA FOR RUNS 1-2

Weight of N_2O_4 in apparatus, g.	107
Inside diameter of flow tube, cm.	3.64
Total time of flow, sec.	690
Pressure of gas at diaphragm, mm.	485
Pressure of gas leaving diaphragm, mm.	5
Temperature of gas arriving at diaphragm, °C.	26.8
Temperature at 0.45 cm. from diaphragm, °C.	-1.7
Temperature at 0.95 cm. from diaphragm, °C.	-3.9
Temperature at 3.55 cm. from diaphragm, °C.	-4.7
Temperature at 9.0 cm. from diaphragm, °C.	-4.7
Temperature at 59.3 cm. from diaphragm, °C.	+1.6

(b) **Corrected Temperatures.**—Before using the data given in Table IV, we must first consider two probable sources of error in the tempera-

ture measurements. The first of these lies in the fact that the gas is colder than the walls of the flow tube and hence presumably receives heat from them on its passage down the tube. The second lies in the fact that the thermocouple wires presumably conduct heat from the point where they pass through the walls down to the thermal junctions, which hence register a higher temperature than that of the gas itself.

To obtain an approximate correction for the first error we note that the measured temperature, after falling sharply in the first few centimeters of the flow tube, then rises a moderate amount from -4.7 to 1.6° in the relatively long distance of 50.3 cm. between the last two thermocouples. If we correlate this rise of 0.125° per cm. with the actual heating up of the gas, we can then obtain an approximate correction to the preceding thermocouple readings with the help of this ratio. Doing so we then obtain the corrected temperature readings given in Table V, with a roughly estimated lower limit at -6.0° .

TABLE V

CORRECTED TEMPERATURES FOR RUNS 1-2

Temperature of gas arriving at diaphragm, $^\circ\text{C}$.	26.8
Temperature at 0.45 cm. from diaphragm, $^\circ\text{C}$.	-1.8
Temperature at 0.95 cm. from diaphragm, $^\circ\text{C}$.	-4.0
Temperature at 3.55 cm. from diaphragm, $^\circ\text{C}$.	-5.1
Temperature at 9.0 cm. from diaphragm, $^\circ\text{C}$.	-5.8
Estimated lower limit, $^\circ\text{C}$.	-6.0

To obtain a direct correction for the fact that all the thermocouples in the flow tube are probably reading too high, owing to the conduction of heat down through the wires from the walls, is not made possible by any data that we have obtained. If the method were further developed, this error could presumably be decreased by going to very fine thermocouple wire, and a direct experimental determination of the proper correction be made.

In the absence of a direct method of correcting for this error, we may proceed instead by calculating the drop in temperature that might theoretically be expected on expanding the tetroxide and comparing the result with the measured drop from 26.8 to -6.0° . To make such a calculation, which at best can only be rough, we shall assume that the heat of reaction Q_p absorbed when one mole of tetroxide dissociates is a constant independent of pressure and temperature, and that the heat capacity C_p of one mole of tetroxide is also a constant independent of pressure, temperature and the degree of dissociation of the tetroxide. For the drop in temperature we can then write the following expression, derivable from the first law of thermodynamics

$$(T - T_0) = (\alpha_0 - \alpha) \frac{Q_p}{C_p} \quad (1)$$

where T and α are the original temperature and degree of dissociation of the tetroxide before passage through the diaphragm and T_0 and α_0 are the final values of these quantities. Furthermore, for the values of α and α_0 we may use Schreber's¹⁵ expression for Natanson's empirical determination of the equilibrium constant, which gives us the two further equations

$$\log \frac{4\alpha^2 p}{1 - \alpha^2} = -\frac{2866.2}{T} + \log T + 9.13242 \quad (2)$$

and

$$\log \frac{4\alpha_0^2 p_0}{1 - \alpha_0^2} = -\frac{2866.2}{T_0} + \log T_0 + 9.13242 \quad (3)$$

where p and p_0 are the initial and final pressures in millimeters and the logarithms are to the base 10.

We thus have three equations for determining the three unknowns T_0 , α and α_0 . For the known quantities we take the initial and final pressures and the initial temperatures from Table IV, and we take the ratio Q_p over C_p to be 1000, corresponding to the heat of reaction 13,600 cal. per mole¹⁶ and an assumed constant heat capacity for a mole of partially dissociated tetroxide of 13.6 cal. per degree,¹⁷ the calculated value of the final temperature T_0 being very insensitive to the value used for this ratio. Solving the equations by a method of approximation, we then obtain for the initial and final degrees of dissociation $\alpha = 0.2344$ and $\alpha_0 = 0.2812$, and for the final temperature -19.5° .

Since the result obtained is very dependent on the accuracy of Schreber's equation, and no allowance has been made for the true Joule-Thomson effect, the value -19.5° cannot be regarded as very certain. It is nevertheless gratifying to find that the calculated drop from 26.8 to -19.5° is not so very much greater than the measured drop from 26.8 to -6.0° , and the result confirms our interpretation of the drop as mainly due to the increased dissociation which occurs.

Since the actual final temperature is certainly less than the measured value of -6.0° , we shall make our further calculations of the rate of dissociation not only on the assumption that the final temperature is -6° , but also assuming -13 and -20° for this quantity.

(c) **Theory of Reaction Rate Calculation.**—We must now consider the theory on which we shall base our calculation of the reaction rate from the rate at which the temperature is falling as the material is passing down the flow tube. At a given point in the flow tube let v be the

¹⁵ Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

¹⁶ Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 561.

¹⁷ Compare with the measurements of McCollum, *THIS JOURNAL*, **49**, 28 (1927). and the estimates of Kistiakowsky and Richards, Ref. 10.

volume containing one mole of the partially dissociated tetroxide, and α be the actual degree of dissociation which it has attained, so that

$$C_1 = (1 - \alpha)/v \quad (4)$$

is the actual concentration of nitrogen tetroxide and

$$C_2 = 2\alpha/v \quad (5)$$

is the actual concentration of nitrogen dioxide at that point. Substituting into the familiar expression for rate of reaction

$$-\frac{dC_1}{dt} = k_1 C_1 - k_2 C_2^2 \quad (6)$$

we then obtain

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) - k_2 \frac{4\alpha^2}{v} \quad (7)$$

for the rate at which the degree of dissociation is increasing in terms of the specific reaction rates k_1 and k_2 , for the forward and reverse reactions. On the other hand, if we let K_c be the equilibrium constant for the reaction and v_e and α_e be the volume and degree of dissociation which would obtain under equilibrium conditions with the pressure and temperature at the point in question, we may write from the well-known relation connecting the specific rates for the forward and reverse reactions

$$K_c = \frac{k_1}{k_2} = \frac{4\alpha_e^2}{(1 - \alpha_e)v_e} \quad (8)$$

and in addition

$$\frac{v_e}{v} = \frac{1 + \alpha_e}{1 + \alpha} \quad (9)$$

as a relation connecting the actual volume v and the equilibrium volume v_e at the given pressure and temperature. Combining (7), (8) and (9) and solving for k_1 we then easily obtain

$$k_1 = \frac{(1 + \alpha) d\alpha/dt}{1 - \alpha^2/\alpha_e^2} \quad (10)$$

or substituting

$$dl/dt = u \quad (11)$$

where u is the velocity of flow down the tube, we can write as our equation for determining the specific rate of decomposition

$$k_1 = \frac{u(1 + \alpha) d\alpha/dl}{1 - \alpha^2/\alpha_e^2} \quad (12)$$

where $d\alpha/dl$ is the change in degree of dissociation with distance down the tube.

To use this equation we must determine α and α_e from the thermocouple temperatures as functions of the distance from the diaphragm. And we must have a value for the velocity of flow u .

To determine the value of the actual degree of dissociation, we may use our previous equation (1), which gives

$$(\alpha - \alpha_1) = (T_1 - T) \frac{C_p}{Q_p} \quad (13)$$

where α_1 and T_1 are the known degree of dissociation and temperature of the gas before passage through the diaphragm, and T is the temperature of the gas at the point of interest.

To obtain a value for the theoretical equilibrium degree of dissociation α_e , it would not be safe to use any empirical formula for the equilibrium constant such as Schreber's, owing to the uncertainty in the formulas when extrapolated to the low temperatures involved, and even more owing to the uncertainty in the absolute magnitude of the lower temperature T which we have discussed in section 8b above. We may, however, proceed satisfactorily as follows.

Using an equation similar to (13)

$$(\alpha_0 - \alpha_1) = (T_1 - T_0) \frac{C_p}{Q_p} \quad (14)$$

we may obtain a value for the final degree of dissociation α_0 ultimately attained by the gas at its final temperature T_0 . The desired degree of dissociation α_e will then differ only moderately from α_0 . To calculate α_e from α_0 , we may then write in accordance with well-known relations

$$K_T = \frac{4\alpha_e^2 p}{1 - \alpha_e^2} \quad (15)$$

and

$$K_0 = \frac{4\alpha_0^2 p}{1 - \alpha_0^2} \quad (16)$$

where p is the pressure, and K_T and K_0 are the values of the equilibrium constant K_p at the temperature T of interest and the final lowest temperature T_0 , and by combination easily obtain

$$\log \frac{\alpha_e^2}{1 - \alpha_e^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \log \frac{K_T}{K_0} \quad (17)$$

Moreover, the difference between the temperature of interest T and the final temperature T_0 will be so small that we can now safely apply the integrated van't Hoff equation in its simplest form to determine the last term in (17) and write

$$\log \frac{\alpha_e^2}{1 - \alpha_e^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \frac{Q_p(T - T_0)}{2.303 RTT_0} \quad (18)$$

as the desired equation for calculating α_e in terms of α_0 .

Finally, to calculate the velocity of flow u at the point of interest, we may evidently write

$$u = \frac{m}{M} (1 + \alpha) \frac{RT}{p} \frac{1}{\pi r^2 t} \quad (19)$$

where m is the mass of gas passing down the tube in time t , M the molecular weight of the tetroxide, r the inside radius of the flow tube and the other quantities have their previous significance.

The expressions (12), (13), (14), (17) and (19) now provide all the theoretical apparatus that is necessary for a calculation of the specific rate of decomposition k_1 of the tetroxide.

(d) **Calculated Values of the Reaction Rate.**—Collecting the equations which are necessary for a calculation of the specific reaction rate, we can write with some simple modifications

$$k_1 = \frac{u(1 + \alpha) \frac{d\alpha}{dl}}{1 - \alpha^2/\alpha_e^2} \quad (12)$$

$$\alpha = \alpha_1 + (T_1 - T) \frac{C_p}{Q_p}, \quad \frac{d\alpha}{dl} = - \frac{C_p}{Q_p} \frac{dT}{dl} \quad (13)$$

$$\alpha_0 = \alpha_1 + (T_1 - T_0) \frac{C_p}{Q_p} \quad (14)$$

$$\log \frac{\alpha_e^2}{1 - \alpha_e^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \frac{Q_p(T - T_0)}{2.303 RTT_0} \quad (18)$$

$$u = \frac{m}{M} (1 + \alpha) \frac{RT}{p} \frac{1}{\pi r^2 l} \quad (19)$$

To obtain a satisfactory calculation of k_1 from these equations, it is evident that we must first determine the slope dT/dl at a point on the curve of descending temperatures sufficiently above the final temperature T_0 so that α and α_e will not be too nearly equal, and at a point where the data are such as to give a reliable value for the slope. With these considerations in mind we have plotted the temperatures given in Table V as a function of the distance from the diaphragm, and chosen as a basis for the calculations a point on the curve at -2.9° half-way between the temperatures of the first two thermocouples in the flow tube, taking the slope at this point as -4.4° per cm., which is the average drop per cm. between the two thermocouples. It may be noted that the glass sockets for these two thermocouples were sealed to the flow-tube at the *same* distance from the diaphragm, and the thermocouples then bent to the desired positions.

With the value thus obtained for the slope we have then calculated k_1 from the data in Tables IV and V, together with $\alpha_1 = 0.2344$, which is the value given by Schreiber's equation at 26.8° and 485 mm., and using $Q_p = 13,600$ and $Q_p/C_p = 1000$ as in section 8b. The result obtained is given in the first line in Table VI.

Since the correct value for C_p is not known, we have then repeated the calculation, assuming $Q_p/C_p = 800$, which corresponds to a value of $C_p = 17$ cal. per degree instead of 13.6. The result is given in the second line of the table.

Since the final temperature -6.0° depends on an uncertain extrapolation and from our plot of temperature against position seems possibly too high, the calculations have again been repeated, using -5.5° as the final temperature. The result is given in the third line of the table.

Finally, since all the temperatures in the flow tube are presumably lower than what is given by the thermocouple readings, as already discussed in section 8b, the calculations have further been repeated, lowering all

the flow tube temperatures first 7° below the values in Table V and then 14° below these values. This last would make T_0 equal to -20° , which is close to the theoretical final temperature calculated in section 8b from Schreber's equation. The results are given in the last two lines of Table VI.

TABLE VI

CALCULATED VALUES FOR SPECIFIC RATE OF DECOMPOSITION k_1

Assumptions for calculation	Q_p/C_p	$k_1, \text{sec.}^{-1}$
Temperatures as in Table V	$Q_p/C_p = 1000$	15.1
Temperatures as in Table V	$Q_p/C_p = 800$	18.9
Final temperature -5.5	$Q_p/C_p = 1000$	17.6
Temperatures in flow tube lowered 7°	$Q_p/C_p = 1000$	14.4
Temperatures in flow tube lowered 14°	$Q_p/C_p = 1000$	13.6

It is evident from the table that the calculated result is not greatly affected by moderate changes in the assumptions, and we may take $k_1 = 15 \text{ sec.}^{-1}$ as a reasonable figure for the order of magnitude of the calculated specific rate of decomposition.

9. Conclusion.—We have thus obtained a quite definite figure, $k_1 = 15 \text{ sec.}^{-1}$, for the specific rate of decomposition of nitrogen tetroxide at the low pressure and temperature in our flow tube. At higher pressures and temperatures, the specific rate would presumably be much greater. Assuming the reaction rate actually second order, as is perhaps probable, and taking the heat of activation the same as the heat of reaction at constant volume, 13,000 cal., we calculate at 1 atm. and 25° , $k_1 = 2.2 \times 10^4$, assuming the final temperature to have been -6° as given in Table V, $k_1 = 4.2 \times 10^4$, assuming a final temperature of -13° , and $k_1 = 8.2 \times 10^4$, assuming a final temperature of -20° . The last of these figures is perhaps the most justifiable estimate, and is not far from the lower limits set by Grüneisen and Goens and Kistiakowsky and Richards using the acoustic method.

Nevertheless, in spite of the reasonably definite result which we have thus obtained for the rate of decomposition of nitrogen tetroxide, it must be strongly emphasized that our considerations have completely neglected disturbing effects which might arise from a persistence of jets in the flow back of the diaphragm. Study of this question would be very important for the further development of the method, and in the absence of this study it would be unwise to make any undue claims for the reliability of the figures which we have presented. If jets do persist in the flow behind the diaphragm, it is possible that the actual rate might be considerably higher than we have calculated, both because the velocity in the jets would be higher than we have assumed, and because the gradual expansion of the jets as they pass down the tube would delay the attainment of final equilibrium.

In addition to a study and possible improvement in the conditions of flow back of the diaphragm, the further development of the method would also demand more reliable temperature measurements in the flowing gas. This could perhaps be achieved by using much finer thermocouple wire, sealed across the tube to provide the stiffness necessary to withstand the flow of gas.

In conclusion it may be remarked that the experiments which we have described are in any case of considerable interest, since they at least exhibit qualitatively a definite positive effect which can only be explained by a high rate of dissociation of nitrogen tetroxide, in contrast to the acoustic experiments which so far have led only to negative effects from which a high rate can be inferred.

PASADENA, CALIFORNIA

II. THE THERMODYNAMIC CONSTANTS OF BROMINE CHLORIDE

1. Historical Summary.

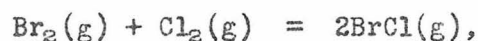
In 1826, Balard (1) published a statement to the effect that when chlorine gas was passed into cold liquid bromine, a highly refractive, yellow liquid was formed which he thought to be bromine chloride. Since that time controversy has been almost continual as to whether or not bromine chloride really did exist. In 1880, Berthelot (2) noted that little heat was produced when chlorine gas mixed with liquid bromine, and from this result concluded that no compound such as bromine chloride was formed. Lebeau (3) in 1906 by studying freezing point curves for the system $\text{Br}_2\text{-Cl}_2$ decided that only solid solutions and no compounds were formed. This result was confirmed by Karsten (4) in 1907.

The first real evidence for the existence of the compound BrCl , was put forward in 1929 by Barratt and Stein (5). Working in carbon tetrachloride solutions, they determined the bromine chloride present by light absorption measurements, and found as an average of 17 measurements that the dissociation constant of bromine chloride in this medium was 0.28. This work was checked in the same year by Gillam and Morton (6).

In 1931 Jost (7) published results of a photometric investigation of the gaseous equilibrium giving as his dissociation constant at room temperature, 0.16. Murdoch (8) in this laboratory using light in the absorption continuum of the gases instead of in the discontinuous region which Jost used, found a dissociation constant at 298°Abs. of 0.12.

2. Pressure Measurements of Gaseous Equilibria.

To most chemists determination of gaseous equilibrium constants by means of pressure measurements seems much more direct and certain than the other methods discussed above. The general procedure consists of measuring the total pressure of a mixture containing known amounts of the gaseous components at some definite temperature in a container of known volume after equilibrium has been reached. From this one measurement, the equilibrium constant for the reaction can usually be determined. In the case of the equilibrium



there is no pressure change as the reaction proceeds, and so pressure measurements on mixtures of bromine, chlorine, and bromine chloride alone can tell nothing about the composition of such a mixture. In order that the composition of the mixture may have an influence on the total pressure, some other substance must be added to this mixture which reacts with chlorine to give a pressure change. A reaction involving chlorine rather than one involving bromine must be used, else the more easily reduced chlorine would tend to displace the bromine from any of its compounds taking part in the reaction, thereby rendering the equilibria involved uncertain. This difficulty does not occur if the auxiliary reaction is one in which a chlorine compound gives chlorine. Several examples of such auxiliary reactions will be seen in the work below.

Another experimental difficulty in working with such corrosive gases as chlorine and bromine is their rapid action on any mercury in manometers with which they might come in contact. Such a difficulty has been met in the past by the use of sulphuric acid manometers

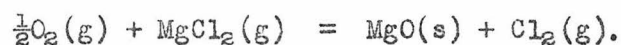
which often dissolve the reacting gases, or by using so-called "cushions" of unreactive gases between the reaction chamber and the manometer, thus introducing errors due to diffusion of the reacting gases into the "cushioning" gas. However, in this work the pressure of the corrosive equilibrium mixture was measured by means of a "click" arrangement. This device consists essentially of a thin membrane of glass so constructed that when the pressure difference on its two sides reaches a very definite value (within 0.01 mm. of mercury), the so-called "click-constant," it changes its shape abruptly with a sharp "click". On one side of this membrane is a supply of air the pressure of which can be adjusted and measured quite exactly. On the other side of the membrane is the corrosive reaction mixture. The pressure of the air is allowed to increase till the clicker "clicks," the air pressure read, and by subtracting the click constant, the pressure of the reaction mixture ascertained. Therefore the pressure measurements discussed below will be as exact as the manometer can be read. The manometer consisted of a U-tube of glass about one centimeter in diameter. This tube was partly filled with mercury, one arm of the U-tube exhausted thoroughly, and then sealed up. The scale attached was provided with a screw and vernier device by which the pressure could be read to 0.1 mm.

3. Attempts with Solid-Gas Auxiliary Equilibria.

The first type of auxiliary reactions which were tried were reactions in which a solid substance gives gaseous chlorine. There are many advantages in the use of this type of equilibrium. In the first place, the pressure change due to the reaction is generally large, un-

like gaseous reactions as will be seen later. In the second place, for the simple case of a solid compound giving chlorine gas and another solid compound, the pressure of the chlorine is fixed at any definite temperature as long as both the solid phases are present. This would make calculations of the dissociation constant of bromine chloride very simple. Various disadvantages of the solid-gas type of auxiliary equilibrium are occasional extreme slowness in reaching equilibrium, the possibility of reactions or solid solutions among the solid phases, and an irreversibility of the reaction due to other further changes of the solid phase.

The first attempt to measure the bromine chloride dissociation was by aid of the equilibrium

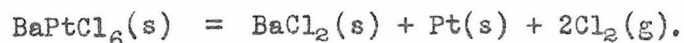


This reaction was found to reach apparent equilibrium very slowly, and then instead of remaining fixed, the pressure continued to change. Only then was it found that this "equilibrium" as it was designated in standard works (9), was only a pseudo-equilibrium, the second reaction which followed the first at once being probably



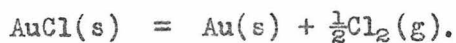
This reaction was abandoned.

The second attempt was made with the help of the equilibrium



Data on this reaction had been obtained in 1922 by Gire (11); this data was checked in our apparatus. Unfortunately bromine seemed to react either with BaPtCl_6 or the reaction products, possibly to form BaPtCl_5Br , or an analogous compound. At any rate this reaction also was abandoned.

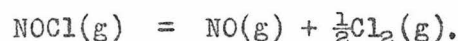
A third attempt was made with the help of the equilibrium (12)



This reaction seemed ideal. The dissociation constants of auric chloride and bromide, and of aurous bromide were known, and were of such an order of magnitude that none of these compounds could exist at the temperatures at which the work was to be done. The gold used was carefully purified from silver, copper, and other ordinary impurities in the standard way, and was finally precipitated as a fine powder with sulphur dioxide. This powder was placed in the reaction vessel and pure dry chlorine from a tank passed over it at such temperatures and pressures that only aurous and not auric chloride could be formed. After pumping out excess gas, the equilibrium data for this reaction were carefully checked, and then a known amount of bromine admitted. Instead of obtaining the large pressure increase to be expected from the formation of bromine chloride and the maintenance of the chlorine pressure, almost no change was found. The experiment was repeated at various temperatures with the same result. No really satisfactory explanation of this fact is known, but possibly a solid solution of aurous bromide in aurous chloride was formed, and was far more stable than pure aurous bromide at this temperature. In support of this it can be mentioned that both silver chloride and bromide, and cuprous chloride and bromide form a complete series of solid solutions with each other (13). In any case, this reaction was also dropped.

4. The Use of the Decomposition of Nitrosyl Chloride as an Auxiliary Reaction.

Nitrosyl chloride decomposes reversibly according to the equation



The thermodynamic data for this reaction have recently been determined by Dixon (14). It is an entirely gaseous reaction and should therefore be free of the difficulties inherent in solid-gas equilibria. Unfortunately the total pressure change for the completed reaction is small since one molecule of nitrosyl chloride gives only $1\frac{1}{2}$ molecules of products. Still worse, the equilibrium is not very sensitive to the chlorine pressure since the latter enters the equilibrium constant expression as a square root while the nitric oxide and the nitrosyl chloride pressures enter as first powers. Because of this, total pressures had to be measured accurately to secure only mediocre accuracy in the bromine chloride constant.

(a) Preparation of Chemicals. The nitrosyl chloride used was prepared by the method outlined by Scott and Johnson (15) without, however, using all the minor refinements which they used for atomic weight work. Dry sulphur dioxide from a tank was passed into fuming nitric acid cooled to 0°C in an all-glass apparatus until all the material solidified to a white crystalline mass. Concentrated sulphuric acid was added to this nitrosylsulphuric acid to dissolve it, and the mixture heated to 100°C on a water bath. Dry air was passed through the hot liquid for about three days till the gas above the clear yellow liquid was entirely free of the brown fumes of nitrogen

dioxide. At this point by turning a greaseless stopcock the gases leaving the mixture were diverted through a new set of tubes protected from moisture of the air by a calcium chloride tube. By cooling these tubes with an ether-solid carbon dioxide mixture while dry hydrogen^{chloride} gas was passed into the solution of nitrosylsulphuric acid, liquid nitrosyl chloride was condensed out. This more or less crude product, contaminated particularly with hydrogen chloride, was distilled back and forth at low pressures between various tubes, a mercury pump protected by a liquid-air trap being connected to the system at all times. The nitrosyl chloride was condensed by an ether-solid carbon dioxide mixture. This series of distillations was believed to separate out the hydrogen chloride, the only impurity present in appreciable amounts, quite effectively. Samples of this nitrosyl chloride were used alone to check the values of the dissociation constant at various temperatures as given by Dixon, which they did within the limits of experimental error. The nitrosyl chloride was finally distilled and sealed into a number of small tubes carrying easily broken tips. From these, as will be described, it passed directly into the reaction chamber.

The bromine used was made by heating pure cupric bromide in an evacuated apparatus, passing the resulting gas through a tube containing potassium bromide to remove chlorine, through various drying tubes, and finally condensing it in a large tube. From this it was poured onto a small watch glass and immediately sucked into a small weighed glass tube with an easily breakable tip, by alternately heating and cooling this tube. The tube was then sealed up and weighed again on an analytical balance to find the amount of bromine in it. The

total weight of the tube was about a gram and of the bromine inside from 0.1 to 0.4 gram.

(b) Apparatus. The furnace in which the reaction tube was heated was constructed according to specifications of the Bureau of Standards (16). It consisted of a copper tube, two inches in diameter, two feet long, and with walls $1/4$ inch thick. This was wrapped in asbestos paper and around this a coil of chromel resistance wire was wound. All this was heavily lagged with a magnesia insulating material. To insure even heating, two copper plugs pierced with holes for inserting thermocouples, etc., were placed in each end of the copper tube. The reaction tube of Pyrex glass had an internal volume of 321.6 cubic centimeters measured by weighing it before and after filling it with water, and also by measuring the volume of water contained with a volumetric flask and a burette. It was connected with parts of the apparatus outside the furnace by means of a capillary tube which ran to the clicker system described above, and to bromine and nitrosyl chloride fillers. These fillers were small tubes of about three cubic centimeters internal volume containing a piece of iron sealed inside a smaller glass tube, and the small tubes containing the bromine and nitrosyl chloride respectively. By the use of a solenoid, the fragile tips of these latter tubes could be broken with the iron hammer. In this way these corrosive gases were admitted to the reaction cell without ever coming in contact with any form of stopcock. Temperatures in the furnace were measured by a calibrated chromel-alumel thermocouple, the electromotive force produced being read on a Leeds and Northrup Type K potentiometer.

(c) Conduct of the Experiments. In making a run, the reaction tube, sealed to the bromine and nitrosyl chloride fillers, to the clicker system, and to a mercury pump, was heated to 500°C., the mercury pump acting meanwhile for several hours. The tube to the pump was then sealed off and the furnace allowed to cool to room temperature. Then the nitrosyl chloride tube was broken, the pressure and temperature of the resulting gas measured carefully several times, and the nitrosyl chloride filler sealed off from the rest of the apparatus. Next the bromine was admitted, the gas in the bromine filler mixed thoroughly by alternately heating and cooling it, and this filler also sealed off. The reaction vessel containing the gases now remained connected only to the clicker system. The total volume of connecting capillaries and clicker outside the furnace was about 1/2 cubic centimeter, a negligible amount compared to the 321.6 cubic centimeter volume of the reaction cell and so no correction was applied for the volume of the gases which remained at room temperature. In making a measurement the temperature of the furnace was held constant for some time and then several pressure readings were taken by means of the clicker. These had to be very closely the same if the measurement was to be considered satisfactory.

(d) Calculation of Results. The data for any given run consists of the pressure of nitrosyl chloride present at some low temperature where no dissociation has taken place, the weight of bromine admitted, and a series of total pressure measurements at various temperatures. An important complication entering into these calculations is the fact that a certain amount of nitrosyl bromide is formed under the experimental conditions. Account must be taken of this fact in the

calculation of the final bromine chloride equilibrium constant. It is easier to do this if a method of successive approximations is used. The total pressure of nitrosyl chloride that would be present at the given temperature if no dissociation had occurred is computed, P_{NOCl}° , and likewise the total pressure of bromine present if no reaction of any sort had taken place, $P_{\text{Br}_2}^{\circ}$. Subtracting the sum of these two from the measured pressure, P , and multiplying the difference by two gives accurately the pressure of nitric oxide actually there, P_{NO} . Subtracting this from the pressure of nitrosyl chloride without dissociation gives roughly the actual pressure of nitrosyl chloride, P_{NOCl}' . By making use of the known equilibrium constant for the nitrosyl chloride dissociation, K_{NOCl} , the real pressure of chlorine, $P_{\text{Cl}_2}^{\circ}$, can be approximately calculated. These operations are summarized in the following equations:

$$P_{\text{NO}} = 2 \left[P - (P_{\text{NOCl}}^{\circ} + P_{\text{Br}_2}^{\circ}) \right] \quad (1)$$

$$P_{\text{NOCl}}' = P_{\text{NOCl}}^{\circ} - P_{\text{NO}} \quad (2)$$

$$P_{\text{Cl}_2}^{\circ} = \frac{K_{\text{NOCl}} P_{\text{NOCl}}'^2}{P_{\text{NO}}^2}$$

Twice this approximate pressure of chlorine subtracted from the nitric oxide pressure gives roughly the pressure of bromine chloride present, P_{BrCl}' . Subtracting half this bromine chloride pressure from the original bromine pressure gives the remaining bromine pressure as a first approximation, P_{Br_2}' . Using this, the known pressure of nitric oxide, and the dissociation constant for nitrosyl bromide, K_{NOBr} , we get our final value for the pressure of the latter, P_{NOBr} .

$$P'_{\text{BrCl}} = P_{\text{NO}} - 2 P'_{\text{Cl}_2} \quad (4)$$

$$P'_{\text{Br}_2} = P^{\circ}_{\text{Br}_2} - \frac{1}{2} P'_{\text{BrCl}} \quad (5)$$

$$P_{\text{NOBr}} = P_{\text{NO}} \sqrt{\frac{P'_{\text{Br}_2}}{K_{\text{NOBr}}}} \quad (6)$$

The values of K_{NOBr} used were those obtained as described in Part III of this thesis. By subtracting the pressure of nitrosyl bromide from the first approximation for the nitrosyl chloride pressure we get the final value for the latter, P_{NOCl} . Using this as in equation (3) we get a final value for P_{Cl_2} . The pressure of bromine chloride is next obtained by adding the nitric oxide and nitrosyl bromide pressures and subtracting twice the chlorine pressure; and the final bromine pressure by subtracting from $P^{\circ}_{\text{Br}_2}$ half the nitrosyl bromide pressure and half the final bromine chloride pressure.

$$P_{\text{NOCl}} = P'_{\text{NOCl}} - P_{\text{NOBr}} \quad (7)$$

$$P_{\text{Cl}_2} = \frac{K_{\text{NOCl}} P_{\text{NOCl}}^2}{P_{\text{NO}}^2} \quad (8)$$

$$P_{\text{BrCl}} = P_{\text{NO}} + P_{\text{NOBr}} - 2 P_{\text{Cl}_2} \quad (9)$$

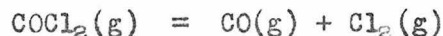
$$P_{\text{Br}_2} = P^{\circ}_{\text{Br}_2} - \frac{1}{2} P_{\text{NOBr}} - \frac{1}{2} P_{\text{BrCl}} \quad (10)$$

Our final equilibrium constant is obtained from the equation

$$K = \frac{P_{\text{Cl}_2} P_{\text{Br}_2}}{P_{\text{BrCl}}^2} \quad (11)$$

5. Use of the Phosgene Decomposition as an Auxiliary Reaction.

In addition to the work with nitrosyl chloride, measurements on the bromine chloride equilibrium were made by Dr. D.M. Yost of this laboratory with the aid of the equilibrium



This reaction, also an entirely gaseous equilibrium, has been studied and its constants quite accurately determined by Bodenstein and Plaut (17). The values of these constants were checked closely by Yost in the apparatus in which the bromine chloride equilibrium was to be studied. In general this apparatus was very similar to that used when the nitrosyl chloride dissociation was the auxiliary reaction. In making a run, first bromine alone was admitted and its pressure measured. Next some chlorine was admitted and the combined pressures of bromine and chlorine measured. Then both these gases were frozen out in liquid air and the desired pressure of carbon monoxide let in. After determining the original pressures of the gases thusly, the reaction cell was heated to various temperatures near and above 400°C, and at these temperatures the total pressure of the mixture of gases accurately determined. From these measurements the dissociation constant of bromine chloride can be computed directly.

These results have the advantage over the results obtained through the use of nitrosyl chloride that the pressure change to be found is considerably larger due to the nature of the auxiliary reaction. Also the computations are direct as compared with the approximations necessary when nitrosyl chloride was used. However, since the dissociation constant of phosgene changes more rapidly with temperature than that of nitrosyl chloride, the temperature had to be con-

trolled more rigidly. In addition to this the dissociation constant of nitrosyl chloride is probably better known than that of phosgene.

6. Results of the Equilibrium Measurements.

The results of the two latest runs using nitrosyl chloride are shown in the following table.

TABLE I

Run	Temperature °Abs	Equilibrium Constant = $\frac{P_{Cl_2} P_{Br_2}}{P_{BrCl}^2}$
4	437	0.24
4	448	0.23
4	454	0.25
4	456	0.25
4	465	0.21
4	476	0.24
4	481	0.24
5	456	0.28
5	485	0.35
5	490	0.22
5	510	0.31
5	537	0.21
5	558	0.31

TABLE II

All pressures in millimeters of mercury

T °Abs	P ^o _{Br₂}	P ^o _{NOCl}	K _{NOCl}	K _{NOBr}	P(meas)	P _{NO}	P _{NOBr}	P _{NOCl}	P _{Cl₂}	P _{BrCl}	P _{Br₂}
Run No. 4											
436.7	142.4	464.5	0.961	2512.	651.5	89.2	19.1	356.2	15.3	77.7	93.9
446.7	145.7	475.1	1.544	3389.	672.3	103.0	18.9	353.2	18.2	85.6	93.4
456.4	148.9	485.5	2.398	4467.	692.5	116.2	18.7	350.6	21.2	91.3	93.8
465.0	151.7	494.6	3.484	5370.	711.8	131.0	19.0	344.6	24.1	101.8	91.3
475.9	155.2	506.2	5.830	6918.	735.7	148.6	19.1	338.5	30.3	107.1	92.0
480.9	156.9	511.2	6.703	7763.	746.3	155.6	18.0	338.0	31.6	110.4	92.7
454.1	148.8	483.1	2.164	4074.	688.3	112.8	19.0	351.3	21.0	89.8	94.4
Run No. 5											
455.6	147.6	358.9	2.314	4295.	553.6	94.2	15.7	250.8	16.4	77.1	101.1
489.8	158.7	385.8	9.484	9772.	615.0	141.0	15.4	229.4	25.1	106.2	97.9
485.4	157.3	382.4	8.013	8710.	604.2	129.0	15.4	238.4	27.4	89.6	104.8
536.9	174.7	423.0	37.90	25120.	698.7	202.0	13.9	207.1	39.8	136.3	99.5
557.7	180.7	439.3	90.85	35480.	738.7	201.9	14.2	187.7	56.8	138.0	104.6
510.7	165.5	402.4	20.37	14790.	651.1	166.4	15.2	220.8	35.9	109.8	103.0

Because these constants show so little trend with temperature we can take the average value for the whole of one run and consider it the equilibrium constant at the mean temperature of the run. These averages are set down in Table III, together with average results using the phosgene equilibrium and results obtained by photometric methods by Murdoch and by Jost.

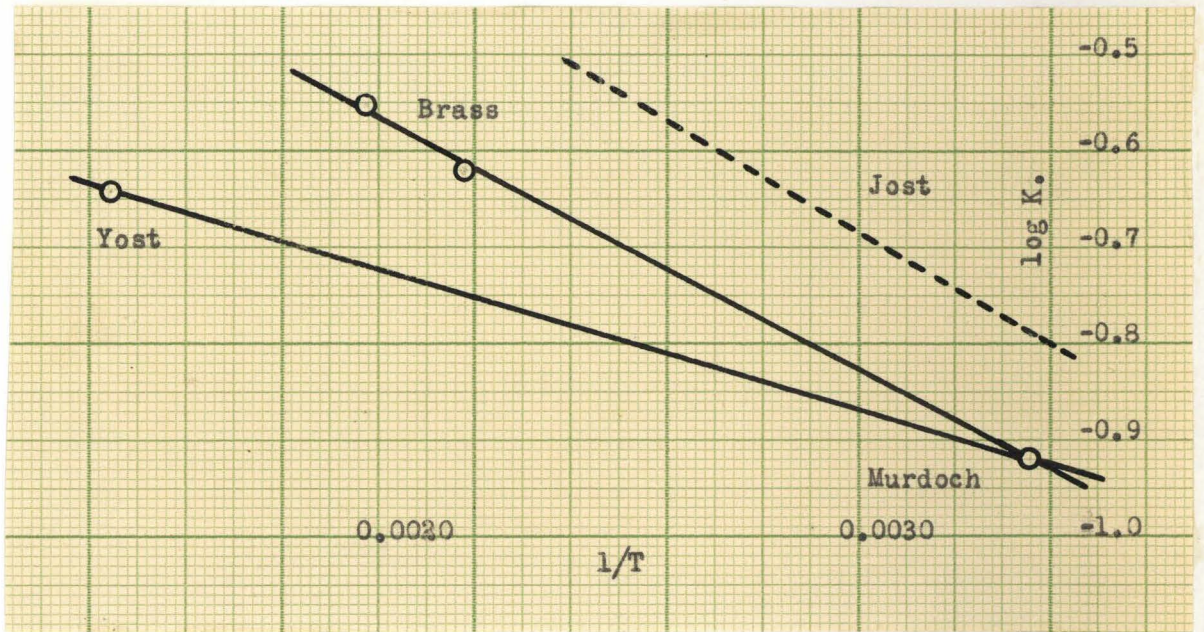
TABLE III

Source	Temperature, °Abs	Equilibrium Constant
Murdoch	298	0.12
Jost	298	0.16
NOCl, Run 4	460	0.24
NOCl, Run 5	506	0.28
Yost, COCl ₂	690	0.23

The logarithms of these constants are plotted against $1/T$ in the figure. The dotted line is the curve given by Jost to represent his measurements.

It is difficult to draw a satisfactory straight line through these points, but if, instead, we assume that the photometric value for the gaseous reaction obtained at room temperature by Murdoch is correct and that (a) the value from the phosgene equilibrium, and (b) the values from the nitrosyl chloride equilibrium are correct, we get the two straight lines shown. From the slopes of these lines ΔH for the reaction can be calculated, since

$$\Delta H = -4.57 \frac{d \log K}{d(1/T)} .$$



Also making use of the fact that

$$\Delta F = \Delta H - T \Delta S$$

and assuming the value of the constant obtained by Murdoch at 298°Abs. to be correct, we get for case (a) $\Delta H = -681$ cal.,

$$\Delta F = -681 - 1.59 T, \text{ and } \Delta S = 1.59 \text{ cal/degree; and for case (b),}$$

$$\Delta H = -1256 \text{ cal., } \Delta F = -1256 + 0.34 T, \text{ and } \Delta S = -0.34 \text{ cal/degree.}$$

From his measurements, Jost finds $\Delta H = -1320$ cal.

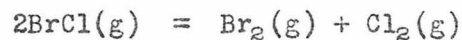
It is obvious that the significance of these calculations is not very great. All that can be said with certainty is that bromine chloride does exist.

7. Calorimetric Measurement of ΔH .

Because of the great uncertainty in the value of ΔH obtained from the equilibrium measurements, it was decided to attempt a calorimetric measurement of this quantity. Due to the unusually small heat effect expected, a sort of flow calorimeter was devised. A stream of chlorine gas was caused to mix with a stream of bromine vapor in a vacuum jacketed, silvered tube which was two centimeters in diameter and a meter long. The temperature of the gases just before entering this tube was measured and at various points within the tube itself it was measured again by means of a glass enclosed thermocouple. It was hoped that the heat of reaction would manifest itself by an ~~occasional~~ increase in the temperature of the gases. It might also be possible by comparing temperatures at various points in the flowing gases to find out something about the rate of the reaction in a way somewhat analogous to that used in Part I of this thesis. These measurements are now in progress, but have not proceeded far enough to make any definite statements about the results.

8. Summary.

(a) Attempts to determine the equilibrium constant of the reaction



by means of pressure measurements have been described. This constant was found to lie somewhere between 0.2 and 0.3 at temperatures near 200°C.

(b) Calculations to determine the thermodynamic constants of this reaction have been given and were shown to be very uncertain.

(c) A projected method for measuring ΔH for the above reaction calorimetrically has been described, and possible applications to rate measurements indicated.

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III. THE DISSOCIATION OF NITROSYL BROMIDE

1. Introduction.

Trautz and Dalal (1) measured the dissociation of nitrosyl bromide at various temperatures using a "cushion" of nitrogen gas between the reaction vessel and a mercury manometer. They obtained results which were not very concordant for the main equilibrium and postulated moreover the existence of nitrosyl dibromide, NOBr_2 , and nitrosyl tribromide, NOBr_3 . Since a rather accurate knowledge of the dissociation constants of nitrosyl bromide was needed for the calculation of the constant of the bromine chloride equilibrium (Part II of this thesis), and since the existence of nitrosyl dibromide and tribromide would change the form of that computation, an investigation was made of the nitrosyl bromide equilibrium. The apparatus used was about the same as that used in the bromine chloride investigation. The nitrosyl chloride filler however was replaced by a large glass bulb carrying stopcocks through which it could be pumped out and filled. It was a storage flask for holding the nitric oxide before letting it into the reaction cell.

2. Preparation of Chemicals.

The bromine used was prepared in the same way as that for the bromine chloride investigation, and was sealed up in the same sort of tubes. The nitric oxide was made by dropping a dilute sulphuric acid solution into a strong solution of sodium nitrite, the evolved gas then passing through a wash bottle containing a strong sodium hydroxide solution, and then through a bottle of concentrated sulphuric acid. From this it was conducted into the storage bulb mentioned above. A side

trap was provided containing sulphuric acid through which the excess nitric oxide could escape if the pressure inside the apparatus became somewhat greater than atmospheric. The various glass tubes of the generating apparatus were connected together with rubber tubing. In filling the storage bulb, this latter was pumped out thoroughly with a mercury pump, nitric oxide meanwhile escaping from the generating apparatus by the side trap, a positive pressure being maintained at all times to keep out air. Then an atmosphere of nitric oxide was admitted to the bulb, and again it was pumped out. This operation was repeated and then a third and final filling was made. Immediately after filling and always thereafter the storage bulb (200 centimeters in diameter) appeared perfectly free of the brown color of nitrogen dioxide which is visible through this thickness in quite high dilutions. In runs No. 1 and No. 4 some nitric oxide was passed at once through the storage vessel to the reaction tube and the latter sealed off immediately. In the other runs the nitric oxide remained in the storage vessel for some days without however becoming colored with nitrogen dioxide as it would have if air had leaked into it.

3. Conduct of a Run.

In making a run, a convenient pressure of nitric oxide was admitted to the evacuated reaction cell, the cell sealed off, and the pressure and temperature accurately measured. Then the small tube containing a known amount of bromine was broken, the gases mixed by heating and cooling the bromine filler, and finally this filler sealed off. Next a series of pressure measurements were made at various temperatures

between 25°C and 300°C by means of the clicker system, the temperature being measured by a calibrated chromel-alumel thermocouple. From these data the dissociation constants for nitrosyl bromide at the various temperatures can be calculated directly.

4. Calculations

From the data obtained on any run the pressure of nitric oxide and bromine which would be present at any given temperature, if no reaction had occurred, can be calculated. If from the sum of these two pressures the measured pressure is subtracted, the difference is the decrease in the pressure of the bromine due to the reaction, and twice this difference is equal to the decrease in pressure of the nitric oxide, and to the existing pressure of nitrosyl bromide.

$$P_{\text{NO}}^{\circ} + P_{\text{Br}_2}^{\circ} - P = \Delta P$$

$$P_{\text{Br}_2}^{\circ} - \Delta P = P_{\text{Br}_2}$$

$$P_{\text{NO}}^{\circ} - 2 \Delta P = P_{\text{NO}}$$

$$2 \Delta P = P_{\text{NOBr}}$$

Having thus obtained the pressures of nitric oxide, of nitrosyl bromide, and of bromine in the equilibrium mixture the constant is calculated by the equation,

$$K = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2}$$

5. Results

Five separate runs were made. Runs No. 1 and No. 5 were made with a ratio of 0.377 mols of bromine to 1.00 of nitric oxide present in the first case, and 0.380 mols of bromine to 1.00 mols of nitric oxide in the second. Runs No. 2, No. 3, and No. 4 were made with ratios of bromine to nitric oxide of 2.70 : 1.00, 2.74 : 1.00 and 2.56 : 1.00, respectively. The greatest chance for experimental error comes in the latter runs where the bromine is far in excess of the nitric oxide. For instance in run No. 4 at 90°C, an error of 0.1 mm. of mercury in the measured pressure causes an error of 2% in K. The logarithms of the constants obtained in runs No. 1, 3, 4, and 5 are shown in the figure plotted against the reciprocal of the absolute temperature. The best fitting straight line has been drawn through these points. The equation for the constant given by Trautz and Dalal gives the dotted line shown in the figure. In the case of run No. 2 the bromine was thought to have been impure since when the whole mixture was heated to 500°C, the total pressure obtained was about 13 mm. greater than to be expected for complete dissociation of the nitrosyl bromide supposedly present. Therefore this run is not included in the plot of results. The results of the most significant runs, No. 1 and No. 5, are given in the following tables, together with the results of runs No. 3 and No. 4.

TABLE I

Run No. 1

T, °Abs	log K (in mm. of Hg)	1/T
295.6	0.874	3.383
334.2	1.755	2.992
346.1	1.996	2.890
360.1	2.248	2.777
372.8	2.515	2.682
396.0	2.769	2.525
423.7	3.223	2.360
447.3	3.506	2.236
472.2	3.756	2.118
512.6	4.159	1.951
557.7	4.441	1.793
583.1	4.520	1.715
437.2	3.388	2.287
301.8	1.012	3.314
319.9	1.442	3.126

Run No. 5

297.7	1.015	3.359
327.4	1.688	3.051
346.1	2.045	2.890
377.3	2.612	2.650
406.6	3.073	2.459
444.9	3.565	2.247
489.3	4.050	2.045

Run No. 3

300.8	1.091	3.324
307.3	1.317	3.255
349.1	2.138	2.864
455.4	3.816	2.196

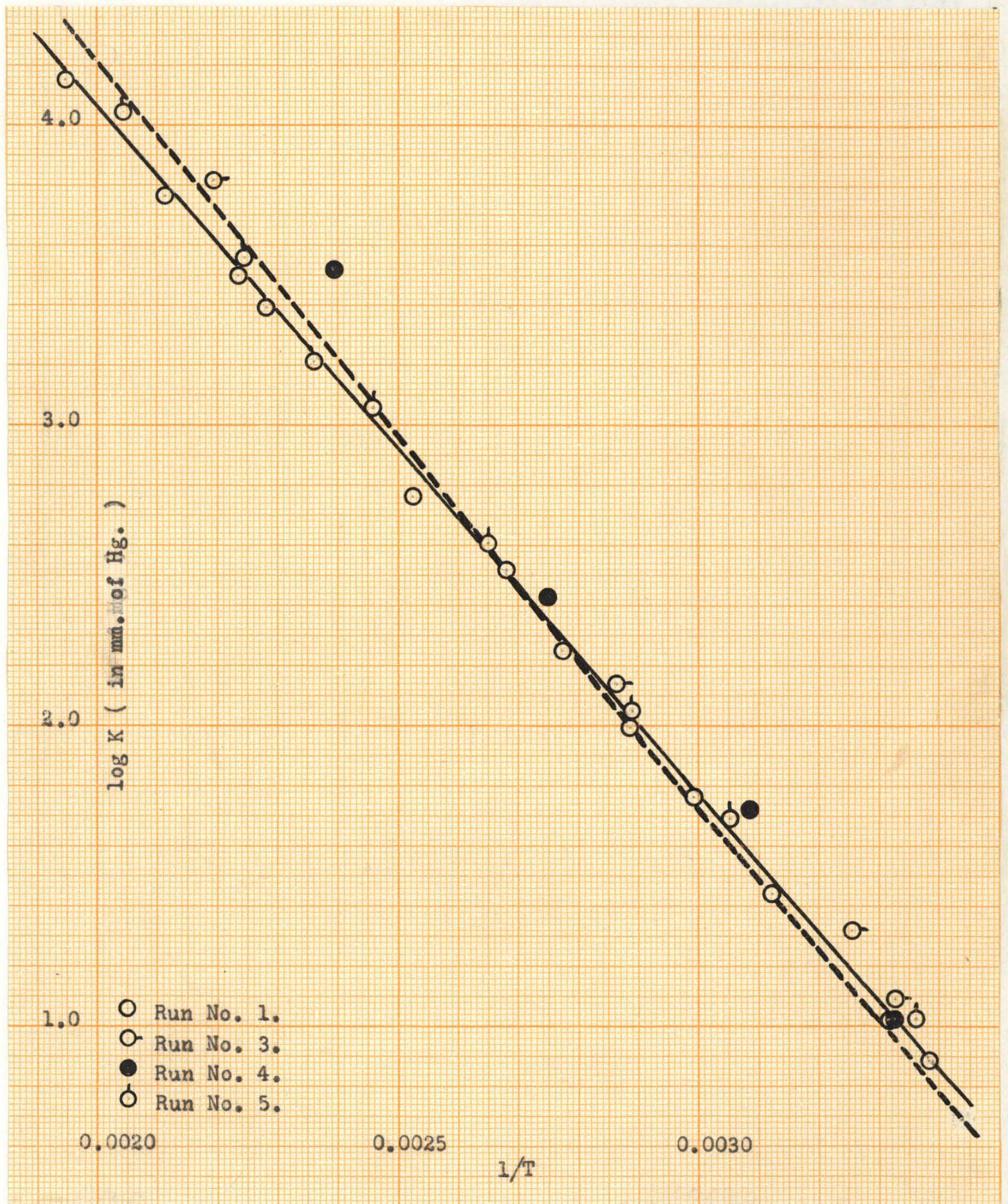
Run No. 4

300.7	1.0173	3.326
324.2	1.7166	3.085
363.5	2.4269	2.751
417.8	3.5253	2.393

TABLE II

All pressures in millimeters of mercury

T °Abs	P° Br ₂	P° NO	P(measured)	P Br ₂	P NO	P NOBr
Run No. 1						
295.6	42.7	113.3	124.7	11.4	50.7	62.6
334.2	48.3	128.1	151.4	23.3	78.1	50.0
346.1	50.0	132.6	159.8	27.2	87.0	45.6
360.1	52.0	138.0	169.4	31.4	97.8	41.2
372.8	52.6	142.8	177.8	35.0	107.6	35.2
396.0	57.2	151.7	193.0	41.3	119.9	31.8
423.7	61.2	162.4	211.7	49.3	138.6	23.8
447.3	64.6	171.4	226.1	54.7	151.6	19.8
472.2	68.2	180.9	240.7	59.8	164.1	16.8
512.6	74.0	196.4	264.1	67.7	183.8	12.6
557.7	80.5	213.7	288.9	75.2	203.1	10.6
583.1	84.2	223.4	302.4	79.0	213.0	10.4
437.2	63.1	167.5	219.9	52.4	146.1	21.4
301.8	43.6	115.6	128.6	13.0	54.4	61.2
319.9	46.2	122.6	141.2	18.6	67.4	55.2
Run No. 5						
297.7	47.8	125.7	139.7	14.0	58.1	67.6
327.4	52.5	138.2	162.2	24.0	81.2	57.0
346.1	55.5	146.1	176.5	30.4	95.9	50.2
377.3	60.5	159.8	200.6	41.3	120.9	38.4
406.6	65.2	171.6	222.1	50.5	142.2	29.4
444.9	71.4	187.8	248.5	60.7	166.4	21.4
489.3	78.5	206.5	277.4	70.9	191.3	15.2
Run No. 3						
300.8	200.5	73.3	244.9	171.6	15.1	57.8
307.3	204.8	75.5	251.8	176.9	19.1	55.8
349.1	232.8	85.8	294.4	209.3	38.1	47.0
455.4	303.6	111.9	404.9	293.9	91.6	19.4
Run No. 4						
300.7	210.6	82.8	259.9	187.1	15.8	67.0
324.2	227.0	89.3	286.8	197.5	30.3	59.0
363.5	254.6	100.1	330.6	230.5	51.9	48.2
417.8	292.6	115.1	394.8	279.7	89.3	25.8



6. Conclusions.

From the slope of the solid line in the figure ΔH at 100°C , the mean temperature of the runs, for the reaction



is found to be 10,640 calories per mol. In the absence of data on the specific heat of nitrosyl bromide it may be assumed the same as that of carbon dioxide. The heat capacity at constant pressure of two mols of carbon dioxide or nitrosyl bromide at 150°C is 19.24 cal/ $^\circ\text{C}$, of two mols of nitric oxide 13.75 cal/ $^\circ\text{C}$, and of one mol of bromine 7.77 cal/ $^\circ\text{C}$. Therefore ΔC_p for the reaction is 2.28 cal/ $^\circ\text{C}$. Since $\Delta H = \Delta H_0 + \Delta C_p T$, we find from the value of ΔH at 100°C that $\Delta H_0 = 9,790$ cal. Then the equation for the heat of reaction becomes

$$\Delta H = 9790 + 2.28 T$$

The equation for the free energy change in a chemical reaction is

$$\Delta F = \Delta H_0 - \Delta C_p T \ln T + IT$$

$$\text{Since } \Delta F_{373^\circ} = -R T \ln K_{373^\circ}$$

$$= 2.308 R T \cdot 0.36$$

$$= 615 \text{ cal.},$$

$$I = -10.82 \text{ cal}/^\circ\text{C}$$

Therefore, for the dissociation of nitrosyl bromide,

$$\Delta F = 9790 - 2.33 T \ln T - 10.82 T.$$

Although runs No. 2, 3, and 4 were made with a very large excess of bromine present at room temperature, no indication of a higher bromide than NOBr was found. Indeed any variation from the solid line obtained in these runs was opposite in direction to what

would have been obtained had nitrosyl dibromide or tribromide been present. In the light of these facts we can only conclude that these two bromides do not exist in the gas phase at room temperature.

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