Magnetic Susceptibility Study of the Liquid Phase Equilibrium N2O42NO2 in Pure Nitrogen Tetroxide

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Magnetic Susceptibility Study of the Liquid Phase Equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ in Pure Nitrogen Tetroxide*

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The magnetic susceptibility of liquid nitrogen tetroxide was measured by the Gouy method over the temperature range 0°C to 30°C. The liquid was found to be diamagnetic throughout this temperature range although the diamagnetism decreased as the temperature increased. The magnetic measurements were found to be in good agreement with the spectrophotometrically determined equilibrium composition of the liquid as reported by Steese and Whittaker.

INTRODUCTION

THE evaluation of the equilibrium constant of the reaction $N_2O_4 \rightleftharpoons 2NO_2$ in the liquid phase by spectrophotometric methods[1] involves an assumption of doubtful validity. Namely, it has to be assumed that the optical absorption coefficient of NO_2 is the same in both liquid and gas phases. Consequently, it was desirable to try to evaluate the constants by a method which does not involve the same assumption. This condition is satisfied when the nitrogen dioxide concentration is determined by magnetic susceptibility measurements. Unfortunately, the concentrations of the major species were such that this method could not yield equilibrium constants of good accuracy. However, the method was accurate enough to establish a measure of the validity of the questionable assumption used in the spectrophotometric study. Also the spectrophotometric study yielded values for the heat of liquid phase dissociation of N_2O_4 and the heat of vaporization of NO_2 that were somewhat unexpected. The magnetic susceptibility study may be expected to give data that will provide a measure of the validity of these thermodynamic results.

Materials

The nitrogen tetroxide used in this study was prepared according to the method described by Steese and Whittaker.[1] Nickel chloride was used as a susceptibility standard for this work, and it was obtained as Baker's analyzed cp crystals of the hexahydrate. Analysis for ions of cobalt, iron, and manganese were made. They were found to be absent within the limits of ordinary gravimetric methods of analysis.

Apparatus and Procedure

The magnetic susceptibilities were determined by the Gouy method.[2] The magnetic field was produced by a Consolidated Engineering Corporation Electromagnet and Power Supply plus a large Sola transformer. This produced a magnetic field constant to within 0.1% and the reproducibility of the magnetic field from one experiment to another was approximately 0.5%. Pyrex susceptibility tubes were suspended by means of aluminum wire from one arm of a microbalance of approximately one microgram sensitivity. At the working load the precision of the microbalance was approximately ±20 micrograms.

Temperature control of the sample was obtained by surrounding the sample tube with a double-walled glass jacket, so that liquid of constant temperature could be circulated through the annular space between the glass walls. The temperature was measured by a platinum resistance thermometer that was suspended alongside the sample tube and temperature measurements to 0.01°C could be made. Temperature control during an experiment could be maintained constant within ±0.05°C. During temperature equilibration a low-velocity flow of dry nitrogen was maintained around the sample tube. During measurements the flow was stopped. Most measurements were made at a field strength of 5700 gauss; a few were made at 3200 gauss.

The magnetic field and sample tubes were calibrated using nickel chloride solution as a standard. Calculation of the gram susceptibility of the nickel chloride solution was made according to the results reported by Nettleton and Sugden.[3] Analysis of the nickel chloride solution was carried out by a gravimetric method using dimethylglyoxime.[4] Calibration of the apparatus was carried out at room temperature in all cases; however, the susceptibility of the nickel chloride solution was determined at −1°C in order to evaluate the effectiveness of temperature equilibration and the ability of the apparatus to measure susceptibilities at reduced temperatures. The susceptibility of the nickel chloride solution was calculated assuming Curie's law to hold and the calculated value was then compared with the experimentally determined value. Experimental and calculated values agreed within 0.9%. This was taken as an indication that temperature equilibrium was

[1] C. M. Steese and A. G. Whittaker, J. Chem. Phys. 24, 776 (1956).
[2] L. G. Gouy, Compt. rend. 109, 935 (1889).
[3] H. R. Nettleton and S. Sugden, Proc. Roy. Soc. (London) A173, 313 (1939).
[4] H. Willard and H. Diehl, *Advanced Qualitative Analysis* (D. Van Nostrand Company, Inc., 1943), p. 385.

achieved and that the apparatus showed satisfactory operation at the lower temperature.

Nitrogen tetroxide was transferred to the susceptibility tubes in an all glass initially evacuated apparatus. Two susceptibility tubes of different calibration constants were used in the study to minimize the chance of inadvertent errors.

RESULTS

The basic equation used to calculate susceptibility is as follows:

$$\Delta W_s - \Delta W_c = (1/2g)(\kappa_s - \kappa_n)A(H_1{}^2 - H_2{}^2), \quad (1)$$

where

$\Delta W_s =$ the change in weight due to sample and susceptibility tube,

$\Delta W_c =$ the change in weight due to the empty susceptibility tube,

$g =$ acceleration due to gravity,

$\kappa_s =$ volume susceptibility of the sample,

$\kappa_n =$ volume susceptibility of nitrogen,

$A =$ cross section of the sample,

$H_1 =$ field strength at the bottom of the susceptibility tube, and

$H_2 =$ field strength at the top of the susceptibility tube.

For the experimental arrangement used in this study the following conditions were satisfied:

$$(1/2g)A(H_1{}^2 - H_2{}^2) = C, \quad (2)$$

where C is a constant at a given magnet current and its value was determined by using the nickel chloride solution as a standard of known susceptibility. All of the susceptibility measurements were made with respect to nitrogen whose volume susceptibility[5] is -4.0×10^{-10}. Since the susceptibility of nitrogen was small compared to the susceptibility for liquid N₂O₄, it was considered to be zero in all calculations. As a result of the above simplifications, the gram susceptibility χ_s of all solutions was calculated according to the following equation:

$$\chi_s = (1/\rho C)(\Delta W_s - \Delta W_c), \quad (3)$$

where ρ was the density of the liquid nitrogen tetroxide, and was taken from the work of Mittasch, Kuss, and Schlueter.[6]

The results obtained when experimental values were substituted in Eq. (3) are given in Table I. These data show that the liquid is diamagnetic over the entire temperature range studied and that the diamagnetism of the liquid decreases as the temperature increases. Results obtained by Sone[7] on the magnetic susceptibility of nitrogen oxides appear to be quite accurate except for the value obtained for NO₂. This value appears to be in error by a factor of about 6.5 assuming

[5] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, p. 354.

[6] Mittasch, Kuss, and Schlueter, Z. anorg. Chem. **159**, 1 (1927).

[7] T. Sone, Science Repts. Tôhoku Imp. Univ. **11**, 139 (1922).

TABLE I. Magnetic susceptibility of liquid nitrogen tetroxide at various temperatures.

Temperature °C	Susceptibility per gram, $-\chi \times 10^7$
30.6	2.40±0.04
22.1	2.50±0.07
15.0	2.57±0.06
8.3	2.67±0.07
−0.1	2.72±0.07

Havens'[8] more recent result to be correct. The error in this value seems to be related to the fact that certain assumptions concerning the behavior of the N₂O₄⇌2NO₂ equilibrium at high temperature had to be made and the experimental difficulties at high temperature caused some large uncertainties. Unfortunately, Sone published only one value of the susceptibility of the liquid equilibrium mixture. This was $-2.62 \pm 0.05 \times 10^{-7}$ for the gram susceptibility at 12.3°C, and there appears to be no reason to believe that there is any serious error in this value. It is evident that this value is in good agreement with the results obtained in this study.

DISCUSSION

The results obtained in this study and in the spectrophotometric study[1] of the liquid-phase equilibrium N₂O₄⇌2NO₂ can be compared if the following assumptions are made:

1. The only species present in significant amounts are NO₂ and N₂O₄.

2. The magnetic susceptibility of NO₂ is the same in the liquid and gas phases.

3. The system is sufficiently magnetically dilute so that the Wiedemann additivity relation holds.

4. The correct mole susceptibility of NO₂ (χ_m) is given by Havens[8] according to the equation $\chi_m = 1380(293/T) \times 10^{-6}$, where T is the absolute temperature.

5. The gram susceptibility of N₂O₄ is correctly given by Sone as -2.76×10^{-7}.

6. The equilibrium is not significantly displaced by the magnetic field. This last assumption can be shown to be quite good since simple calculation indicates that the free energy of the reaction is not changed by more than 1 part in 19 000 due to a change of 5000 gauss in magnetic field strength.

Under these assumptions the susceptibility of the liquid can be calculated from the data obtained in the spectrophotometric study[1] by means of the Wiedemann additivity relation:

$$\chi_1 = \chi_a f_a + \chi_b (1 - f_a), \quad (4)$$

where χ_1, χ_a, and χ_b are the gram susceptibilities of the liquid equilibrium mixture, pure NO₂, and pure N₂O₄, respectively, and f_a is the weight fraction of NO₂ in the

[8] G. G. Havens, Phys. Rev. **41**, 337 (1932).
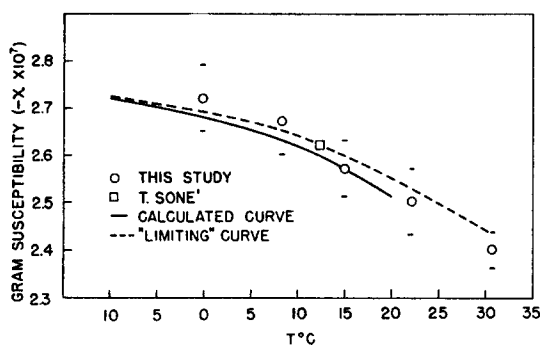
Fig. 1. Magnetic susceptibility of liquid nitrogen tetroxide *vs* temperature.

TABLE II. Magnetic susceptibility of liquid nitrogen tetroxide calculated from spectrophotometric results.

Temperature °C	NO$_2$ concentration[a] (g/cc) X10^5		Magnetic susceptibility per gram, $-\chi_1$ X10^7	
	B	V,D	B	V,D
20	128.8	117.1	2.51	2.53
15	97.6	88.4	2.57	2.59
10	72.3	65.3	2.62	2.63
0	39.7	35.4	2.68	2.69
−10	19.3	16.9	2.72	2.73

[a] Data taken from reference 1. B—Based on Bodensteins vapor phase data. V,D—Based on Verhoek and Daniels vapor phase data.

liquid. The results obtained from a set of such calculations are given in Table II. Calculated and observed magnetic susceptibilities are plotted in Fig. 1. It can be seen in Fig. 1 that the agreement between the experimental and calculated susceptibilities is quite good in that the curve through the calculated points falls well within the average deviations of the observed points. The calculated points in Fig. 1 are for NO$_2$ concentration values based on Bodenstein's[9] vapor-phase data. It can be seen from Table II that the calculated values based on Verhoek and Daniels'[10] vapor-phase data agree even better with the observed susceptibilities. Consequently it appears that no serious error was introduced in the spectrophotometric study by calculating concentrations of NO$_2$ on the assumption that the optical absorption coefficient of NO$_2$ is the same in both liquid and gas phases.

If it were assumed that the optical absorption coefficient in the liquid phase (α_l) was greater than that in the vapor phase (α_g) as one might suspect from the work of other investigators,[11,12] then the NO$_2$ concentration would be smaller than those given in Table II. Indeed, if the ratio α_l/α_g were assumed to be 1.12, a new calculated curve would appear as the dashed curve in Fig. 1. Since this curve passes through the average deviation limit of the 30.6°C data point it may be considered a "limiting" curve. Hence, it can be said that the ratio α_l/α_g cannot exceed 1.12 and still preserve compatibility of the spectrophotometric and magnetic susceptibility results. Certainly the experimental data are not good enough to establish that the ratio α_l/α_g is exactly unity. However, in view of the fact that the solid curve in Fig. 1 fits the experimental data much better than the dashed curve, it seems reasonable to conclude that the value of the ratio α_l/α_g is much closer to unity than 1.12.

[9] M. Bodenstein, Z. physik. Chem. **100**, 68 (1922).
[10] F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).
[11] E. Rabinowitch and W. C. Wood, Trans, Faraday Soc. **32**, 540 (1936).
[12] G. Kortum and E. Muller, Z. Naturforsch. **1**, 439 (1926).

THERMODYNAMIC ASPECTS

The results of this study of the magnetic susceptibility of liquid N$_2$O$_4$ lend support to the somewhat unexpected thermodynamic values derived from the spectrophotometric study of this system. In the latter study the heat of dissociation of N$_2$O$_4$ in the liquid phase (ΔH_1) was found to be greater than its heat of dissociation in the gas phase (ΔH_g), and the heat of vaporization of NO$_2$ from the equilibrium mixture at its boiling point was found to be surprisingly small. S. H. Bauer[13] has pointed out that the reverse situation would be expected to exist for the heats of dissociation. Thus, for pure dipole-dipole interaction between NO$_2$ molecules simple theory gives:

$$\frac{\Delta H_1}{\Delta H_g} = \left(\frac{\epsilon+2}{3\epsilon}\right)_1 = 0.594, \qquad (5)$$

where ϵ is the dielectric constant for liquid N$_2$O$_4$ and 2.8 is taken as its value.[14] Hence, if ΔH_g is taken as 14.6 kcal,[9] the value of ΔH_1 is 8.67 kcal, which is considerably different from the 19.5 kcal obtained in the spectrophotometric study. Moreover, if one assumes a valence type bond between the monomer units, thermodynamic equations lead to a similar result. For the case at hand the following equation holds to good approximation:

$$\Delta H_g = \Delta H_1 + 2L_1 - L_2, \qquad (6)$$

where L_1 and L_2 are the heats of vaporization of NO$_2$ and N$_2$O$_4$, respectively. Both ΔH_g and ΔH_1 are positive and one might expect L_1 and L_2 to be about equal in magnitude. Therefore, it is clear that ΔH_1 would be expected to be less than ΔH_g.

A decrease in the value of ΔH_1 has the effect of decreasing the curvature of the curves in Fig. 1 and making them more nearly parallel to the temperature axis. Thus, the "limiting" dashed curve in Fig. 1 has a ΔH_1 of approximately 17.9 kcal as contrasted to 19.5 kcal for the full curve in Fig. 1. Consequently, any value of ΔH_1 equal to or less than ΔH_g would be in complete

[13] S. H. Bauer, Department of Chemistry, Cornell University, private communication.
[14] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, p. 76.

disagreement with the magnetic results. From Eq. (6) it follows, therefore, that a low value for the heat of vaporization of NO_2 from the equilibrium mixture is probably correct. Finally, it is interesting to note that the effect of increasing the ratio α_l/α_g is in the same direction as decreasing the value of ΔH_1. Thus, if the ratio α_l/α_g

were much greater than unity, even higher values of ΔH_1 would have to be assumed to make the spectrophotometric results compatible with the magnetic data. Since ΔH_1 cannot reasonably be expected to exceed 21.5 kcal[1] it follows that this puts another upper limit of about 1.15 on the ratio α_l/α_g.

Homogeneous Exchange Reaction Between Hydrogen and Deuterium

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The homogeneous exchange reaction between hydrogen and deuterium has been reinvestigated, to see whether a more satisfactory quantitative test of the transition state method could be obtained in this simple chemical reaction.

The reaction was studied in the temperature range from 916°K to 1010°K, where the heterogeneous contribution from the walls was found to be negligible. Preventing air from diffusing into the reaction vessel trough the walls, exchange rates lower by a factor of 2.0 than those obtained by previous authors were found in the whole temperature interval. The total activation energy was determined as 59.8±0.4 kcal/mole.

The validity of the transition state method was tested by extrapolation of the experimental data to a lower temperature region (283°–373°K) where independent experimental data were available. Comparison of the extrapolated values with the experimental ones leads to a very good agreement.

THE homogeneous exchange reaction in the gas phase between hydrogen and deuterium was first studied experimentally in 1935 by A. and L. Farkas[1] in the range 740–600°C, and, more recently, by M. Van Meersche[2] in the range 600–450°C. Its importance lies in the simplicity of the reacting system, which together with the *ortho-para* conversions of H_2 and D_2 is more amenable to a theoretical treatment than any other chemical reaction. These reactions were therefore used as the first test of the activated state method developed by Polanyi, Wigner, and Eyring. Among the many theoretical papers in which the *a priori* calculation of the rate of these reactions has been attempted, we may particularly refer to that by Hirschfelder, Eyring, and Topley,[3] where with an assumed percentage of ionic terms the calculated values of the reaction constant fitted the experimental results within a factor of two at 1000°K. To check the activated state method independently from the quantum-mechanical calculation of the potential energy of the system, Farkas and Wigner[4] used the experimental *ortho-para* hydrogen conversion values at high temperature to obtain the

unknown constants of the activated complex, such as the vibrational frequencies, etc. With these constants determined, the *ortho-para* hydrogen conversion at low temperature and the H_2-D_2 exchange reaction data were calculated. The experimental values of the exchange reaction were fairly consistent with this treatment, but for the low temperature conversion this treatment gave values differing by more than a factor of three from the experimental ones of Geib and Harteck.[5] We want to stress that the disagreement was no longer due to possible errors in calculation of the potential surface, but to the transition state method itself or to the experimental values. In fact Farkas and Wigner concluded their paper stating, "it is planned to revise the experimental data in a wide temperature range, since it seems very important to decide whether the present theory of reaction velocities, as developed recently, is correct or not."

Since then the activated state method has been an object of interest for many theoreticians. The quantum-mechanical corrections to the point motion on the potential surface have been evaluated,[6] and the equilibrium hypothesis assumed in the method has also been

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[1] A. and L. Farkas, Proc. Roy. Soc. (London) A152, 152 (1935).

[2] M. Van Meersche, Bull. Soc. Chim. Belg. 60, 99 (1951).

[3] Hirschfelder, Eyring, and Topley, J. Chem. Phys. 4, 170 (1936).

[4] L. Farkas and E. Wigner, Trans. Faraday Soc. 39, 708 (1936).

[5] K. H. Geib and P. Harteck, Z. physik. Chem. (Bodenstein Festband) 849 (1931).

[6] J. O. Hirschfelder and E. Wigner, J. Chem. Phys. 7, 616 (1939); H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. 11, 276 (1943).