will permit us definitely to decide between these two mechanisms; there is also the possibility that there are other mechanisms which will give a unimolecular rate.

Summary

1. The absorption spectrum of nitrogen pentoxide has been measured and shows continuous absorption commencing at 3050 Å. and extending to the far ultraviolet.

2. The long wave length limit of this continuous spectrum corresponds very closely to the energy change in the reaction $N_2O_5 = 2NO_2 + O$ and indicates that this may be the primary photochemical reaction.

3. The mechanism of the thermal decomposition has been discussed and two possible mechanisms have been pointed out which are analogous to the radioactive decomposition of nuclei and the spontaneous dissociation of the excited hydrogen molecule.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY OF NITRIC OXIDE FROM 14°K. TO THE BOILING POINT AND THE HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID PHASES. THE ENTROPY FROM SPECTROSCOPIC DATA

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In a recent paper[1] the entropy of oxygen has been discussed. This was particularly interesting due to the effect of two spinning electrons. In this paper nitric oxide will be considered.

Jenkins, Barton and Mulliken[2] have measured the fine structure of the β-bands of nitric oxide and have given a very satisfactory interpretation of them. It is evident from their work that the nitric oxide gas molecules exist in a double electronic level under ordinary conditions. This arises from one-half unit of electronic spin which may couple with or against the one unit of electronic angular momentum which is directed along the figure axis of the molecule. The energies and probabilities associated with the rotation of the molecule as a whole are much influenced by the nature of the electronic coupling and are correspondingly different for the two cases referred to above.

The unbalanced angular momentum responsible for the strong paramagnetism of the nitric oxide molecule has a considerable effect on the entropy to be considered in the latter part of this paper. The theoretical treatment of the magnetic susceptibility of the nitric oxide molecule has

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[1] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

[2] Jenkins, Barton and Mulliken, *Phys. Rev.*, **30**, 150 (1927).

been considered by Van Vleck,[3] who arrived independently at the same electronic configuration for the molecule as was indicated by the band spectra. The above spectroscopic data and interpretation make possible the calculation of a very accurate value of the entropy.

The object of the present investigation was to obtain reliable heat capacity data for solid and liquid nitric oxide from the boiling point of nitric oxide to temperatures obtainable with liquid hydrogen under reduced pressure. Our object was to determine whether the third law of thermodynamics, as ordinarily used, would give a value for the entropy agreeing with that calculated from spectroscopic data. In the light of opinions advanced in earlier papers[4,5] it may be expected that for some substances, due to lack of thermodynamic equilibrium or to effects occurring close to the absolute zero, or both, the integral $\int C_p \mathrm{d} \ln T$ might give too small a value.

The entropy of nitric oxide from the calorimetric data is considerably lower than that obtained from spectroscopic data although the entropy calculated from the latter may be considered reliable.

Preparation and Purification of Nitric Oxide.—The difficulty of preparing pure nitric oxide has been recognized by various investigators and probably accounts for the discordant data on the physical properties. Adwentowski[6] expressed doubt that the gas could be prepared in a high state of purity. Difficulty arises from the fact that all processes for the preparation of the gas depend on the reduction of either NO_3^- ion or of NO_2^- ion and the NO produced always contains traces of other oxides or reduction products not easily removed, particularly NO_2, N_2O_3 and N_2. A comparatively large amount of nitric oxide was desired in a higher state of purity than any previously obtained in order to fix certain physical constants with great accuracy. A careful study was made to determine the best method of preparation and purification. The investigations of Moser[7] indicated that the best method for the preparation is that described by Winkler.[8] A dilute solution of sulfuric acid is dropped into a solution of potassium nitrite and potassium oxide. The nitric oxide is produced by the reaction $2NO_2^- + 4H^+ + 2I^- = 2NO + I_2 + 2H_2O$. When the preparation is carried out under proper conditions and the product is passed through wash bottles containing in turn sulfuric acid and potassium hydroxide solutions, Moser finds that nitric oxide of 99.8% purity may be produced. Germann[9] showed that fractional distillation was usually more

[3] Van Vleck, *Phys. Rev.*, **31**, 587 (1928).

[4] Giauque, THIS JOURNAL, **49**, 1870 (1927).

[5] Giauque and Johnston, *ibid.*, **50**, 322 (1928).

[6] Adwentowski, *Anz. akad. Wiss. Krakau*, S142 (1909).

[7] Moser, *Z. anal. Chem.*, **50**, 401 (1911).

[8] Winkler, *Ber.*, **34**, 1408 (1901).

[9] Germann, *J. Phys. Chem.*, **19**, 437 (1915).

effective for final purification than the use of chemical purifying agents. Gray,[10] however, has shown that the usual methods of fractionation become ineffective for nitric oxide and describes an effective means of distillation which relies for its efficacy on the high solubility of the oxides in liquid nitric oxide and their low vapor pressures at the boiling point of nitric acid. Nitrogen is best removed by evacuating the freshly sublimed solid.

The preparation and purification were based on the suggestions above. The measurements were carried out with three different preparations of nitric oxide. In Preparation I a six-liter pyrex round-bottomed reaction flask was employed. This could be emptied or filled with fresh reagents through a pyrex stopcock without contamination with air. It was initially half filled with a nearly concentrated solution made by dissolving 5 kilograms of potassium nitrite and 2.5 kilograms of potassium iodide in 15 liters of distilled water. Nitric oxide was generated by dropping a 50% solution of sulfuric acid from an acid reservoir. Regulation of stopcocks controlled the rate at which the gas was generated. During operation the mixture was stirred by an electromagnetic stirrer. Platinum–iridium in the form of a wire spring, which served to prevent injury to the apparatus, was the only material other than pyrex glass in contact with solution or evolved gas. It was necessary to refill the reaction flask several times in the course of a preparation in order to obtain the amount of nitric oxide desired. Some annoyance was experienced in this operation due to the precipitation of large amounts of iodine, and to the formation of hard crystals of potassium sulfate which clogged the drainage tube. Accordingly in Preparations II and III a 20-liter bottle was substituted, which held enough of the reagents to avoid the necessity of refilling. This was made of common glass and was fitted with a two-holed rubber stopper through which projected the dropping stem from the acid reservoir and the outlet tube for the gas. To make certain that it was vacuum tight the stopper was covered externally with de Khotinsky cement. The solution was unstirred but the gas generated was subjected to one more fractionation in the later stages of purification than Preparation I and, as the data will show, there was no appreciable difference in purity between Preparation I and Preparations II and III.

As a practical precaution, the 20-liter bottle was placed in a small barrel to avoid danger in case it should collapse when evacuated. This precaution was found necessary for on one occasion a similar bottle which had been previously tested and frequently evacuated collapsed under a vacuum and threw pieces of glass with considerable violence.

From the generator the crude gas entered the purifying train. It was first bubbled through a tall column of 90% sulfuric acid and then through a tall column of 50% potassium hydroxide solution. Both columns contained glass beads to break up the bubbles. Next was included a trap immersed in a bath of solid carbon dioxide and ether. The principal purpose of this trap was to remove the bulk of the moisture but it also served to condense a further portion of the higher oxides that might have passed through the potassium hydroxide. The gas was condensed in a bulb surrounded with liquid air. When sufficient nitric oxide had collected, the generator was stopped, and the gas was distilled, passing on its way through about two meters of tubing packed alternately with phosphorus pentoxide and plugs of glass wool, the first and last portions being discarded. Following this the nitric oxide was distilled into a bubbling bulb until it had collected to a depth of four or five centimeters, after which the depth was kept constant by regulating the height of liquid air in an unsilvered Dewar flask while

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[10] Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

the remainder was slowly bubbled through in accordance with the suggestion of Gray, mentioned above. Two such stages of bubbling were included in each cycle, the liquid in the first stage, with the relatively non-volatile other oxides of nitrogen being discarded, and the liquid remaining in the second bubbling bulb being transferred to the first to serve as the initial concentrate for the next operation. The nitric oxide was then solidified, pumped for several minutes, sublimed under a pressure of about 5 cm. of mercury and pumped again for several minutes. Finally the nitric oxide was returned to the beginning of the cycle and the distillation and sublimation process repeated. This cycle was carried through three times for Preparation I and four times for Preparations II and III. During the process about 450 cc. of liquid nitric oxide initially collected was reduced to about 150 cc. of purified liquid. The middle 105 or 110 cc. was then distilled into the calorimeter. Except during the sublimation process the pressures in the generator and purifying line were kept close to atmospheric. The pressures were observed on five manometers, which also served as safety valves in case of need.

Great care was taken to avoid contamination by air since Moser[7] had shown that small amounts of air had a catalytic action in the decomposition of nitric oxide. Except for the reaction bottle and its rubber stopper the entire generating and purifying system was constructed of pyrex glass with fused joints. The stopcocks used were special high vacuum stopcocks and were greased with rubber stopcock grease[11] previously saturated with nitric oxide gas at 150°. Before the liquid reagents were added to the generator or purifying columns, the entire line was evacuated to a pressure of about 10^{-5} mm. of mercury and was pumped for several days with occasional sparking and heating to remove adsorbed gases from the phosphorus pentoxide and from the walls of the glass line. All solutions were boiled to expel air. After supplying the reagents the system was again evacuated for several hours. A slow stream of nitric oxide was passed through the line for several minutes before any was collected. The gas was generated slowly in order to avoid loss of efficiency in the purifying columns. For the same reason distillation and sublimation were carried out at a moderate rate. With continuous day and night operation a period of four or five days was consumed from the time that the generator was started until the nitric oxide was distilled into the calorimeter.

No analyses of the gas were made since accurate melting point and heat capacity data provide a more sensitive test of impurity than are given by chemical analysis. Following the presentation of the data there will be given a full discussion of the question of purity.

Heat Capacity Measurements and Data.—The calorimetric measurements and the measurements of the amounts of material were carried out in the same manner and with the same apparatus described for the measurements on oxygen.[1] The discussion given in the latter work relative to the sources of error and treatment of the data applies practically without change in the work on nitric oxide. Since the amount of gas was measured volumetrically, we made use of certain physical constants of nitric oxide which are given below. The molecular weight was taken as 30.008.[12] The density used was 1.34018 as given by Scheuer.[13] The

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[11] "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, **1922**, p. 654.

[12] Thirty-Fourth Annual Report of the Committee on Atomic Weights, THIS JOURNAL, **50**, 603 (1928).

[13] Scheuer, *Sitzb. Akad. Wiss. Wien*, **123**, 2A, 1029 (1914).

mean coefficient of expansion between 0 and 25° as given by Leduc[14] is 0.003677. The coefficient of deviation from Boyle's law per atmosphere is given by Batuecas[15] as −0.00112.

Two series of measurements, described as IIIa and IIIb, were carried out to determine the heat capacities of solid and liquid nitric oxide. Both were made with Preparation III. Within each series the measurements were made in order of rising temperature and between the two series a small measured amount of nitric oxide was removed from the calorimeter in the process of removing the plug of solid nitric acid which had distilled into the glass tube above the calorimeter during the period of recooling. The two series of measurements taken together covered the temperature interval from about 14.3 to about 122.1°K. The data are recorded in Table I, in which the first column gives the serial number of the run, the second column the mean absolute temperature, the third column the temperature interval covered and the fourth the heat capacity in calories per mole per degree.

TABLE I

HEAT CAPACITY OF NITRIC OXIDE

Molecular weight, 30.008. Series IIIa 3.7691 moles. Series IIIb 3.7476 moles

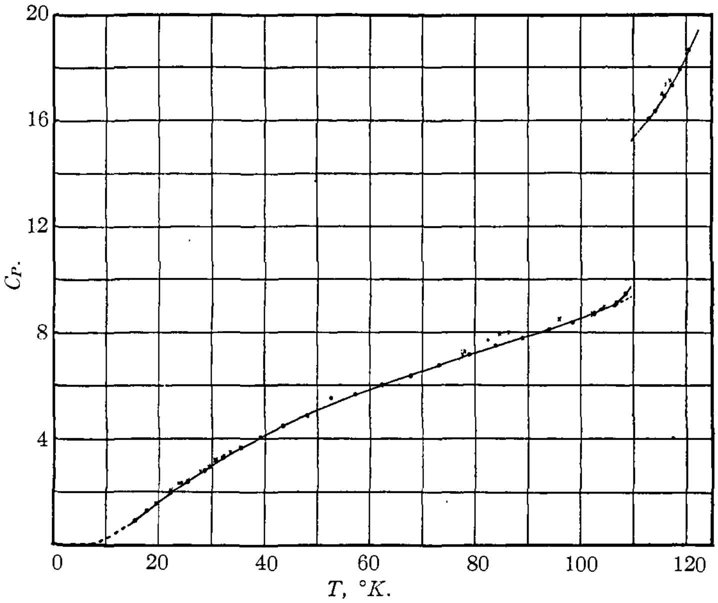
Series	T, °K.	ΔT, °K.	C_p/mole in cal./deg.	Series	T, °K.	ΔT, °K.	C_p/mole in cal./deg.
IIIb	15.57	2.447	0.935	IIIb	83.83	4.949	7.516*
IIIb	17.75	1.733	1.303	IIIb	88.96	4.996	7.795
IIIb	19.51	1.685	1.590	IIIb	94.04	4.998	8.130
IIIb	22.27	3.006	1.964	IIIb	98.51	3.773	8.397
IIIb	25.36	2.960	2.389	IIIb	102.55	4.153	8.713
IIIb	28.59	3.399	2.807	IIIa	106.39	2.409	9.033
IIIb	32.08	3.490	3.274	IIIb	106.65	3.882	9.120
IIIb	35.50	3.375	3.691	IIIa	108.39	1.525	9.456
IIIb	39.20	3.930	4.060				
IIIb	43.51	4.679	4.481	Melting point at 109.49°K.			
IIIb	48.16	4.621	4.895	IIIb	112.81	2.844	16.067
IIIb	52.64	4.324	5.543	IIIa	114.01	3.298	16.362
IIIb	57.25	4.796	5.686	IIIb	115.79	2.896	16.915
IIIb	62.32	5.319	6.016	IIIa	117.35	3.293	17.329
IIIb	67.90	5.515	6.392	IIIb	118.86	3.125	17.935
IIIb	73.24	5.030	6.760	IIIa	120.56	3.024	18.667
IIIb	78.84	4.942	7.158				

The results tabulated above are also shown graphically by the dark circles in Fig. 1. The results of all runs have been tabulated and plotted, but the value marked with an asterisk in this table is known definitely to be in error due to improper experimental conditions for which adequate corrections could not be applied. The point at 52.64° may be in error although a careful study of data taken in that and adjacent runs failed

[14] Leduc, *Ann. Physik,* **5**, 180 (1916).

[15] Batuecas, *Anales soc. españ. fís. quím.,* **20**, 441 (1922).

to reveal any factor to which might be assigned an error within reasonable limits sufficient to account for the deviation. It is possible that a transition of very small energy change has been included. A transition heat of about 1.3 calories per mole would account for this point. It is also possible that the point falls on the maximum of a gradual transition. This region could readily have been studied in detail had this situation been suspected but unfortunately the calorimeter was emptied before it was discovered. From the standpoint of the entropy calculation this is immaterial since the area concerned, if real, would affect the entropy by only 0.02 of an entropy unit.



●, This Research; ×, Eucken and Karwat.

Fig. 1.—Heat capacity in calories per mole of nitric oxide.

The short interval runs taken in Series IIIa just below the melting point were for the purpose of evaluating the degree of impurity and will be discussed in a later paragraph. The sharp rise in the solid curve is assumed to be due to the influence of premelting and the dotted curve represents the extrapolation for the pure solid.

For the sake of comparison the results of Eucken and Karwat[16] have been plotted and are represented by crosses. It will be observed that their values are in general higher than ours and show large deviations among themselves. Compared with the curve of Fig. 1, their results for solid nitric oxide from 22 to 34° show an average deviation of 2.3% with a maxi-

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[16] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924).

mum deviation of 6%. In the region from 82 to 104°, their results differ from the curve by 2.5% on the average and show a 5% maximum deviation. These deviations are somewhat larger than the probable error claimed by those authors, who believed their values for solid nitric oxide to contain no larger maximum error than 2% with an average error of only 1%. The points they secured for liquid nitric oxide agree more closely with ours and the deviations are within the limits of error which they claimed.

Among our values, with the exception of these points already discussed, only six of the points above 30° deviate from a smooth curve by more than 0.1 of 1%. Of these only two deviate by more than 0.2 of 1%. It is believed that for the region from 35° to the boiling point the smooth curve represents correct values of C_p to within 0.2 of 1%. Below 35° the accuracy is lessened somewhat, due partly to the lowered heat capacity but principally to the lower temperature coefficient of the resistance thermometer. At 20° the error may be 0.7 of 1% and at 14° may be as large as 2 or 3%.

Melting Point.—The melting point was determined for each of three preparations of nitric oxide. On each occasion readings were taken at intervals of three or four hours over a period of about two days. When constancy of successive readings indicated that thermal equilibrium was attained, a further fraction of the solid was melted and more readings were taken at subsequent intervals. This was done to avoid the influence of impurity in the final value chosen for the melting point, although the data make it evident that very little influence of this sort existed. Table II records the measurements. The data for Preparations I, II and III are arranged in order. Column one indicates the date and approximate hour at which observations were recorded. Column two indicates the approximate percentage melted. Column three records the absolute temperatures determined. These were calculated from the reading of the standard thermocouple soldered to the bottom of the calorimeter. The readings of the thermocouple are ordinarily reproducible to 0.01°, so differences of that amount are without significance in this column. For that reason, there is included in column four the resistance (in ohms) of the gold resistance thermometer wound on the outer surface of the calorimeter. The readings of this thermometer are ordinarily reproducible to 0.001 or 0.002 of an ohm and the resistance at this temperature is changing by almost exactly an ohm per degree. The comparison of resistance is only significant as between values in a single series of measurements, since in the period between the readings on Preparations I and II the wire had been subjected to strain and the calibration changed, and between the measurements of Preparations II and III a new resistance thermometer was wound. These are referred to as thermometers A, A′ and B.

TABLE II

MELTING POINT OF NITRIC OXIDE

Date and time		Percentage melted	*T*, °K. (from thermocouple)	*R*, ohms, from resist. thermometer
		Preparation I		
12/14/27	4:00 P.M.	Heated into melting point		Thermometer A
	9:00 P.M.	15	109.49	169.402
	12:00 P.M.	15	109.49	169.401
12/15/27	9:30 A.M.	15	109.50	169.397
	9:45 A.M.	Supplied heat		
	2:00 P.M.	50	109.49	169.401
	6:00 P.M.	50	109.50	169.398
	9:30 P.M.	50	109.51	169.402
	12:00 P.M.	Supplied heat		
12/16/27	9:30 A.M.	75	109.49	169.399
		Preparation II		
1/ 6/28	9:00 P.M.	Heated into melting point		Thermometer A'
1/ 7/28	12:30 A.M.	3	109.49	169.437
	2:00 A.M.	Supplied heat		
	7:00 A.M.	50	109.51	169.437
	10:00 A.M.	50	109.48	169.438
		Preparation III		
3/24/28	12:30 P.M.	Heated into melting point		Thermometer B
	9:00 P.M.	5	109.48	.....
	10:00 P.M.	Supplied heat		
3/25/28	11:00 A.M.	50	109.49	173.161
	7:00 P.M.	50	109.53	173.162
3/26/28	10:00 A.M.	50	109.49	173.166
	2:00 P.M.	50	109.51	.....

Accepted value, 109.49 ± 0.05°.

It will be observed that among the temperatures recorded by the thermocouple at various times, only four differ by more than 0.01° from the value chosen as the melting point. In other words, they lie within the precision of the thermocouple to distinguish them. The resistance thermometer likewise shows this constancy of temperature since the extreme readings

TABLE III

TRIPLE POINT DATA FOR NITRIC OXIDE

Observer	*T*, °K.	*P*, int. cm.
This research	109.49 ± 0.05	16.438 ± 0.004
Henglein and Kruger[17]	109.4	16.57
Goldschmidt[18]	109.88	17.02
Eucken and Karwat[16]	About 110	...
Adwentowski[6]	112.4	16.8
Olszewski[19]	106.1	13.8

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[17] Henglein and Kruger, *Z. anorg. allgem. Chem.*, **130**, 181 (1923).

[18] Goldschmidt, *Z. Physik*, **20**, 159 (1923).

[19] Olszewski, *Compt. rend.*, **100**, 940 (1885).

in any one series differ by only 0.005 of a degree. The chosen value, 109.49°, is then subject only to the uncertainty of temperature scale, which amounts to about 0.05°.

For the sake of comparison, in Table III are listed melting point values reported by various authors. Values of the triple point pressure are also included.

Heat of Fusion.—The heat of fusion was measured in the usual manner. Correction was applied for $\int C_p dT$ and also for the small amount of premelting that had occurred below the temperature at which the energy input was begun. The latter correction was determined from the area between the solid and dotted curves in Fig. 1.

The results are given in Table IV, in which column one gives the amount of material melted (in moles); column two the temperature interval covered; column three the total heat input in calories corrected for all factors except $\int C_p dT$ and the premelting correction referred to above; column four the total of these last two corrections for calorimeter plus contents; and columns five and six the individual values and the mean value of our determinations. The latter value is believed to be correct to within 0.2 of 1%. Both measurements were made with Preparation III. At the bottom of the table, for comparison, are included the experimental values obtained by Eucken and Karwat and the values calculated by Henglein and Kruger and by Goldschmidt from vapor pressure measurements.

TABLE IV

HEAT OF FUSION OF NITRIC OXIDE

Melting Point 109.49°

This research

Amount, moles	Temp. interval	Corr. total heat input, cal.	$\int C_p dT$ + premelting	ΔH, cal. per mole	Mean
3.7691	109.20–112.32	2276.3	204.0	549.8	549.5 ± 1.0
3.7476	109.12–111.02	2177.9	119.8	549.2	
Eucken and Karwat[16]		Henglein and Kruger[17]		Goldschmidt[18]	
	552	900			539

Heat of Vaporization.—The heat of vaporization was measured in the manner previously described[1] for oxygen. During the determinations the surroundings were maintained at a temperature slightly above the boiling point of the liquid in order to avoid errors due to condensation. By means of the automatic pressure control device referred to in a previous paper,[1] the pressure during the measurements was kept constant at 76 cm. of mercury within 0.1 mm. Heat was supplied to the bottom half of the calorimeter and no measurements were taken after the liquid level had fallen close to the heated portion. They were all made with Preparation III. Energy was supplied for a period of fifty-three minutes in each case. The results are given in Table V, in which the first column gives the number of moles evaporated in each determination, column two the values of the heat of vaporization obtained from the individual measurements and column three the mean value. It will be observed that no individual value differs from this mean by more than 0.04 of 1%. We believe 0.1 of 1% to be the limit of error of this determination.

Table V

Heat of Vaporization of Nitric Oxide

Boiling point, 121.36°. Molecular weight, 30.008

Moles of NO evaporated	0.21677	0.21729	0.21711	0.21646	
ΔH, 760 mm., cal./mole	3292.8	3291.8	3293.8	3292.1	Av. 3292.6 ± 3.3

No other calorimetric values for the heat of vaporization of nitric oxide are to be found in the literature.

Vapor Pressures of Nitric Oxide.—The best recent determinations of the vapor pressures of solid and liquid nitric oxide are those of Henglein and Kruger[17] and of Goldschmidt.[18] Both claimed high accuracy for their values, yet there is comparatively wide disagreement between the two sets of data. Since we had very pure nitric oxide and since the calorimetric apparatus employed was likewise admirably suited to the accurate measurement of vapor pressures, it seemed desirable to make a redetermination of vapor pressures. The data were obtained by the procedure already used by Giauque, Johnston and Kelley[20] for oxygen and hydrogen. For each vapor pressure point the calorimeter, nearly full of the liquid or solid nitric oxide, was heated to the desired temperature and allowed to stand for nearly an hour to insure thermal equilibrium before the temperature and pressure were taken. To avoid distillation the surroundings were maintained at a temperature slightly above that of the calorimeter. Pressures were read with the aid of a standard meter scale and a Société Génévoise Cathetometer. Corrections for temperatures of mercury and scale and for meniscus height were applied as described in connection with the measurement of the amount of gas in a previous paper.[1] The measurements were obtained with a precision of 0.002 cm. The measurements for solid nitric oxide began at 94.62°K. and were all made with Preparation II. Those for the liquid were begun with Preparation II and carried to about 116°. An accident occurred which interrupted the measurements at this point and subsequently the measurements were repeated with Preparation III and extended to nearly 123°K. The triple point pressure was investigated with Preparations I, II and III in turn.

The results are tabulated in Table VI. In this table the first column gives the preparation number; the second, the observed temperature in degrees absolute; the third, the observed pressure in international centi-

[20] Giauque, Johnston and Kelley, This Journal, **49**, 2367 (1927).

meters; the fourth, the temperature calculated by substituting the observed pressures in the vapor pressure equations which we have derived; the fifth, the pressure calculated by substituting the observed temperatures in our vapor pressure equations; the sixth, pressure observed minus pressure calculated; the seventh, temperature observed minus temperature calculated and the eighth, the physical state of the nitric oxide.

TABLE VI

THE VAPOR PRESSURE OF NITRIC OXIDE

Prepn.	T, °K., obs.	P, int. cm., obs.	T, calcd.	P, calcd.	ΔP, int. cm.	ΔT, °K.	Remarks
II	94.62	0.918	94.64	0.912	+0.006	−0.02	Solid
II	96.47	1.366	96.45	1.372	− .006	+ .02	Solid
II	98.77	2.227	98.76	2.230	− .003	+ .01	Solid
II	100.84	3.396	100.85	3.389	+ .007	− .01	Solid
II	102.92	5.082	102.93	5.075	+ .007	− .01	Solid
II	104.41	6.700	104.40	6.711	− .011	+ .01	Solid
II	106.68	10.101	106.67	10.121	− .020	+ .01	Solid
I	109.49	16.442					Triple point
II		16.440					Triple point
II		16.441					Triple point
III		16.442					Triple point
III		16.433					Triple point
III		16.432					Triple point
	Average	16.438 ± 0.004	109.49	16.438	0.000	0.00	Triple point
III	110.75	19.662	110.75	19.660	+0.002	0.00	Liquid
II	111.67	22.267	111.65	22.339	− .072	+ .02	Liquid
III	112.67	25.651	112.68	25.609	+ .042	− .01	Liquid
II	113.90	30.143	113.89	30.199	− .056	+ .01	Liquid
III	114.95	34.646	114.95	34.646	.000	.00	Liquid
II	116.18	40.604	116.19	40.571	+ .033	− .01	Liquid
III	117.28	46.588	117.28	46.584	+ .004	.00	Liquid
III	119.53	61.296	119.53	61.301	− .005	.00	Liquid
III	121.18	74.328	121.16	74.465	+ .063	+ .02	Liquid
III	122.93	90.990	122.93	90.990	.000	.00	Liquid

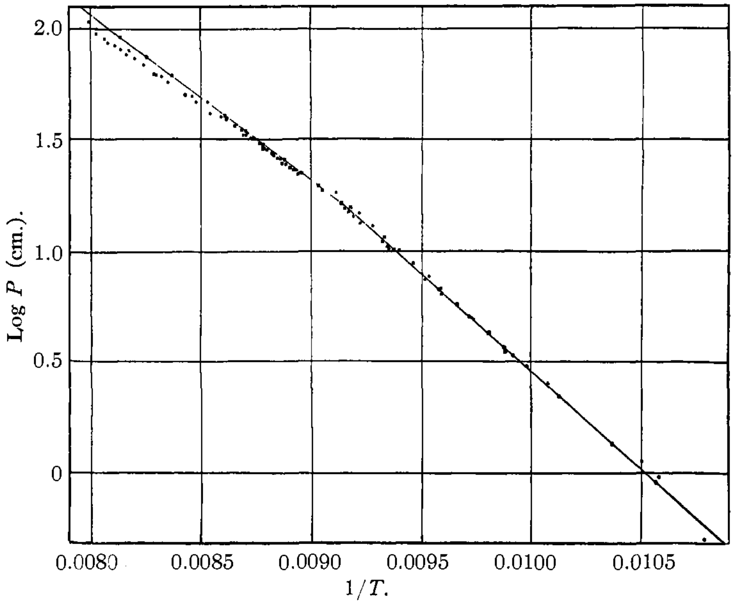
The data are represented by vapor pressure equations which take the form, for solid

$$\log_{10} p(\text{cm.}) = \frac{-867}{T} + 0.00076\,T + 9.05125$$

and for liquid

$$\log_{10} p(\text{cm.}) = \frac{-776}{T} - 0.002364\,T + 8.562128$$

As shown from the ΔT column of Table VI, the agreement between experimental values and the values given by these equations is exceptionally good. Almost without exception the experimental points fit these equations within the limits of the thermocouple readings. The results are shown graphically in Fig. 2, where log p is plotted against $1/T$. The nearly linear curves intersecting at the triple point represent the above two equations. Our experimental points are plotted in dark circles. For comparison the results of Henglein and Kruger are plotted in dark squares and those of Goldschmidt in dark triangles. The scale of the graph is really too insensitive to indicate the extent of the disagreement. Table VII shows a comparison of the smoothness of these data with those of Henglein and Kruger and of Goldschmidt, by comparing the mean deviations and the extreme deviations of each observer's data from the vapor pressure equations derived by the respective workers. The comparison is made over the same range of temperature for each set of data, a little above 90° to the boiling point. The first line lists the research, Line 2 the extremes of ΔT from the vapor pressure equation derived to fit and the third line the average deviation in degrees absolute.



●, This Research; ■, Henglein and Kruger; ▲, Goldschmidt.

Fig. 2.—Vapor pressure of solid–liquid and liquid nitric oxide.

Table VII

Deviation of Experimental Data from the Equations Which Represent Them

	Henglein and Kruger[17]	Goldschmidt[18]	This Research
Extremes of ΔT, °K.	+0.30 to −0.30	+0.30 to −0.50	+0.02 to −0.02
Average ΔT, °K.	0.12	0.08	<0.01

Comparisons of triple point pressures are made in Table III, where the triple point temperatures were recorded. The present value is the mean of the six direct determinations recorded in Table VI and is consistent for three separate lots of nitric oxide. It is believed to be correct to within

0.004 cm. The triple point pressure of Henglein and Kruger was not determined from direct measurement but was calculated from their vapor pressure equations, and was likewise their triple point temperature. Goldschmidt's value was obtained from a single direct measurement.

In Table VIII are given the values for the boiling point of nitric oxide as determined by the vapor pressure measurements of various observers.

TABLE VIII

BOILING POINT OF NITRIC OXIDE

Observer	T, °K.	Observer	T, °K.
Olszewski[19]	119.5	Henglein and Kruger[17]	122.4
Ramsey and Travers[21]	123.2	Goldschmidt[18]	121.87
Adwentowski[6]	122.8	This Research	121.36 ± 0.05

Differences in temperature scales undoubtedly are a contributing factor to the vapor pressure differences found by various observers. This cannot account, however, for differences in the triple point pressure. It is believed that the difficulty of preparing nitric oxide in a high state of purity has been a prominent factor. It is a significant fact that the present measurements, which were carried out with very pure nitric oxide, lead to a lower value for the boiling point and to higher vapor pressures for the liquid than do other recent researches.

Purity of Nitric Oxide.—Measurements of heat capacity just below the melting point serve as a very sensitive test of impurity. Measurements were purposely made close to the melting point in order to make such a test. Insoluble impurities would not cause premelting but they could hardly be present under the circumstances of preparation and purification.

For the most probable case of pure solid in equilibrium with impure liquid, we have, assuming Raoult's law, the equation

$$\ln N_1 = \frac{-\Delta H}{R}\left(\frac{T_m - T}{T_m T}\right)$$

where N_1 refers to the mole fraction of nitric oxide, ΔH is its heat of fusion and T_m is the melting point. This equation gives us the mole fraction of nitric oxide in any liquid which may be formed by premelting at temperature T. The heat effect accompanying premelting will depend on $\Delta H \times (A'' - A')$, where A'' and A' refer, respectively, to the amounts of liquid nitric oxide at T'' and T'. The heat effect is obtained by taking the difference between the observed input from T' to T'' and that which would be calculated from an assumed curve such as is indicated by the dotted line in Fig. 1. We now have sufficient information to solve for the number of moles of impurity, which must be a constant. The results are given in Table IX. The amount of impurity is expressed in mole percentage rather than in mole fraction.

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[21] This value was quoted in Ref. 17.

TABLE IX

MOLE PERCENTAGE OF IMPURITY IN NITRIC OXIDE

Preparation III

T'	T''	Heat of pre-melting calories	N'_1	N''_1	Impurity, mole per cent.
104.71	108.59	0.171	0.8956	0.9795	0.00079
107.63	109.15	.365	.9580	.9922	.00064
From melting point change of Preparation II					.0004

At the bottom of the table a value obtained from the less sensitive method of melting point rise is included. In determining the melting point of Preparation II, a measurement was purposely made with only about 3% melted in order to make as severe a test as possible. From the data recorded in Table II the amount of impurity was evaluated. It should be a reasonable conclusion that the nitric oxide contained less than 0.001 mole per cent. of impurity.

Some Physical Characteristics of Liquid and Solid Nitric Oxide.—The assignment of physical characteristics to solid and liquid nitric oxide has been influenced by the recognized impurity of the substance examined by those who have reported. Adwentowski[6] describes the liquid as colorless in thin layers and light blue in thick layers and ascribes the blue color to the presence of nitrogen trioxide impurity. Henglein and Kruger refer to the liquid as pale blue, resembling liquid oxygen. Nearly all writers refer to the solid as a "snow white" solid and this description is accepted without question in books of reference. In this investigation, we dealt with large quantities of solid and liquid in a high state of purity. The liquid was blue in color, a much darker and more brilliant blue than liquid oxygen with which we had every opportunity of comparison since in the course of the oxygen investigation liquid oxygen was collected in some of the same collecting bulbs used for the nitric oxide. If this blue were due to the small traces of impurity present a marked change in color intensity should have been observed in the course of the purification; no such change was observed. The appearance of the solid depended on our method of freezing it. If collected as a sublimate on the walls of the collecting bulb it had the appearance of a white frost, the "snow white" solid of the literature, but if this same sublimate were allowed to warm to the melting point, it was converted into a clear blue ice. Freezing the liquid always produced this clear blue ice, resembling in shade and intensity the coloration of the liquid. If a glass bulb filled with this clear blue solid was suddenly immersed in liquid air the nitric oxide became filled with innumerable cracks which made the solid appear white and opaque, although blue splotches of varying shades of intensity remained in places where the cracking was not as complete. Further investigation convinced us that the white appearance of the solid secured under certain conditions of freezing is a purely superficial effect caused by the crystalline state of aggregation throughout the mass and that the true color of the solid is blue. Thus both liquid and solid are blue in color.

Entropy from Heat Capacity Data.—The entropy of nitric oxide gas at the boiling point of the liquid was calculated from the calorimetric measurements by integration of the heat capacity data with respect to the logarithm of temperature. A summary of the entropy calculation is given in Table X. The extrapolation below 14.35°K. was carried out by means of a Debye function with a $\beta\nu = 119$.

TABLE X

ENTROPY OF NITRIC OXIDE FROM HEAT CAPACITY DATA

	Cal. per degree per mole
0 to 14.35°K. (extrapolated)	0.27
14.35 to 109.49° (graphical)	8.79
Fusion 549.5/109.49	5.02
109.49 to 121.36 (graphical)	1.73
Vaporization 3292.6/121.36	27.13
Entropy of nitric oxide gas at the boiling point	42.94 ± 0.1 E. U.

This value is for the actual gas. For the purpose of later comparison with the entropy derived from band spectra, it is necessary to have the entropy of the hypothetical perfect gas. Assuming Berthelot's equation of state, a correction of 0.09 cal./deg. per mole results, leading to a value of 43.03 for the entropy of nitric oxide gas in the hypothetical ideal state at 121.36°K.

The entropy has also been calculated with the assistance of the thermodynamic equation $\mathrm{d}\,P/\mathrm{d}\,T = \Delta S/\Delta V$ and our vapor pressure data for both solid and liquid. The entropy of vaporization was calculated at the triple point temperature in each case, making use of Berthelot's equation in order to correct for gas imperfection. The entropy of solid or liquid at the melting point may be obtained from Table X. In order to obtain the entropy change in heating the gas from the triple point to the boiling point, we assumed that C_p was $7/2\ R$ and corrected for the error in this assumption by an approximate calculation of the entropy change accompanying the changing distribution of the $^2P_1$ and $^2P_2$ states. From the solid $S_{\mathrm{NO}} = 43.3$ E. U., and from the liquid $S_{\mathrm{NO}} = 43.0$ E. U., each calculated to the temperature of the boiling point, as compared to 43.0 E. U. obtained from the calorimetric measurements. This agreement is all that could be expected of the vapor pressure calculations and we give these two calculations no weight as compared to the calorimetric data.

The heat of vaporization at the boiling point has also been calculated from the vapor pressure data for liquid nitric oxide, again using Berthelot's equation to represent gas imperfection. The value obtained for $\Delta H_{121.36^\circ\mathrm{K.}}$ is 3316 cal. per mole as compared with the more accurate calorimetric value 3293. Similar calculations by Henglein and Kruger[17] and by Goldschmidt[18] from their respective vapor pressure data lead to the values 3024 and 3199.

Spectroscopic Interpretation of Nitric Oxide.—Jenkins, Barton and Mulliken[2] have obtained measurements of the fine structure of the β-bands of nitric oxide and have made an analysis of the lines in keeping with Hund's theory[22] of molecular electronic states and with recent developments in the interpretation of band spectra as reviewed and extended in a number of papers by Mulliken.[23] The classification of the lines revealed the presence of two distinct band systems. The application of the combination principle taken in conjunction with the positions of missing lines in the various branches led to the assignment of proper j values and to the proper term formulation for the initial and final electronic levels of the two band systems. The term formulations show that the two band systems originate from respective transitions from a double initial electronic level to a double final electronic level ($^2P_1 \longrightarrow {}^2P_1$) ($^2P_2 \longrightarrow {}^2P_2$). In the lower states the $^2P_2$ level has a higher energy than the $^2P_1$ level. The separation is 124.4 cm.$^{-1}$. The magnitude of separation was obtained from the analysis by Frl. Guillery[24] of the γ-bands of nitric oxide, which are likewise a double band system, having the same final double electronic state as do the β-bands. From the fact that both β- and γ-systems appear in the absorption spectra of nitric oxide,[25,26] it is evident that this lower double level is the normal state of the nitric oxide molecule.

A physical concept of alignment and quantization of momenta within the molecule is desirable to make clear the assignment of j values and of *a priori* probabilities necessary in the application of the spectroscopic data to the calculation of entropy. Hund has shown that molecules containing resultant electronic angular momentum and electron spin will have their rotation states defined by the three vectors: σ_k, the component of electronic angular momentum directed along the figure axis of the molecule; S, the electron spin and m, the rotational momentum of the molecule. Any component of electronic angular momentum other than that directed along the axis of the molecule is assumed to be without effect on the molecular motion due to the rapid procession. This latter assumption is, of course, in agreement with the observed facts of band spectra.

For nitric oxide $s = {}^1/_2$ and $\sigma_k = 1$. Neglecting at first the molecular rotation, the spin s sets itself either with or against σ_k, thus leading to the

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[22] Hund, *Z. Physik*, **36**, 657 (1926).

[23] Mulliken, *Phys. Rev.*, **28**, 482 (1926); **28**, 1202 (1926); **29**, 391, 637 (1927); **30**, 138, 785 (1927).

[24] Guillery, *Z. Physik*, **42**, 121 (1927).

[25] Liepson, *Astrophys. J.*, **63**, 73 (1926).

[26] Sponer and Hopfield, *Phys. Rev.*, **27**, 640 (1926).

doublet state referred to above. In the ${}^2P_1$ state s opposes, σ_k and in the ${}^2P_2$ state, s is with σ_k. When the rotation of the molecule is taken into account, Hund has shown that for increasing values of m, the influence of σ_k is relatively weakened as compared to that of m. The spin, s, gradually breaks away from its close coupling with σ_k and, in the limit, aligns itself either directly with or directly against the vector j_k (j_k is the vector sum of σ_k and m).

The vector sum of σ_k, s and m leads to the single vector j, which represents the total angular momentum of the molecule. Under all circumstances j is rigidly quantized. It is significant to observe in this connection that in meeting the conditions of quantization in the several instances referred to above, m itself is not quantized and, except for the special case of a molecule with $\sigma_k = 0$, cannot be quantized. Indeed, when a σ_k is present, the various m states not only differ by non-integral amounts of momentum but even the increments in momentum change in passing from one pair of rotation states to the next. The various rotational energy states are thus correlated with quantized terms which are j terms. Particular attention is called to this point because in the past m rather than j has frequently been regarded as the significant quantity in applying band spectra to the heat capacity and the entropy calculations.

It may be seen from the geometry of the model built up in the paragraphs above that j may be equal to the vector sum of σ_k and s (for $m = 0$) but never less. Hence the ${}^2P_1$ state has associated with it j values $= {}^1/_2$, ${}^3/_2$, ${}^5/_2 \ldots$, while the ${}^2P_2$ state can include no value $j = {}^1/_2$ but has associated with it the j values $= {}^3/_2$, ${}^5/_2$.

In fixing the *a priori* probability of a particular state of the molecule j, and not m, is the significant quantity to be considered. The *a priori* probability of a particular state is given by the wave mechanics as $(2j + 1)$.

The above was shown very definitely by the fine line structure photographed by Jenkins, Barton and Mulliken and by the intensity measurements of the same authors.[27] The j values used by the latter and by Mulliken[23] are larger by ${}^1/_2$ unit than the wave mechanics j values, but as they used $2j$ as the *a priori* probability, the same results are attained. In the tables the wave mechanics values for the vibrational quantum number n are used to replace the values given in their tables, which were one-half unit lower.

One further important consequence of the theory of Hund must be considered. From the equations of Hund it follows that for a molecule like nitric oxide, possessing a component σ_k, associated with every value of j there should be not two (corresponding to ${}^2P_1$ and ${}^2P_2$ states) but four states of the molecule of equal *a priori* probability. This should lead to four series of bands provided the energies corresponding to the states of

[27] Jenkins, Barton and Mulliken, *Phys. Rev.*, **30**, 175 (1927).

the last two members of the multiplet were sufficiently different from the first two. Jenkins, Barton and Mulliken did find a fine scale doubling in the lines of the $^2P_1$ band series and, where resolution was sufficiently great for intensity measurements, the intensity relations corresponded to the equal *a priori* probability assignment. No such fine scale doubling was found in the lines of the $^2P_2$ band system but it is probable that double states of almost equal separation existed in the initial $^2P_2$ level as well as in the final level so that the doubling could not be observed in the spectra. This type of superfine doubling is well recognized in other spectra of molecules possessing a component σ_k and is referred to as σ-type doubling. Mulliken[23] refers to the energy levels that give rise to the members of the doublets as A and B sub-levels.

The Entropy Calculated from the Spectroscopic Data.—The entropy of nitric oxide gas has been calculated for a temperature of 121.36°K. and also for 298.1°K. To obtain that portion of the entropy resulting from the translational energies of the molecules, we have employed the Sackur equation for the entropy of a monatomic gas

$$S = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V - 11.06$$

M is the molecular weight, T the absolute temperature, V the molal volume in cc. and R is the gas constant taken as 1.9869 cal./deg. per mole.

To obtain that portion of the entropy contributed by the degrees of freedom other than translation, we have used the summation method[28,1]

$$S_{E+R+V} = R \ln \Sigma_{e,n,m} p_{e,n,m} \mathbf{e}^{-\epsilon_{e,n,m}/kT} + \frac{1}{kT} \frac{\Sigma_{e,n,m} p_{e,n,m} \epsilon_{e,n,m} \mathbf{e}^{-\epsilon_{e,n,m}/kT}}{\Sigma_{e,n,m} p_{e,n,m} \mathbf{e}^{-\epsilon_{e,n,m}/kT}}$$

$\epsilon_{e,n,m}$ is the energy of a certain state with respect to electronic configuration, molecular vibration and molecular rotation, respectively; $p_{e,n,m}$ is the corresponding *a priori* probability, $\mathbf{e}$ the base of the natural logarithms and k the gas constant per molecule.

The above equation has been used in conjunction with the data and spectroscopic interpretation of Jenkins, Barton and Mulliken[2] as outlined above.

In carrying out the required summations in the calculations which follow, it has been convenient to make the summations as though σ-type doubling did not exist. Then each sum was doubled before incorporating it in the entropy equation. This method is justified since the energy differences of A and B substates are so small that the same energy may be assigned for each state (the spectroscopic measurements were taken at the middle of the double lines) and the total energy and total numbers in both A and B states will be double that in either one.

Table XI shows the values obtained for the significant sums which appear in the entropy equation for T = 121.36°K.

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[28] Giauque and Wiebe, This Journal, **50**, 101 (1928).

TABLE XI

SUMS IN THE ENTROPY EQUATION FOR NITRIC OXIDE

$n = 1/2 \quad T = 121.36°\text{K.}$

e	$\Sigma_m p_m e^{-\epsilon_m/kT}$	$1/kT\ \Sigma_m \epsilon_m p_m e^{-\epsilon_m/kT}$
$^2P_1$	51.364	50.529
$^2P_2$	11.053	27.553
$\Sigma_{e,n,m}$	62.417	78.082
Doubled for σ-type doubling	124.834	156.164

It is interesting to note that the distribution of molecules between the $^2P_1$ and $^2P_2$ states at the boiling point of nitric oxide is 82.29% of $^2P_1$ molecules to 17.71% of $^2P_2$ molecules. This unequal distribution is a result of the 124 odd wave numbers difference in energy between the two forms of coupling. The fraction of molecules in higher vibration states has been calculated and found to be inappreciable for this temperature. Putting the above sums into the entropy equation

$$S_{E+R+V} = 12.08 \text{ E. U.}$$

Combining this value with the 31.67 entropy units contributed by the translation of the molecules, the entropy of the hypothetical perfect nitric oxide gas at one atmosphere pressure and 121.36°K. has the value 43.75 calories per degree per mole.

The result of a similar calculation for a temperature of 298.1°K. is given in Table XII.

TABLE XII

SUMS IN THE ENTROPY EQUATION FOR NITRIC OXIDE

$T = 298.1°\text{K.}$

e	n	$\Sigma_m p_m e^{-\epsilon_m/kT}$	$1/kT\ \Sigma_m \epsilon_m p_m e^{-\epsilon_m/kT}$
$^2P_1$	1/2	124.864	124.107
$^2P_1$	3/2	0.917	5.419
$^2P_1$	5/2	.007	0.078
$^2P_1$	7/2	.000	.001
$^2P_2$	1/2	65.721	105.804
$^2P_2$	3/2	0.480	3.131
$^2P_2$	5/2	.004	0.043
$^2P_2$	7/2	.000	.001
$\Sigma_{e,n,m}$		191.993	238.584
Doubled for σ-type doubling		383.986	477.168

This leads to the value $S_{298.1} = 50.43$ E. U.

There is one further type of multiplicity which makes a contribution to the absolute entropy of nitric oxide which we have not considered in the above calculation, since it would be expected to affect the spectroscopic and $\int_0^T C_p \mathrm{d} \ln T$ calculations equally. This arises from the one unit of spin associated with the nitrogen nucleus and contributes $R \ln 3$ entropy units to the value of the absolute entropy.

Comparison of Entropy Values.—The theoretical and experimental values of the entropy are compared in Table XIII.

TABLE XIII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF NITRIC OXIDE

T, °K.		121.36	298.1
Entropy from spect. data, cal./deg./mole		43.75	50.43
$\int_0^T C_p d \ln T$	Actual gas	42.94 ± 0.1	...
	Corr. to ideal state	43.0	...

It is clear that the experimental value is in definite disagreement with that calculated from the spectroscopic data.

It appears significant that the entropy obtained from the calorimetric measurements is lower than that obtained by the spectroscopic method by almost exactly $^1/_2$ R ln 2. This can be explained if solid nitric oxide is a solution of two polymerized isomers in equal amount. Liquid nitric oxide is known to be highly associated into N_2O_2 molecules and it appears reasonable that this effect would persist in the solid. Solid isomers would result if, in the process of association, more than one type of pairing could occur between molecules which retained some of the electronic differences they possessed in the gaseous state, such as the differences responsible for σ-type doubling. An equimolal mixture of two such isomers of small energy difference would possess an entropy in excess of that obtained from the heat capacity measurements by an amount equal to R ln 2 entropy units per mole of polymerized molecules. This is equivalent to $^1/_2$ R ln 2 entropy units per stoichiometrical mole. The solid nitric oxide would thus appear to go to the absolute zero with 0.69 entropy units per mole still present. The discrepancy between the entropy values obtained from calorimetric and from spectroscopic data, respectively, is 0.72 entropy unit.

We do not regard this as a contradiction of the third law of thermodynamics, although it has an important bearing on the application of that law to thermodynamic problems. In conformity with views expressed in previous papers,[4,5] it is believed that if nitric oxide could be cooled to the absolute zero and be allowed to reach true equilibrium, a transformation would occur to a single species of molecule having zero entropy. This transformation would result from the energy difference which, though small, must exist between the isomeric forms. Expressed in other terms, we believe that if measurements of the heat capacity of nitric oxide could be carried to the absolute zero under equilibrium conditions, the results would fall on a curve which would show a maximum, close to the absolute zero, which would just account for the observed entropy difference.

We wish to thank Mr. J. O. Clayton for assistance in the experimental work and in the calculations. We also wish to thank Professor R. T. Birge for many discussions of the spectroscopic data and their interpretation.

Summary

Nitric oxide containing less than 0.001 mole per cent. of impurity has been prepared. Both solid and liquid were found to be blue in color. The accepted opinion that solid nitric oxide is colorless is apparently based on observations on material in a fine state of subdivision. Under such conditions it was found to have this appearance.

The heat capacities of solid nitric oxide and of the liquid have been measured from 14°K. to the boiling point. From the boiling point to 35°K. the smooth curve through the points is believed to be accurate to within 0.2 of 1%; below this temperature there is a gradual decrease in accuracy. At 20°K. the results are believed to be reliable to 0.7 of 1%, and at 14°K. to 2 or 3%.

The melting point was found to be 109.49 ± 0.05°K.; the boiling point 121.36 ± 0.05°K.

Calorimetric determinations of the heat of fusion and of the heat of vaporization were made. These were found to be 549.5 ± 1.0 and 3292.6 ± 3 calories per mole, respectively.

The vapor pressures of solid and liquid nitric oxide have been measured between 93 and 123°K.

The entropy of nitric oxide gas at 121.36°K. and one atmosphere was calculated from the above data and the third law of thermodynamics, and found to be 42.94 ± 0.1 calories per degree per mole. With the aid of Berthelot's equation of state this value was corrected to the ideal state, the correction being +0.09 calorie per degree per mole. When compared to the value calculated by the accurate summation method from the molecular spectrum of nitric oxide gas, the value obtained from the heat capacity measurements proved to be too low to the extent of 0.72 calorie per degree per mole. This is not taken as a contradiction of the third law of thermodynamics but is believed to arise from the presence of equimolal amounts of two forms of N_2O_2 in the solid state. This situation, which would lead to a difference of $^1/_2$ R ln 2 or 0.69 E. U. in comparison with the experimental amount of 0.72 ± 0.1 E. U., might be expected from the selective combination of molecules in the A and B substates resulting from the axial component of momentum of the nitric oxide molecule.

The two substates of nitric oxide are practically identical in energy and it is not surprising that the heat capacity measurements do not extend, and possibly cannot be extended, to sufficiently low temperatures to make the thermodynamic equilibrium produce a perfectly ordered crystalline state. This is a matter of considerable practical importance since it indicates that the correct use of the third law of thermodynamics will occasionally require information in addition to that supplied by heat capacity measurements.

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