[Contribution from The Cryogenic Laboratory and Department of Chemistry, The Ohio State University]

The Magnetic Susceptibility of Liquid Nitric Oxide and the Heat of Dissociation of $(NO)_2$[1]

By A. Lee Smith and Herrick L. Johnston

Received January 28, 1952

With the aid of a specially designed cryostat, the magnetic susceptibility of liquid nitric oxide was measured by both the Faraday test-body method and the Gouy method. A temperature variation of susceptibility was found, corresponding to an equilibrium dissociation of feebly magnetic dimer molecules into paramagnetic monomer. Measurements of the susceptibility of liquid nitric oxide–liquid krypton mixtures were used to estimate the contribution of the $(NO)_2$ molecule, which was found to be about 0.026×10^{-3} per mole of $(NO)_2$. The degree of dissociation of liquid nitric oxide varied from 2.7% at 110° to 5.0% at 120°K., and the heat of dissociation of the dimer was found to be 3710 ± 150 cal. per mole.

Introduction

The paramagnetic susceptibility of gaseous nitric oxide is well known both experimentally and theoretically.[2] The NO molecule has one unpaired electron, and the ground state of the molecule is a 2π state with the $2\pi_{1/2}$ component lying 120.9 cm.$^{-1}$ lower than the $2\pi_{3/2}$ level. Since this splitting is of the order of kT and since the magnetic moment of the molecule is zero in the lower state, Curie's law does not hold, but a theoretical expression deduced by Van Vleck gives excellent agreement with the observed susceptibility of NO gas.[2]

It is found, however, that in the liquid state, nitric oxide is almost completely associated into (NO_2) molecules.[3] Since magnetic susceptibility measurements provide a convenient method of evaluating the degree of dissociation in the liquid—the dimer, is, of course, only feebly magnetic—the present work was undertaken in order to find the variation of monomer concentration with temperature, and from this variation to calculate the heat of dissociation of the dimer. The only previous measurement of the susceptibility of the liquid was made by Bizette and Tsai,[4] who reported the value 3.53×10^{-6} per cc. at 110°K. This corresponds to about 97% dimerization.

Experimental Method and Apparatus

The Faraday test body method[5,6] was used because it seemed to offer the best sensitivity[6] and was readily adaptable to restrictions imposed by the nature of the sample. A few measurements were also made with a Gouy balance in order to check the results of the test body method. A special cryostat was designed to give the required temperature range and control. It consisted of a vacuum jacketed copper sample tube which extended downward between the poles of the electromagnet,[7] a reservoir for liquid air, and a heat valve to connect the two.[8] Provision was made to maintain the temperature of the sample at any point between 80°K. and room temperature by means of a suitable thermostating arrangement, which also automatically controlled the sample temperature to better than 0.1°. Temperatures were determined with thermocouples which were calibrated in the region 110–120°K. by observing the vapor pressure of the pure nitric oxide[9] with a mercury manometer and cathetometer. Nitric oxide was prepared by the method of Johnston and Giauque.[10] The test piece and quartz fiber used in the torsion method were carefully calibrated with pure gaseous oxygen, the susceptibility of which has been given as $\chi = 106.3 \times 10^{-6}$/gram at 20°.[10] The Gouy balance was calibrated by measuring the force exerted on a solution of nickel chloride[11] of known composition and density. Correction was made for the change in diameter of the Pyrex sample tube in going from 110°K. to room temperature.

The volume susceptibility of liquid nitric oxide is shown plotted as a function of temperature in Fig. 1. Run A was carefully calibrated and the curve of Run B was adjusted to give the best fit with Run A. Independent points from the Gouy method are also shown, and agreement is well within experimental error. Data for a typical run are shown in Table I. The susceptibility of solid nitric oxide was also checked by the Gouy method, and the results are shown in Table II along with those of Lips.[12] The slight temperature dependence may be real, but the variation is within experimental error. Measurements were also made on the susceptibility of solutions of nitric oxide in liquid krypton (liquid range 116–120°K.) in order to determine the amount of monomer as a function of total nitric oxide concentration. Such data are useful in the estimation of the susceptibility of the $(NO)_2$ molecule, as will be shown later. For these measurements, the gases were metered in a calibrated bulb

Table I

Typical Run, Torsion Method

Temp., °K.	Turns	Volume susceptibility × 10⁶	Molar volume[a]	Molar susceptibility × 10⁵
111.70	13.444	3.619	22.65	8.197
113.65	14.854	4.000	22.86	9.144
115.68	16.464	4.432	23.07	10.22
117.64	18.226	4.907	23.27	11.42
118.77	19.351	5.210	23.38	12.18
119.59	20.143	5.423	23.44	12.71
120.91	21.513	5.792	23.59	13.66

[a] Eugene C. Kerr, private communication.

Table II

Susceptibility by the Gouy Method

Source	Temp., °K.	Weight change, mg.	Susceptibility per mole of NO × 10³
This research	102.8	46.6	0.0208
This research	98.2	45.6	.0204
This research	97.7	45.4	.0203
Lips[12]	63–90	. .	.0198

---

(1) This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1934.

(3) A. L. Smith, W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **19**, 189 (1951).

(4) H. Bizette and B. Tsai, *Compt. rend.*, **206**, 1288 (1936).

(5) E. C. Stoner, "Magnetism and Atomic Structure," E. P. Dutton Co., 1926.

(6) G. C. Havens, *Phys. Rev.*, **41**, 337 (1932).

(7) Consolidated Engineering Corp., Pasadena, Calif.

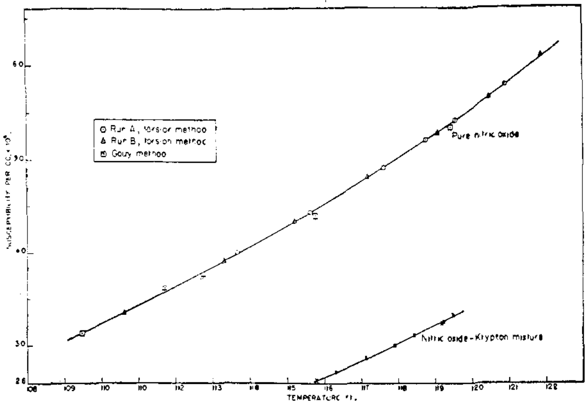
(8) A more detailed description of this apparatus will be submitted to the "Review of Scientific Instruments."

(9) A. Burris and C. D. Hause, *J. Chem. Phys.*, **11**, 442 (1943).

(10) H. L. Johnston and W. F. Giauque, This Journal, **51**, 3194 (1929).

(11) H. R. Nettleton and S. Sugden, *Proc. Roy. Soc. (London)*, **A173**, 313 (1939).

(12) E. Lips, *Helv. Phys. Acta*, **8**, 247 (1935).



Fig, 1.—Volume susceptibility of liquid nitric oxide.

at known temperature and pressure. The susceptibility of liquid krypton was measured directly at several temperatures, and was found to be $(-30.0 \pm 0.2) \cdot \times 10^{-6}$ per mole, as compared with the value -29.2×10^{-6} for the gas.[13] A copper test piece was used because the high density of liquid krypton made it impossible to obtain consistent data with a quartz test body.

Regarding the correction for the susceptibility of krypton in krypton–nitric oxide solutions, we assumed the volume susceptibilities of the components to be linear functions of their volume fractions. In these measurements, it was also necessary to make a correction for the amount of gas which vaporized into the space above the liquid. This was done by observing the total pressure at the time of measurement, and assuming Raoult's law for krypton. The remainder of the pressure was then ascribed to NO, and the amount of each component remaining in the liquid could then be calculated. In the worst case, 15% of the nitric oxide was vaporized. It was noted that even below the boiling points of the pure liquids, the vapor pressure of the mixture was above one atmosphere. This, of course, is because the vapor pressure of liquid nitric oxide is essentially that of monomeric NO.

In all cases, the volume susceptibilities were plotted against temperature and further calculations were carried out on values taken from the smooth curve.

Discussion

If the susceptibility of the dimer is assumed to be zero, the degree of dissociation can be calculated from the data of Table I and from values of the theoretical molar susceptibility.[2] The degree of dissociation α is given by the ratio of the observed to the calculated susceptibility, or

$$\alpha = \chi/\chi^0 \qquad (1)$$

Then for the dissociation reaction

$$(NO)_2 \rightleftarrows 2NO$$

we can calculate an equilibrium constant

$$K = X_1^2/X_2 = 4\alpha^2/1 - \alpha^2 \qquad (2)$$

where X_1 and X_2 are the mole fractions of the monomer and dimer, respectively. For solutions of nitric oxide in krypton, it can be shown that

$$K = \frac{4\alpha_2}{1 - \alpha_2} \times \frac{X_1'(1 + \alpha)}{X_1'(1 + \alpha) + 2X_k} \qquad (3)$$

in which X_1' is the number of moles of nitric oxide expressed in terms of monomer, and X_k is the number of moles of krypton. The heat of dissociation of the dimer is given by

$$\Delta H_D = -R\,\frac{d \ln K}{dT^{-1}} \qquad (4)$$

Preliminary calculations showed that since α for the liquid was quite small (2–6%) considerable error might result from the assumption that the dimer has zero susceptibility. The susceptibility of the dimer could not be measured directly, but with the aid of the magnetic data taken on nitric oxide–krypton solutions, a method of estimating the dimer susceptibility was found.

Our first approach to this problem was to assume that the equilibrium constant K did not vary with the concentration of nitric oxide. An expression for K was developed which involved the observed susceptibility of the solution, X_1' and X_k, and a parameter k, defined as the ratio of the volume susceptibility of the pure dimer to that of the pure monomer. Then by equating K's at different dilutions, but at the same temperature, we could solve the expression for k. It was found, however, that k was negative (indicating a diamagnetic dimer) and varied rapidly with temperature. Such a combination of circumstances did not seem plausible, so it was concluded that the activities of the solution components were not proportional to the mole fractions, *i.e.*, activity coefficients should have been taken into account.

A second and more fruitful method was the following: The molar susceptibility of the pure dimer χ_2^0 was arbitrarily assigned a series of values ranging from -8×10^{-5} to $+8 \times 10^{-5}$. Each of these values was used to compute a corresponding α at 116 and 120°, and from these α's K, and then ΔH_D were calculated. This was done for pure nitric oxide and for one krypton solution.[14] ΔH_D was then plotted as a function of χ_2^0 as shown in Fig. 2. The intersection of the two curves gives both ΔH_D and χ_2^0 directly. The figure brings out the expected result that the influence of the dimer becomes less, the more dilute the solution. This method involves the reasonable assumption that χ_2^0 and the activity coefficients of X_1 and X_2 do not change appreciably over the small temperature range 116–120°K. The degree of dissociation of the liquid nitric oxide and the corrected K's are given in Table III.

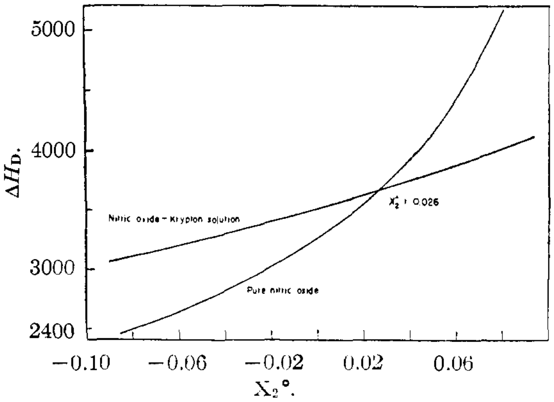


Fig. 2.—Heat of dissociation *vs.* dimer susceptibility.

Figure 3 shows $-R \ln K$ plotted against the reciprocal of the temperature, and from this plot (over a 10 degree temperature range) we find ΔH_D

---

[13] L. Abonnenc, *Compt. rend.*, **208**, 986 (1939).

[14] This was the most concentrated solution, for which X_1'/X_k = 0.615. These data were considered most accurate.

TABLE III

DEGREE OF DISSOCIATION OF LIQUID NITRIC OXIDE

A. Pure nitric oxide

Temp., °K.	α	$K \times 10^3$
110	0.0273	2.032
112	.0311	2.768
114	.0352	3.709
116	.0399	4.922
118	.0449	6.439
120	.0505	8.360

B. Diluted nitric oxide

Temp., °K.	X_1'	X_k	α	$K \times 10^3$
116	0.1452	0.2404	0.1003	9.222
118	.1418	.2367	.1135	11.995
120	.1375	.2331	.1287	15.637

= 3710 cal. per mole of $(NO)_2$. This compares well with the value 3910 cal. obtained by Rice[15] from the entropy of vaporization of liquid nitric oxide at its boiling point. If we had assumed that $\chi_2^0 = 0$, the dissociation heat would have been 3270 cal.

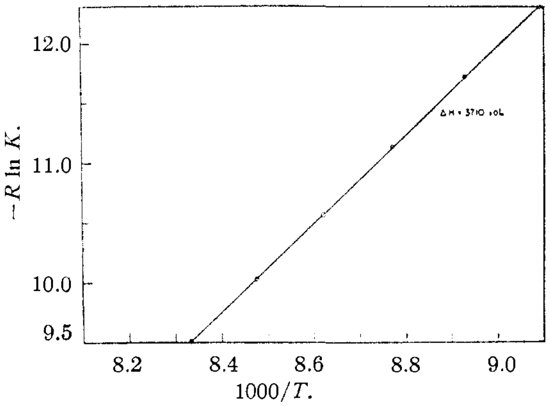


Fig. 3.—$R \ln K$ *vs.* T^{-1} for pure nitric oxide.

Figure 2 shows that the dimer is feebly paramagnetic as is the completely associated solid nitric oxide.[16] The value of $\chi_2^0 = 0.026 \times 10^{-3}$ per mole of $(NO)_2$ is only approximate since it involves the assumption that the molar volume of $(NO)_2$ is twice that of NO. One might state more accurately that the average volume susceptibility of the dimer between 116 and 120°K. is -0.56×10^{-6} per cc.

The chief sources of error in this work are calibration error and uncertainties in the vaporization correction in krypton solution. The former is probably not greater than 3%, and the latter is probably less than 2%. Actually, a small calibration error has a negligible effect on ΔH_D. It is probable that the value for the dissociation heat is reliable to ±150 cal.

As a check on our data we have calculated a synthetic heat capacity curve for liquid nitric oxide, assuming the equipartition value of 12 cal. per mole at the melting point (109.49°) and a slow rise in the heat capacity of the hypothetical normal liquid such as is shown by methane. The excess heat capacity due to dissociation of $(NO)_2$ was calculated using the equation and results are shown

$$C_{xs} = \left(\frac{d\alpha}{dT}\right)\frac{\Delta H_D}{2} \tag{5}$$

in Table IV. The slight discrepancy at higher temperatures may be due to heat of solution or other effects not manifested in the magnetic data.

TABLE IV

CALCULATED HEAT CAPACITY OF LIQUID NITRIC OXIDE, CALORIES PER MOLE

Temp., °K.	C_E	C_{XS}	$C_{calc.}$	$C^{10}_{obsd.}$
111	12.10	3.50	15.60	15.65
113	12.20	3.87	16.07	16.12
115	12.30	4.29	16.59	16.63
117	12.40	4.68	17.08	17.22
119	12.50	5.18	17.68	17.98

It is interesting to calculate the expected degree of dissociation of gaseous nitric oxide near its boiling point. Taking into account the change in density on going from a liquid to a gas, and using the equilibrium constant for the pure liquid, we can calculate that α = 64% at 120°K. Actually, experimental data[13] show that dissociation is nearly complete (99% or more). The reason for this discrepancy is not clear, but it may be that the proximity of the molecules in the liquid inhibits the formation of the three-electron bond which stabilizes the gaseous NO molecule.[17]

Acknowledgments.—We wish to thank Mr. L. E. Cox, shop foreman, for contributing many valuable ideas to the construction of the cryostat. We would like to express our gratitude to the du Pont Company for financial support during a portion of the period of this work.

COLUMBUS, OHIO

---

[15] O. K. Rice, *J. Chem. Phys.*, **4**, 367 (1936).

[16] H. L. Johnston and H. R. Weimer, THIS JOURNAL, **56**, 625 (1934).

[17] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 266.