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## Oxygen and Nitrogen Isotope Effects in the Decomposition of Ammonium Nitrate\*

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The isotopic composition of the products of the controlled thermal decomposition of ammonium nitrate has been studied. It has been found that small amounts of water are necessary to initiate the decomposition of ammonium nitrate.  $N^{15}H_4NO_3$  has been found to yield exclusively the isomer  $N^{15}N^{14}O$ . Some inferences are drawn from this observation regarding the mechanism of the reaction.

Oxygen and nitrogen isotope effects accompanying the decomposition have been studied with material of "natural" isotopic composition. Satisfactory agreement is found between the experimental results and theoretical calculations.

A method for the isotopic analysis of nitrates for  $O^{18}$  is outlined.

## I. INTRODUCTION

AS part of a program aimed at studying the effect of isotopic substitution on chemical equilibria and the rates of chemical reactions, we have investigated the decomposition of ammonium nitrate for nitrogen and oxygen isotope effects both during the course of the reaction and at complete decomposition. In the course of our work we have made some observations which are pertinent to the mechanism of the decomposition. We have prepared a sample of  $N_2O$  containing enriched  $N^{15}$  in the end position exclusively. In view of the current status of the analysis of the vibrational spectrum of  $N_2O$ ,<sup>1</sup> we have investigated the infrared spectrum of  $N^{15}N^{14}O^{16}$ . A similar and concurrent investigation of the infra-red spectrum has been carried out by Richardson and Wilson.<sup>2</sup> At present we are studying the infra-red spectrum of  $N^{14}N^{15}O^{16}$ , and the results of the spectroscopic study of these two isomers as well as their thermodynamic properties will be communicated shortly. The results of the study of the isotope effects accompanying the decomposition are presented in this paper.

II. DECOMPOSITION OF  $NH_4NO_3$ 

The decomposition of ammonium nitrate has been investigated repeatedly.<sup>3</sup> In the temperature region between 180–300°C pure molten ammonium nitrate decomposes according to the equation



We wish to record here an observation which has not been described previously. A three-gram sample of J. T. Baker's "C.P. Analyzed"  $NH_4NO_3$  was put into a glass apparatus shown schematically in Fig. 1. The sample was held at approximately 150°C and pumped overnight by the mercury diffusion pump. The system

closed off from the pump was capable of maintaining a vacuum of better than  $10^{-6}$  mm over a period of hours. During the pumping operation all of the ammonium nitrate sublimed to the cool portion of the tube above the furnace. The furnace was then raised and the temperature gradually increased over a period of hours to about 300°C. There was no decomposition detectable manometrically with the reservoir bulbs shut off from the system. The furnace was removed and a small amount of water vapor was admitted to the system. The furnace was then replaced around the tube containing the  $NH_4NO_3$  and the decomposition commenced at about 180°C. The experiment was completely reproducible, and we find that ammonium nitrate which has been thoroughly dried does not decompose up to 300°C. A similar experiment was tried using dry  $N_2O$ . The  $N_2O$  sufficed to prevent sublimation but did not induce the decomposition.

A qualitative experiment was carried out to determine the role of the water in initiating the reaction. A small amount (4 cc at N.T.P.) of water vapor containing 1.5 percent  $H_2O^{18}$  was used to initiate the decomposition of a three-gram sample of  $NH_4NO_3$ . The reaction was continued until about 4 cc of  $N_2O$  were produced. The  $N_2O$  was examined mass spectrometrically and the  $O^{18}/O^{16}$  ratio was within 0.3 percent of that found in  $N_2O$  samples obtained from the decomposition initiated by ordinary water. From this we conclude that the water does not enter into reactions which lead directly to the formation of  $N_2O$ .

Apart from our observations on the catalytic effect of water, our experimental results on the decomposition are in agreement with those of Kretzschmar.<sup>3c</sup> In our experiments the water from the decomposition was removed in trap A, which was cooled to  $-80^\circ C$  after the decomposition had been initiated by the addition of small amounts of water. The gas, non-condensable at  $-80^\circ C$ , was 98 percent  $N_2O$ ; the remainder was  $N_2$  and may have contained some  $O_2$ .

Kummer<sup>4</sup> has reported some isotopic analyses of nitrogen produced by the reduction of  $N_2O$ , formed from the decomposition of 62 percent  $N^{15}H_4NO_3$ , by

\* J. T. Kummer, J. Am. Chem. Soc. 69, 2559 (1947).

\* Research carried out under the auspices of the AEC.

<sup>1</sup> See G. Herzberg, *Infrared and Raman of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 174.

<sup>2</sup> W. S. Richardson and E. B. Wilson, Jr., J. Chem. Phys. 18, 694 (1950).

<sup>3</sup> See (a) H. L. Saunders, J. Chem. Soc. 121, 698 (1922); (b) M. S. Shah and T. M. Oza, *ibid.* 725 (1932); (c) W. Kretzschmar, Zeits. f. anorg. u. allgem. Chemie 219, 17 (1934); (d) H. Tramm and H. Velde, Angew. Chem. 47, 782 (1934).

iron at room temperature. Kummer finds 0.35 percent  $N^{15}N^{15}$  in the nitrogen as against the expected 0.24 percent if the ammonium ion reacted with the nitrate ion by an N-N bond formation. If the  $N_2O$  were formed from some intermediate such as nitroxyl, Eqs. (3a) and (4a) below, the nitrogen analyzed by Kummer would contain 9.6 percent  $N^{15}N^{15}$ , which figure would also be expected for any mechanism in which the ammonium and nitrate nitrogen atoms become randomly mixed. His results therefore rule out the possibility that  $N_2O$  is formed by an oxidation-reduction mechanism of the type



but they furnish no evidence for or against an alternative oxidation-reduction mechanism proceeding through hyponitrous acid.



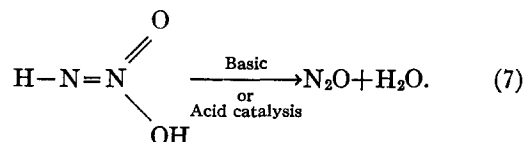
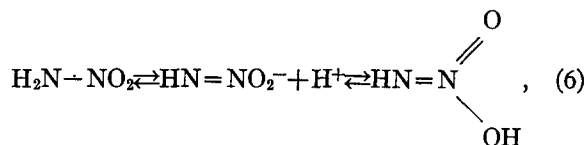
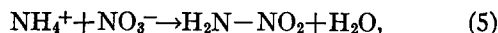
The production of  $N_2O$  from hyponitrous acid predicts equal amounts of the isomers  $N^{15}N^{14}O$  and  $N^{14}N^{15}O$ , apart from small isotope effects, unless one postulates an unsymmetrical structure for hyponitrous acid. Most of the evidence points to the structure  $HONNOH$  for this acid.<sup>5,6</sup>

From Kummer's experiment it is not possible to determine which of the isomers  $N^{15}N^{14}O^{16}$  or  $N^{14}N^{15}O^{16}$  or whether a mixture of these isomers is formed from the decomposition of  $N^{15}H_4N^{14}O_3$ . By means of microwave spectroscopy, Richardson and Wilson<sup>2</sup> have established that  $N^{15}N^{14}O^{16}$  is formed from the decomposition of  $N^{15}H_4N^{14}O_3$ . We have also established this fact independently with the mass spectrometer. A sample of

$N_2O$  was prepared from  $NH_4NO_3$  containing 7.5 percent  $N^{15}$  in the  $NH_4^+$  ion. The  $N^{15}H_4NO_3$  was obtained from the Eastman Kodak Company. A 2.4-gram sample was decomposed after thorough evacuation drying and then the addition of trace amounts of water. The  $N_2O$  was collected and analyzed mass spectrometrically in a Consolidated-Nier "Isotope Ratio" mass spectrometer. The results of the analyses are given in Table I.

If the isomer  $N^{15}N^{14}O^{16}$  is produced then the intensity ratio of 31/30, corresponding to the  $NO^+$  ions, should be that due to normal  $N^{15}$  and  $O^{17}$  isotopic abundance or 0.0042.<sup>†</sup> On the other hand, if the isomer  $N^{14}N^{15}O^{16}$  is produced, then the 31/30 ratio for this experiment should be 0.0830. If a mixture of the two isotopic isomers is formed, the the 31/30 ratio will measure their relative abundances. The possibility of rearrangement on electron impact in the mass spectrometer may give a value intermediate between 0.0042 and the 45/44 ratio corrected for the presence of two N atoms in  $N_2O$ , even if an authentic sample of  $N^{15}N^{14}O^{16}$  were analyzed. However, fortunately such rearrangements appear to be uncommon and, where they do occur, they are usually less than 10 percent of the more normal simple rupture of chemical bonds by electron impact. It is clear from the data in Table I that our sample contains less than seven percent of the  $N^{15}$  from the  $NH_4^+$  in the form of the isomer  $N^{14}N^{15}O^{16}$ . The fact that the 31/30 ratio is 0.010 rather than 0.0042 may be due either to production of  $N^{14}N^{15}O$  in the course of the decomposition reaction or to production of  $N^{15}O^+$  ions from  $N^{15}N^{14}O$  by electron impact or a combination of both. Richardson and Wilson<sup>2</sup> have shown by microwave spectroscopy that no  $N^{14}N^{15}O$  above that expected from the normal abundance of  $N^{15}$  in nitrate is formed in the decomposition of  $N^{15}H_4N^{14}O_3$ . Therefore we infer that there is a seven percent rearrangement on electron impact.

Our results, as well as those of Kummer<sup>4</sup> and Richardson and Wilson,<sup>2</sup> lead us to suggest that the decomposition of ammonium nitrate proceeds by a dehydration mechanism:



Reactions (6) and (7) are the mechanisms which have

<sup>†</sup> This value is calculated from the data in Table II, the "natural" abundance of  $O^{17}$ , and an average value for certain instrumental factors.

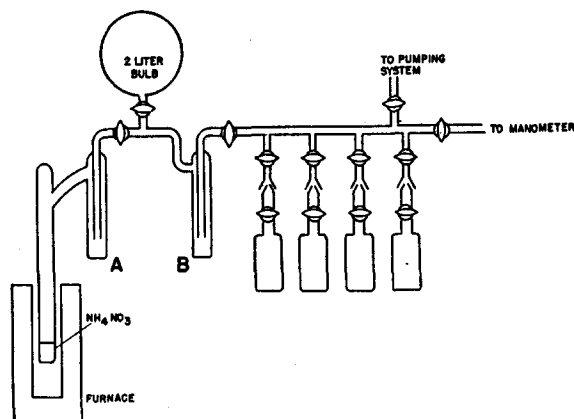


FIG. 1. Vacuum line for the decomposition of ammonium nitrate (schematic).

<sup>5</sup> E. C. E. Hunter and J. R. Partington, J. Chem. Soc. 309 (1933).

<sup>6</sup> A. Hantzsch, Ber. 66, 1555 (1933).

been proposed to explain the acidic<sup>7</sup> and basic<sup>8</sup> catalysis in the decomposition of nitramide. From our analyses of the N<sub>2</sub>O formed from the decomposition of N<sup>15</sup>H<sub>4</sub>N<sup>14</sup>O<sub>3</sub> and Kummer's analysis of the N<sub>2</sub> formed on reduction we conclude that the N—N bond is not broken in the adsorption and reduction of N<sub>2</sub>O on catalytic iron at room temperature.

### III. N<sup>15</sup> AND O<sup>18</sup> ISOTOPE EFFECTS IN THE DECOMPOSITION OF NH<sub>4</sub>O<sub>3</sub>. THE ISOTOPIC COMPOSITION OF NH<sub>4</sub>NO<sub>3</sub>

#### A. Experimental

Prior to measurement of the O<sup>18</sup> isotope effect on the decomposition, we have reinvestigated and extended the exchange study of oxygen between N<sub>2</sub>O and water. Previous investigation by density measurements on water slightly enriched in O<sup>18</sup> showed no exchange between N<sub>2</sub>O and water in 14 days at 20°C.<sup>9</sup> Our experiments were carried out with 1.5 percent H<sub>2</sub>O<sup>18</sup> and the N<sub>2</sub>O was analyzed mass spectrometrically. We find 0.26 percent exchange in three days at 24±1°C between N<sub>2</sub>O gas and liquid water. At 195±2°C we find 0.68 percent exchange in 22 hours between water vapor at a partial pressure of 0.8 atmospheres and N<sub>2</sub>O at a partial pressure of 0.0017 atmospheres. Thus the exchange between N<sub>2</sub>O and water is negligible under the conditions of our experiments.

It is not surprising that N<sub>2</sub>O exchanges slowly with water. Solutions of N<sub>2</sub>O in water show no acidic properties<sup>10</sup> despite the fact that N<sub>2</sub>O is the stoichiometric anhydride of hyponitrous acid and is formed from the decomposition of the latter. Furthermore, N<sub>2</sub>O is salted out of water by all electrolytes, including bases, except nitric acid.<sup>10,11</sup>

The decomposition reactions were carried out by the method described in Section II. The decomposition temperature was 220°±20°C. Temperature control was difficult because of the large heat evolved in the reaction. The N<sub>2</sub>O formed after one percent decomposition was collected in a bulb. The reaction was then carried to completion and the N<sub>2</sub>O and water were separated continuously by cold traps. The N<sub>2</sub>O was purified by the use of cold traps from the small amounts of nitrogen and oxygen that arise from side reactions and analyzed as N<sub>2</sub>O. The water was equilibrated with CO<sub>2</sub> and analyzed according to the method described by Cohn and Urey.<sup>12</sup> It does not seem feasible to obtain and analyze the water at one percent decomposition. Each sample was analyzed at least three times in a Consoli-

TABLE I. Analysis of N<sub>2</sub>O prepared from 7.5 percent N<sup>15</sup>H<sub>4</sub>N<sup>14</sup>O<sub>3</sub>.

Peak ratio measured	Ion	Ratio
45/44	N <sub>2</sub> O <sup>+</sup>	0.0869
31/30	NO <sup>+</sup>	0.010
29/28	N <sub>2</sub> <sup>+</sup>	0.081

dated-Nier "Isotope Ratio" mass spectrometer. The reproducibility of the analyses was better than 0.3 percent of the ratio measured.

The Consolidated-Nier "Isotope Ratio" mass spectrometer is a dual collector instrument and is used to measure isotope ratios directly. In the analysis for N<sup>15</sup> in N<sub>2</sub>O, measurements can be made by measuring the 45/44 ratio directly. Analysis for O<sup>18</sup> in either N<sub>2</sub>O or CO<sub>2</sub> can be made by measuring the 46/44+45 ratio and correcting for the 45/44 ratio. The intercomparison of samples with nearly identical isotopic composition can be made with little error by comparison of the directly determined ratios. Samples of widely different isotopic composition were compared only after correction for incomplete resolution on the isotopic peaks of 45 and 46 from the normal peak at 44 and the relative efficiencies of collection and amplification through the two collectors. The intercomparison between O<sup>18</sup>/O<sup>16</sup> in N<sub>2</sub>O and CO<sub>2</sub> is made here after direct experimental determination of these factors. No correction need be made for a possible mass discrimination effect because both O<sup>18</sup>/O<sup>16</sup> ratios are derived from 46/44 ratios. The intercomparison between N<sub>2</sub>O samples for 45/44 and 46/44+45 is made from the uncorrected ratios. The resolution corrections and collector efficiencies remained constant during the determination of these uncorrected ratios. This was demonstrated by the reproducibility of the measurements and alternate measurements of standard samples of N<sub>2</sub>O and CO<sub>2</sub>.

The ratio of O<sup>18</sup>/O<sup>16</sup> in N<sub>2</sub>O is given by Eq. (8).

$$\frac{O^{18}}{O^{16}} = \frac{N^{14}N^{14}O^{18} + N^{15}N^{14}O^{18} + N^{14}N^{15}O^{18} + N^{15}N^{15}O^{18}}{N^{14}N^{14}O^{16} + N^{15}N^{14}O^{16} + N^{14}N^{15}O^{16} + N^{15}N^{15}O^{16}} = \frac{N^{14}N^{14}O^{18}}{N^{14}N^{14}O^{16}} \quad (8)$$

The experimentally determined 46/(44+45) and 45/44 ratios are given by Eqs. (9) and (10).

$$\frac{46}{44+45} = \frac{N^{14}N^{14}O^{18} + N^{15}N^{14}O^{17} + N^{14}N^{15}O^{17} + N^{15}N^{15}O^{16}}{N^{14}N^{14}O^{16} + N^{15}N^{14}O^{16} + N^{14}N^{15}O^{16} + N^{14}N^{14}O^{17}} \quad (9)$$

$$\frac{45}{44} = \frac{N^{15}N^{14}O^{16} + N^{14}N^{15}O^{16} + N^{14}N^{14}O^{17}}{N^{14}N^{14}O^{16}} \quad (10)$$

For samples containing O<sup>17</sup> close to natural abundance

<sup>7</sup> C. A. Marlies and V. K. La Mer, J. Am. Chem. Soc. **57**, 1812 (1935).

<sup>8</sup> K. J. Pederson, J. Phys. Chem. **38**, 581 (1934).

<sup>9</sup> Winter, Carlton, and Briscoe, J. Chem. Soc. **131** (1940).

<sup>10</sup> G. Geficken, Zeits. f. physik. Chem. **49**, 301 (1904).

<sup>11</sup> G. Lunge, Ber. **14**, 2188 (1881); W. Knopp, Zeits. f. physik. Chem. **48**, 97 (1904); W. Manchot, M. Johrstorfer and H. Zepter, Zeits. f. anorg. Chemie **141**, 45 (1924).

<sup>12</sup> M. Cohn and H. C. Urey, J. Am. Chem. Soc. **60**, 679 (1938).

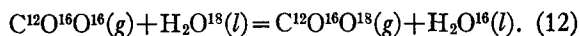
TABLE II. Isotopic analysis of N<sub>2</sub>O and H<sub>2</sub>O formed in the decomposition of ammonium nitrate.

Sample analyzed	Ratio reported	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
Tank CO <sub>2</sub>	C <sup>12</sup> O <sup>16</sup> O <sup>18</sup> /C <sup>12</sup> O <sub>2</sub> <sup>16</sup> Corrected	422.4±0.3×10 <sup>-5</sup>	422.0±0.5×10 <sup>-5</sup>		
CO <sub>2</sub> from H <sub>2</sub> O equilibration	C <sup>12</sup> O <sup>16</sup> O <sup>18</sup> /C <sup>12</sup> O <sub>2</sub> <sup>16</sup> Corrected	432.7±0.6×10 <sup>-5</sup>	431.8±0.4×10 <sup>-5</sup>		
N <sub>2</sub> O complete reaction (t <sub>∞</sub> )	N <sup>14</sup> N <sup>14</sup> O <sup>18</sup> /N <sup>14</sup> N <sup>14</sup> O <sub>2</sub> <sup>16</sup> Corrected	212.6±0.2×10 <sup>-5</sup>	212.5±0.5×10 <sup>-5</sup>		
N <sub>2</sub> O One percent decomposition (t <sub>ε</sub> )	N <sup>14</sup> N <sup>14</sup> O <sup>18</sup> /N <sup>14</sup> N <sup>14</sup> O <sub>2</sub> <sup>16</sup> Corrected		213.5±0.2×10 <sup>-5</sup>		
N <sub>2</sub> O t <sub>ε</sub>	46/44+45 Uncorrected			232.7±0.5×10 <sup>-5</sup>	
N <sub>2</sub> O t <sub>∞</sub>	46/44+45 Uncorrected			233.8±0.4×10 <sup>-5</sup>	
N <sub>2</sub> O t <sub>ε</sub>	45/44 Uncorrected			875.0±2.7×10 <sup>-5</sup>	866.5±0.3×10 <sup>-5</sup>
N <sub>2</sub> O t <sub>∞</sub>	45/44 Uncorrected			880.8±1.0×10 <sup>-5</sup>	873.4±0.5×10 <sup>-5</sup>
	$\left(\frac{45}{44}\right)_{t_{\infty}} / \left(\frac{45}{44}\right)_{t_{\epsilon}}$			1.007±0.004	1.008±0.001
	$\left(\frac{46}{44}\right)_{t_{\infty}} / \left(\frac{46}{44}\right)_{t_{\epsilon}}$		0.9953±0.003	1.0047±0.004	
	(H <sub>2</sub> O <sup>18</sup> /H <sub>2</sub> O <sup>16</sup> ) <sub>t<sub>∞</sub></sub>	208.0±0.3×10 <sup>-5</sup>	207.6±0.2×10 <sup>-5</sup>		
	$\left(\frac{N_2O^{18}}{N_2O^{16}}\right) / \left(\frac{H_2O^{18}}{H_2O^{16}}\right)_{t_{\infty}}$	1.022±0.003	1.024±0.003		

we get from Eqs. (9) and (10)

$$\frac{N^{14}N^{14}O^{18}}{N^{14}N^{14}O^{16}} = \frac{46}{44+45} \left( 1 + \frac{45}{44} \right) - \frac{1}{4} \left( \frac{45}{44} - 0.0004 \right)^2 - (0.0004) \frac{45}{44} \quad (11)$$

For the analysis of water by the equilibration method of Cohn and Urey<sup>12</sup> we need the ratio C<sup>12</sup>O<sup>16</sup>O<sup>18</sup>/C<sup>12</sup>O<sub>2</sub><sup>16</sup>O<sup>16</sup> and the equilibrium constant for the reaction



For CO<sub>2</sub> with both C<sup>13</sup> and O<sup>17</sup> close to natural abundance the ratio C<sup>12</sup>O<sup>16</sup>O<sup>18</sup>/C<sup>12</sup>O<sub>2</sub><sup>16</sup>O<sup>16</sup> is given by Eq. (13).

$$\frac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{16}} = \frac{46}{44+45} \left( 1 + \frac{45}{44} \right) - (0.0008) \frac{45}{44} - (0.0004)^2. \quad (13)$$

The samples of water and CO<sub>2</sub> were equilibrated at 24°C and the equilibrium constant (12) was taken as 2×(1.040).<sup>12-14</sup>

The results of the analysis are given in Table II. The reproducibility of the analysis between the different samples was better than 0.3 percent of the ratio. None of the ratios reported should be considered absolute ratios because of an undetermined mass discrimina-

tion effect. There is a fortuitous agreement between our 46/44 ratio for tank CO<sub>2</sub> and Thode's<sup>15</sup> results for CO<sub>2</sub> equilibrated with Lake Ontario water (422±1×10<sup>-5</sup>). From the analysis of samples 2 and 3 we conclude that the O<sup>18</sup> content of the N<sub>2</sub>O does not change by more than one-half of one percent during the course of the decomposition. Thus the isotopic analysis of any sample of N<sub>2</sub>O from the decomposition of NH<sub>4</sub>NO<sub>3</sub> can be used to analyze nitrates for O<sup>18</sup>. In most cases it might be preferable to analyze nitrates by analysis of the water formed in the decomposition because the precision of CO<sub>2</sub> analysis is in general better than N<sub>2</sub>O analyses and N<sub>2</sub>O pumps out of the mass spectrometer extremely slowly. Samples of N<sub>2</sub>O with abnormal isotopic composition will introduce a memory effect because of the latter fact.

From the CO<sub>2</sub> and N<sub>2</sub>O analyses performed on samples 1 and 2, the fact that tank CO<sub>2</sub> is in equilibrium with fresh water,<sup>12,14</sup> and the stoichiometry of Eq. (1), we can compare the O<sup>18</sup> content of our ammonium nitrate sample with that of fresh water. We get as the average of these two samples the ratio of O<sup>18</sup> to O<sup>16</sup> in ammonium nitrate compared to the similar ratio in fresh water 3×(1.032±0.003). The ammonium nitrate used in this investigation is reported to be entirely of synthetic origin.<sup>16</sup> Synthetic nitrates have most of their

<sup>15</sup> H. G. Thode, Report No. MC-57, National Research Council of Canada, McMaster University, Hamilton, Ontario (April 29, 1944). Also reported by K. T. Bainbridge to the Seventh International Solvay Congress on Chemistry. R. Stoops, Editor, *Rapports et Discussions sur Les Isotopes* (Brussels, 1948), p. 84.

<sup>16</sup> Private communication from Dr. J. R. Stevens, J. T. Baker Chemical Co.

<sup>12</sup> Weber, Wahl, and Urey, J. Chem. Phys. 3, 129 (1935).

<sup>14</sup> H. C. Urey, J. Chem. Soc. 562 (1947).

oxygen derived from atmospheric oxygen, which Dole<sup>17</sup> has shown to be enriched in O<sup>18</sup> over fresh water by 1.030. This is very close to the enrichment found in our nitrate sample. In view of the fact that nitrates do not exchange oxygen with water<sup>18</sup> we conclude that the fractionation in the catalytic synthesis of nitrates is small. Detailed calculations would require more extensive knowledge than is available of the actual processes in the synthesis plants.

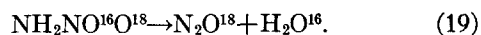
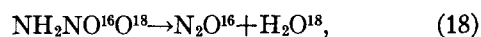
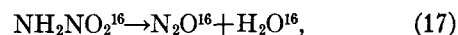
In the intercomparison of the abundance of O<sup>18</sup> in nitrous oxide and water formed from the decomposition of ammonium nitrate as determined from N<sub>2</sub>O<sup>18</sup>/N<sub>2</sub>O<sup>16</sup> and CO<sup>16</sup>O<sup>18</sup>/CO<sub>2</sub><sup>16</sup> respectively we have made the tacit assumption that if there is any isotope effect in the production of the parent ions by electron impact in the mass spectrometer it is the same in both cases. A theoretical estimate of the magnitude of this effect, based on the assumption that there is no isotope effect on the total ions produced by electron impact and a five percent O<sup>18</sup> isotope effect on bond rupture, indicates that the O<sup>18</sup>/O<sup>16</sup> ratio in N<sub>2</sub>O may be too high by as much as one percent. Therefore the assumption with regard to equal isotope effect on the production of the parent ions N<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup> was investigated experimentally. From the data in Table II we find that the ratio of (N<sub>2</sub>O<sup>18</sup>)/(N<sub>2</sub>O<sup>16</sup>)<sub>∞</sub>/(H<sub>2</sub>O<sup>18</sup>)/(H<sub>2</sub>O<sup>16</sup>)<sub>fresh water</sub> is 1.047 ± 0.003. This ratio is based on the N<sub>2</sub>O and tank CO<sub>2</sub> analyses, the equilibrium constant K<sub>12</sub>, and the assumption of no difference in the electron impact isotope effect on the parent ions N<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup>. A sample of N<sub>2</sub>O was decomposed completely to nitrogen and oxygen in a quartz vessel at 1000°K. The O<sup>18</sup> in the oxygen was compared with the O<sup>18</sup> content of atmospheric oxygen by measurement of 34/32+33 ratios. As a result of this intercomparison and Dole's determination of the relative abundance O<sup>18</sup> in atmospheric oxygen and fresh water by density measurements,<sup>17</sup> we get (N<sub>2</sub>O<sup>18</sup>)/(N<sub>2</sub>O<sup>16</sup>)<sub>∞</sub>/(H<sub>2</sub>O<sup>18</sup>)/(H<sub>2</sub>O<sup>16</sup>)<sub>fresh water</sub> is equal to 1.045 ± 0.003. The agreement for this ratio as determined by the latter method, which is independent of the equilibrium constant K<sub>12</sub> and the assumption concerning isotope effects in the production of parent ions, with the ratio calculated from Table II is within the limit of our experimental errors and the uncertainty in K<sub>12</sub>. For the parent ions N<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup> we may therefore neglect any difference in the ratios N<sub>2</sub>O<sup>18</sup>/N<sub>2</sub>O<sup>16</sup> and CO<sup>16</sup>O<sup>18</sup>/CO<sub>2</sub><sup>16</sup> arising from isotope effects on electron impact. The agreement of the intercomparison of O<sup>18</sup> in nitrous oxide and fresh water by these two methods serves as a good check on the reliability of the data in Table II.

### B. Theoretical

The experimental results on the nitrogen isotope effect cannot be interpreted unambiguously. The

nitrogen isotope effect measured at small amounts of reaction is an undetermined combination of two effects: N<sup>15</sup> substitution in the ammonium ion and N<sup>15</sup> substitution in the nitrate ion. The effect of N<sup>15</sup> substitution in each ion has yet to be determined. For this reason, as well as the fact that our knowledge of the mechanism and the kinetics of the decomposition reaction is meager, no calculations of the nitrogen isotope effect have as yet been carried out.

In spite of the limitations of our knowledge of the mechanism and kinetics of the decomposition, some interesting predictions can be made about the oxygen isotope effects from some rather general models of the activated complex and the mechanism of the reaction. For the purpose of the calculations we assume that the reaction proceeds by the successive elimination of two molecules of water from one ammonium ion and one nitrate ion. The intermediate chemical species may be nitramide or some other substance. The oxygen bound to the nitrogen is assumed to be in the form of a nitro group. This mechanism is consistent with our results on the decomposition of N<sup>15</sup>H<sub>4</sub>NO<sub>3</sub>. The following equations are assumed for the purpose of calculation



We shall assume that the nitramide or analogous intermediate formed in reactions (14)–(16) is present in a steady state concentration. With this assumption and the further assumption that the contributions of reactions (16) and (19) to the total amount of H<sub>2</sub>O<sup>16</sup> can be calculated without regard to isotope effects (they contribute a small fraction of the total H<sub>2</sub>O<sup>16</sup> formed), and a similar assumption with regard to the production of N<sub>2</sub>O<sup>16</sup> from NO<sub>2</sub><sup>16</sup>O<sup>18-</sup>, we find

$$\frac{\left(\frac{\text{N}_2\text{O}^{18}}{\text{N}_2\text{O}^{16}}\right)_{\infty}}{\left(\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}^{16}}\right)_{\infty}} = \frac{2\left(\frac{k_{16}}{k_{15}+k_{16}}\right)\left(\frac{k_{19}}{k_{18}+k_{19}}\right)}{\left(\frac{k_{15}}{k_{15}+k_{16}}\right) + \left(\frac{k_{16}}{k_{15}+k_{16}}\right)\left(\frac{k_{18}}{k_{18}+k_{19}}\right)}, \quad (20)$$

and

$$\frac{\left(\frac{\text{N}_2\text{O}^{18}}{\text{N}_2\text{O}^{16}}\right)_{t_e}}{\left(\frac{\text{N}_2\text{O}^{18}}{\text{N}_2\text{O}^{16}}\right)_{t_{\infty}}} = \frac{k_{15}+k_{16}}{k_{14}}. \quad (21)$$

<sup>17</sup> M. Dole, Science **109**, 77 (1949).

<sup>18</sup> N. F. Hall, and O. R. Alexander, J. Am. Chem. Soc. **62**, 3455 (1940).

TABLE III. Distribution of O<sup>18</sup> between N<sub>2</sub>O and H<sub>2</sub>O in the decomposition of ammonium nitrate.

	$\left(\frac{N_2O^{18}}{N_2O^{16}}\right)_{eq} / \left(\frac{H_2O^{18}}{H_2O^{16}}\right)_{eq}$
Model A	1.034
Model B	1.026
Experimental	1.023 ± 0.003

The general theory of the effect of isotopic substitution on the rates of chemical reactions<sup>19</sup> leads to the relation

$$\frac{k_1}{k_2} = \frac{s_1 s_2 \ddagger K_1}{s_2 s_1 \ddagger K_2} \left( \frac{m_2^*}{m_1^*} \right)^{\frac{1}{2}} \times \left[ 1 + \sum_i^{3n-6} G(u_i)(u_{i(1)} - u_{i(2)}) - \sum_i^{3n'-6} G(u_i \ddagger)(u_{i(1) \ddagger} - u_{i(2) \ddagger}) \right] \quad (22)$$

for the ratio of the rate constants of two isotopic molecules.<sup>20</sup> In the comparison of  $k_{16}$  with  $k_{15}$  and  $k_{19}$  with  $k_{18}$  respectively it is to be noted that  $u_{i(15)} = u_{i(16)}$  and  $u_{i(18)} = u_{i(19)}$ . This leads to the ratios necessary for the evaluation of Eqs. (20) and (21).

$$\frac{k_{16}}{k_{15}} = 2 \left( \frac{m_{16}^*}{m_{15}^*} \right)^{\frac{1}{2}} \left[ 1 - \sum_i^{i=21} G(u_i \ddagger)_{15, 16} (u_{i(16) \ddagger} - u_{i(15) \ddagger}) \right] \quad (23)$$

$$\frac{k_{19}}{k_{18}} = \left( \frac{m_{18}^*}{m_{19}^*} \right)^{\frac{1}{2}} \left[ 1 - \sum_i^{i=12} G(u_i \ddagger)_{18, 19} (u_{i(19) \ddagger} - u_{i(18) \ddagger}) \right] \quad (24)$$

$$\frac{k_{14}}{k_{15}} = 3 \left( \frac{m_{15}^*}{m_{14}^*} \right)^{\frac{1}{2}} \times \left[ 1 + \sum_i^{i=6} G(u_i)_{14, 15} (u_{i(14)} - u_{i(15)}) - \sum_i^{i=21} G(u_i \ddagger)_{14, 15} (u_{i(14) \ddagger} - u_{i(15) \ddagger}) \right] \quad (25)$$

The factors 2 and 3 in Eqs. (23) and (25) respectively arise from symmetry considerations. In accord with the previous discussion we take  $K_1/K_2$  equal to unity.<sup>19</sup>

We now consider the implications of the fact that the oxygen content of the N<sub>2</sub>O is the same at one percent decomposition as it is at complete decomposition. We use Eqs. (23) and (25) to evaluate the right-hand side of Eq. (21). All the factors  $G(u_i \ddagger)$  are the same and

we arrive at the empirical relation

$$\sum_i^{i=21} G(u_i \ddagger) (u_{i(14) \ddagger} - \frac{1}{3} u_{i(15) \ddagger} - \frac{2}{3} u_{i(16) \ddagger}) - \sum_i^{i=6} G(u_i) (u_{i(14)} - u_{i(15)}) = 0.333 - \frac{1}{3} \left( \frac{m_{14}^*}{m_{15}^*} \right)^{\frac{1}{2}} \quad (26)$$

The term  $m_{14}^{*1/2}/m_{15}^*$  is less than unity and has been calculated for two models. In model A we simply use the reduced masses<sup>21</sup> of N<sup>14</sup>O<sup>16</sup> and N<sup>14</sup>O<sup>18</sup> for Eqs. (14) and (15) respectively. In model B we assume not only that one of the N—O bonds is ruptured but a water molecule is formed as the activated complex decomposes. This gives for the right-hand side of Eq. (26) 0.009 ± 0.005 and 0.007 ± 0.005 for models A and B respectively.

The empirical Eq. (26) leads to the conclusion, which is valid for any model, that the activated complex in the elimination of water from nitrate ion has some oxygen vibrations which are of higher frequency than the oxygen vibrations in nitrate ion. This can be readily understood if we suppose that one oxygen is loosely bound in the activated complex and at a greater distance from the nitrogen atom than the other two. From chemical considerations we would expect the effect of isotopic oxygen substitution on the difference between the free energy function for the activated complex and the free energy function for the nitrate ions to be similar to the difference in the free energy function of CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> on substitution of O<sup>18</sup> for O<sup>16</sup>. At 500°K this difference is 0.013.<sup>14</sup> This value for the left-hand side of Eq. (26) is in satisfactory agreement with the values calculated for the right hand side.

For the evaluation of Eq. (20) we must know the differences in the vibrational frequencies of activated complexes which differ from one another only in that they are isotopic isomers. We would expect this effect on the free energy function to be smaller than the free energy function which arises from direct isotopic substitution. We have seen from Eq. (26) that the latter is small, which is to be expected for competitive reactions involving oxygen isotopes at 500°K. As a first approximation we shall evaluate Eq. (20) by neglecting the contributions of the free energy functions to Eqs. (23) and (24). The results for the two models discussed above are compared with experiment in Table III. The agreement between theory and experiment is within the limit of the approximations made in  $\sum_i G(u_i \ddagger) (u_{i(16) \ddagger} - u_{i(15) \ddagger})$  and  $\sum_i G(u_i \ddagger) (u_{i(19) \ddagger} - u_{i(18) \ddagger})$  in Eq. (23) and (24) respectively.

It is clear from the calculations presented and their agreement with experiment that the principal factor

<sup>19</sup> J. Bigeleisen, J. Chem. Phys. **17**, 675 (1949).

<sup>20</sup> See Eq. 8(a) reference 19.

<sup>21</sup> N. B. Slater, Proc. Roy. Soc. **194**, 112 (1948).

contributing to the preference of  $O^{18}$  for  $N_2O$  over  $H_2O$  in the decomposition of ammonium nitrate is the greater frequency of rupture of  $N-O^{16}$  bonds than  $N-O^{18}$  bonds. In accord with theoretical expectations we find that there is little isotope effect on the equilibrium between the substrate and activated complex at 500°K.

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We wish to thank Dr. Joseph R. Stevens for making available to us the information on the origin of "Baker's Analyzed" ammonium nitrate. We also wish to thank Mr. W. S. Richardson and Professor E. B. Wilson, Jr., for sending us a copy of their manuscript on the infrared spectrum of  $N^{15}N^{14}O^{18}$  in advance of publication.

## Ultrasonic Velocities of Sound in Some Metallic Liquids. Adiabatic and Isothermal Compressibilities of Liquid Metals at Their Melting Points\*

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The ultrasonic velocities of sound at 12 mc in 12 pure liquid metals at their melting points under atmospheric pressure and in 4 equi-atomic liquid metallic mixtures have been determined by the use of the electronic pulse-circuit technique.

For the pure metals the adiabatic and isothermal compressibilities have been computed. The compressibilities were generally found to be somewhat larger than for the corresponding solids at room temperatures. A calculation of Grüneisen's  $\gamma$  for the liquid metals shows that this quantity, in the case of normal metals, does not change appreciably on going from the solid state at room temperature to the liquid at moderately elevated temperature. These facts support the familiar view that the liquid metals at temperatures not far above their melting points are in a "solid like" state, and that equations of state for the solid state may be applicable to such liquids.

## INTRODUCTION

IN view of the experimental difficulties associated with the measurement of isothermal compressibilities at elevated temperatures, it is not surprising that such data are not generally available for liquid metals. However, the well-known relationship between velocity of sound  $u$ , density,  $\rho$ , and adiabatic compressibility,  $K_s$ ,

$$K_s = 1/\rho u^2$$

makes an alternative approach to the problem possible, if velocities of sound can be measured. Under these circumstances we get the isothermal compressibility  $K_T$  through the relationship

$$K_T = (C_P/C_V)K_s,$$

where

$$\frac{C_P}{C_V} = \frac{1}{1 - (TM\alpha^2/\rho C_P K_T)}.$$

If data are available for specific heat,  $C_P$ , and coefficient of thermal expansion,  $\alpha$ , and with temperature,  $T$ , and atomic weight,  $M$ , fixed by the investigator, the isothermal compressibility can be derived readily by successive approximations.

With the obvious exception of mercury, reliable measurements of velocity of sound have not, to the

knowledge of the author, been carried out for liquid metals. The present investigation was started in order to secure such information. In other communications the author will discuss some of the consequences of these measurements with respect to the thermodynamic properties of liquid alloy systems.

Through the development of the electronic pulse-circuit technique during and after the war, a new and experimentally simple approach has been opened up, by which velocities of sound in solids and liquids can be measured with considerable accuracy.<sup>1</sup> The method was previously applied by Pellam and Galt<sup>2</sup> in the case of a number of simple liquids at room temperatures, and more recently by Galt<sup>3</sup> and by Galt and Squire<sup>4</sup> for investigation of liquids at low temperatures.

The author has previously reported briefly<sup>5</sup> on the use of the same technique for the study of metallic liquids at moderately elevated temperatures. In the present paper will be given a more complete account of this work, which covers measurements at atmospheric pressure on 12 pure liquid metals at and above their melting points and on 4 equi-atomic liquid metal mixtures.

<sup>1</sup> Cefola, Droz, Frankel, Jones, Maslach, and Teeter, Jr., MIT Radiation Laboratory Report 963 (March 1946).

<sup>2</sup> J. R. Pellam and J. K. Galt, *J. Chem. Phys.* **14**, 608 (1946).

<sup>3</sup> J. K. Galt, *J. Chem. Phys.* **16**, 505 (1948).

<sup>4</sup> J. K. Galt and C. F. Squire, *Phys. Rev.* **72**, 1245 (1947).

<sup>5</sup> O. J. Kleppa, *J. Chem. Phys.* **17**, 668 (1949).

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