For arsenic(V) chloride, however, the *SR* would be 4.74, indicating that the chlorine would have expanded only enough to change in *SR* by 0.19. Here the bond would be even less ionic, and this compound would be expected not only to be an even more active chlorinating agent, but also it would be less stable. When it is considered that phosphorus(V) chloride is 13.5% dissociated in the vapor at 160°,[25] and wholly dissociated above 300°, and that antimony(V) chloride is likewise considerably dissociated even at its boiling point of 140°,[26] it is not surprising that arsenic(V) chloride has not been prepared.

There are, of course, other factors which complicate such chemical interpretations, especially for the compounds of the heavier atoms. One is the bond length, which together with the polarity of the bond has its effect on ionization. The ease of separation of a molecule into ions depends not only on the polarity of the bonds but also on the bond lengths; ionization may occur as easily for a less polar bond if the bond length is greater. This may help to explain the trend toward "increasing basicity" in a periodic group where the electronegativity actually alternates.

Another complicating factor is the apparent decrease in availability for bond formation, in certain elements, of the *s* electrons in the higher principal quantum levels. That is, the so-called "inert pair,"[27] (which may contribute to the instability of mercury compounds, causes the major valence of thallium to be one instead of three, causes lead to exhibit a valence of two in preference to four, and contributes largely to the instability of bismuth(V)) probably exerts an influence on the oxidizing properties of such elements as antimony and tellurium in their higher valence states, which would not be predicted on the basis of stability ratios alone.

Independent of such factors, the stability ratio theory seems both to be strengthened by its consistency with the many known chemical "anomalies" and to be useful in helping to explain them.

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[25] W. Fischer and O. Jübermann, *Z. anorg. Chem.*, **235**, 337 (1938).

[26] Reference 23b, p. 794.

[27] (a) H. G. Grimm and A. Sommerfeld, *Z. Physik*, **36**, 36 (1926), (b) ref. 23b, pp. 287, 481, 617, 795, 798, 951.

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[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

# Vapor Pressures and Freezing Points of the System Nitrogen Tetroxide–Nitric Oxide

BY A. G. WHITTAKER, R. W. SPRAGUE, S. SKOLNIK AND G. B. L. SMITH

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The freezing points and vapor pressures of the system $N_2O_4$–NO have been determined in the composition range 0 to 16.85% by weight of NO, and in the temperature range 15 to −40°.

## Introduction

The system nitrogen tetroxide–nitric oxide represents a rather unique combination of compounds. Nitrogen tetroxide in the liquid phase as well as in the gas phase dissociates reversibly into two molecules of nitrogen dioxide. Nitric oxide reacts either with nitrogen tetroxide or nitrogen dioxide to form nitrogen trioxide ($N_2O_3$) which also dissociates. The system, therefore, is complicated by at least two sets of equilibria which are not independent. Data on the freezing points and vapor pressures of mixtures of nitrogen tetroxide and nitric oxide are not only important parameters of the system, but can contribute to an understanding of the properties of $N_2O_4$–NO solutions. Wittorf,[1] and Baume and Robert[2] both investigated this system, but unfortunately the agreement between the results reported by these investigators is poor. The freezing points and vapor pressures, therefore, were redetermined in 1948 at the U. S. Naval Ordnance Test Station, Inyokern. The results of this investigation are in substantial agreement with those of Baume and Robert[2] over the range of compositions studied.

**Purification of Nitrogen Tetroxide.**—Nitrogen tetroxide about 99.5% pure as obtained from Mathieson Chemical Company was used as starting material. It was boiled in the presence of phosphorus pentoxide for about 16 hours, and then distilled into a container which was arranged so that dry oxygen could be bubbled through the dried nitrogen tetroxide to oxidize the last traces of nitric oxide. The purified material was then frozen and pumped on to remove as much oxygen as possible. All these operations were carried out in all glass apparatus containing no ground joints or stopcocks.

The purified material had a melting point of −11.23° (this is in good agreement with −11.20° obtained by Giauque and Kemp[3]) and froze to a colorless solid. The water content was about 0.024 ± 0.01% by weight according to the analytical work as carried out by the method of Whitnack and Holford.[4]

**Preparation of Nitric Oxide.**—The method given by Johnston and Giauque[5] for the preparation of nitric oxide appears to give a very pure material, but has the disadvantage of requiring a dependable supply of liquid nitrogen. It was therefore advisable to seek another method. Several methods of generation were tried, and the nitric oxide analyzed qualitatively to determine the impurities present. Nitrous oxide was detected by observing the transmission of a sample in the infrared region. Inert impurities were determined by oxidizing a sample in a eudiometer tube with an acid permanganate solution. The inert material was taken as the volume of gas remaining after all reaction had ceased. The method of preparation finally adopted consisted of adding a saturated solution of sodium nitrite to a saturated solution of ferrous sulfate in 35% sulfuric acid. This method was found to give no detectable amounts of $N_2O$, and a minimum amount of inert material, assumed to be nitrogen because it was not affected by solutions of permanganate, persulfate or thiosulfate, and did not support combustion.

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[1] N. V. Wittorf, *Z. anorg. Chem.*, **41**, 85 (1905).

[2] G. Baume and M. Robert, *Compt. rend.*, **169**, 968 (1919).

[3] W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

[4] G. C. Whitnack and C. J. Holford, *Anal. Chem.*, **21**, 801 (1949).

[5] H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929).

A modified version of the method of purification used by Johnston and Giauque[5] was used to purify the gas from the generator. The generated gas was passed through a medium sintered glass disk into a column containing 50% KOH; it was then bubbled in the same manner through a column containing 95% sulfuric acid; from the acid it was passed through a trap immersed in a Dry Ice–alcohol-bath, and then was condensed in a trap immersed in liquid nitrogen. While the gas was being condensed it was pumped on with a vacuum pump capable of producing a vacuum of $10^{-3}$ mm. After a sufficient quantity had been condensed, the solid NO was pumped on for an additional half hour. The purity of the final material was about 99.8% by weight, as determined by the method of Whitnack, Holford, Gantz and Smith.[6]

**Apparatus.**—Since this work was undertaken to clarify points brought out by previous study, an effort was made to obtain more accurate results. A primary requisite was that all apparatus coming in contact with the mixtures should be entirely glass to avoid corrosion errors. It was also felt that adequate temperature control was essential to accurate temperature measurements.

**Freezing Cell.**—The freezing cell (Fig. 1) was designed so as to allow about 30 cm. of the thermocouple to be immersed in the liquid to be frozen in an effort to avoid errors due to heat conduction along the thermocouple wires. The thermocouple well was filled with paraffin to provide lubrication when inserting the thermocouple and to afford better heat transfer. Uniform stirring conditions were obtained by use of a solenoid-actuated, plunger-type stirrer furnished with current pulses from a thyratron controlled by a multivibrator circuit. The stirring rate in all cases was 60 strokes per minute. The freezing cell unit (Fig. 1) was immersed in a stirred, refrigerated, alcohol-bath and temperature control was accomplished by controlling the temperature of this bath.

The copper–constantan thermocouple in the cell was calibrated in place by measuring the freezing points of pure water (0.00°) carbon tetrachloride (−22.85°) mercury (−38.87°) and the transition point of sodium sulfate (+32.383°). From these points corrections for the standard copper–constantan thermocouple calibration curve[7] were determined. The value −278.18° was taken as zero for the Kelvin scale.

It was desired to obtain linear cooling rates so that the break in the cooling curve at the freezing point would be sharply defined. It was also desirable to be able to hold the bath at any fixed temperature for vapor pressure measurements. An automatic controlling device was designed to meet these requirements which was capable of maintaining the alcohol-bath temperature constant to 0.02°, or maintaining a bath temperature different from the cell temperature by any desired amount constant to 0.04°.

A glass Bourdon type gage was used to measure vapor pressures. The design used four collapsed bulbs in series to retain sensitivity and increase strength. A paddle on the tip of the pointer dipping in a mercury pool served as a vibration damper. The gage was used as a null gage, the null point being taken as the point at which the platinum contacts on pointer and gage envelope make contact as determined by a Fisher–Serfass electronic relay. In measuring vapor pressures the pressure on the envelope side of the gage was read with mercury manometers and the gage constant added to give the pressure on the freezing cell side of the gage. Over the pressure range involved, the gage constant and sensitivity were independent of pressure. The gage sensitivity was about 0.01 mm. Pressures up to one atmosphere were read on a single manometer; pressures greater than one atmosphere were read on a series manometer consisting of three manometers in series with the space above the mercury filled with redistilled toluene.

**Procedure.**—A weighed amount of purified nitrogen tetroxide was added to the cooled and evacuated freezing cell from an ampule equipped with a breakoff. The nitric oxide was prepared as needed and distilled from the collecting trap into a gas measuring buret. The pressure of the nitric oxide was determined by raising mercury to a reference level in the gas buret and noting the atmospheric pressure and the level in a standpipe open to the atmosphere. The gas buret and the pressure of nitric oxide were recorded for the purpose of calculating the quantity of nitric oxide, assuming it to behave as a perfect gas. The nitric oxide then was displaced by mercury into the freezing cell, through a glass breakoff. The contents of the freezing cell were maintained at −40° during the addition. The above procedure was repeated until the desired quantity of nitric oxide had been added to the cell. Pressure readings were corrected for meniscus height according to the data of Cawood and Patterson[8] and were reduced to international centimeters of mercury using the value of 979.504 cm./sec.$^{-2}$ for the acceleration of gravity at this location as calculated from the data of Landolt, Börnstein, Roth and Scheel.[9]

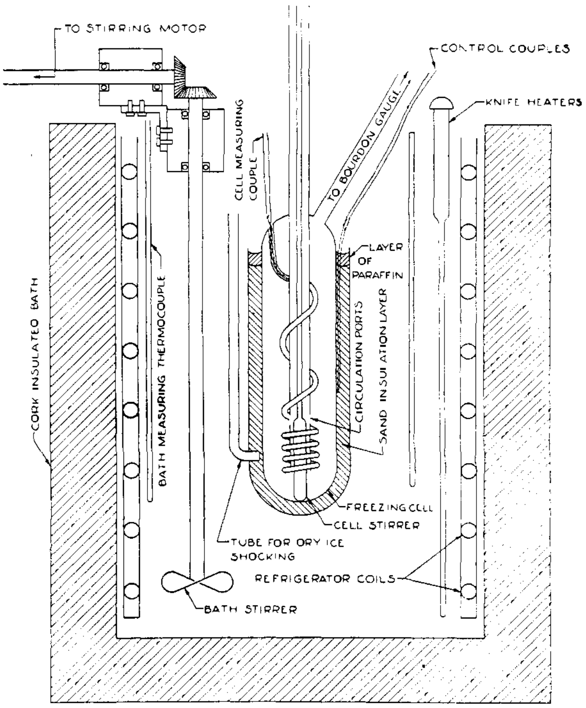

Fig. 1.—Freezing cell.

Samples were withdrawn by an isothermal distillation method for each composition.

The vapor pressure of each composition was studied over a limited temperature range. These results have been expressed in the following equations covering the liquid range studied:

| | Equation | Temp. range, °C. | Wt. % NO | Av. deviation, mm. |
|---|---|---|---|---|
| (1) | $\log_{10} P_{\text{mm}} = 9.0121 - 1782.2\,(1/T)$ | 15 to −14.1 | 2.89 | 2.8 |
| | (Extends into metastable region) | | | |
| (2) | $\log_{10} P_{\text{mm}} = 8.9700 - 1751.3\,(1/T)$ | 15 to −17.1 | 5.55 | 2.3 |
| (3) | $\log_{10} P_{\text{mm}} = 9.0105 - 1745.3\,(1/T)$ | 15 to −20.4 | 8.30 | 1.4 |
| (4) | $\log_{10} P_{\text{min}} = 9.1163 - 1760.46\,(1/T)$ | 9 to −23.5 | 10.67 | 2.3 |
| (5) | $\log_{10} P_{\text{mm}} = 8.9847 - 1704.6\,(1/T)$ | 2 to −28.8 | 14.11 | 2.2 |
| (6) | $\log_{10} P_{\text{mm}} = 9.0347 - 1702.4\,(1/T)$ | 5 to −33.6 | 16.85 | 1.8 |

The standard deviation of $\log_{10} P_{\text{mm}}$ for equation 1

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[6] G. C. Whitnack, C. J. Holford, E. S. Ganzt and G. B. L. Smith, *Anal. Chem.*, **23**, 464 (1951).

[7] "International Critical Tables," Vol. 1, p. 58 (1926).

[8] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 518 (1933).

[9] Landolt, Börnstein, Roth and Scheel, *Phys. Chem. Tabellen*, **5**, 25 (1923).

was 0.0092 and for equation 3, 0.0018. The vapor pressure of the system NO–$N_2O_4$ containing solid $N_2O_4$ was also studied. These results are contained in the equation

$$(7)\quad \log_{10} P_{mm} = -9.938688 + 6719.285\ 1/T - 0929534\cdot 1/T^2\ (-13 \text{ to } -40°)$$

The standard deviation for only two of the equations was calculated. These values, along with the data presented in Table I, gives an indication of how well these equations fit the vapor pressure data.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED VAPOR PRESSURES FOR 8.30% NO

| T, °C. | P calcd. | P obsd. | T, °C. | P calcd. | P obsd. |
|---|---|---|---|---|---|
| 15.39 | 917 | 915.1 | −20.68 | 123.8 | 123.3 |
| 2.46 | 477.2 | 479.9 | −24.38 | 112.6 | 112.2 |
| − 4.04 | 335.6 | 336.1 | −29.25 | 96.7 | 95.7 |
| −15.08 | 177.2 | 176.9 | −39.44 | 62.3 | 62.8 |

A fit of the data with Antoine[10] type equations was tried, and no better fit was obtained. These equations had the disadvantage that the virtual ice point was different for each equation, and no suitable average value could be used in all equations and still have the equations fit the data as well as the least squares fit. Some vapor pressure measurements were made on pure nitrogen tetroxide for the purpose of checking our equipment. The average of these results agree with the data of Giauque and Kemp[3] within our experimental accuracy. Some of the vapor pressure data are presented in graphical form in Fig. 2. Although the curves appear linear for all compositions in the liquid–vapor regions, a close examination of the results for the first two compositions appears to show a slight curvature. The slopes increase slightly as the freezing point is approached. This effect decreases as the concentration of NO increases and within the accuracy of the data, it was impossible to detect any curvature for concentrations greater than about 8% NO. For purposes of comparison, Table II gives the freezing points as determined by cooling curves (perhaps the most accurate values), by observed vapor pressure data, and by the simultaneous solutions of equations 1 through 6 with equation 7. It would appear from this table that although the equations represent the best line through the points in the least squares sense, they give the least accurate values of the freezing points. Figure 3 shows this same data plotted in terms of ml. fraction $N_2O_3$ for the system $N_2O_3$–$N_2O_4$, and compared with the data of other workers.

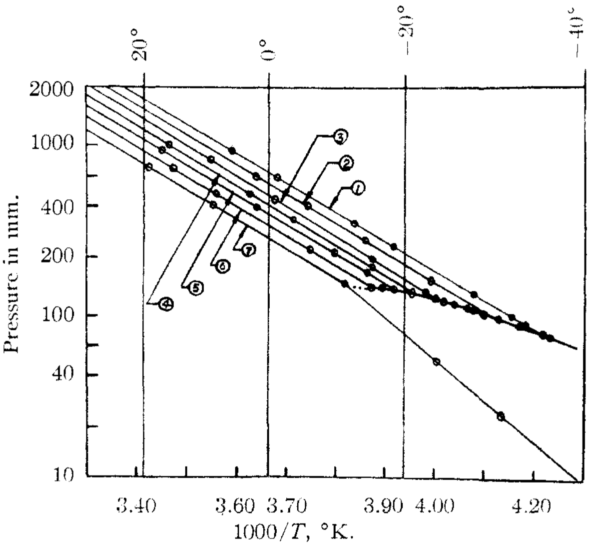

Fig. 2.—Vapor pressure of $N_2O_4$–NO mixtures: 1, 16.85% NO; 2, 14.11% NO; 3, 10.67% NO; 4, 8.30% NO; 5, 5.55% NO: 6, 2.89% NO; 7, pure $N_2O_4$.

TABLE II

COMPARISON OF FREEZING POINTS

| Wt. % NO | Observed f.p. cooling curve, °C. | Observed f.p. vapor p. data, °C. | Calculated f.p. vapor Pmm equations, °C. |
|---|---|---|---|
| 0 | −11.30 | −11.20 | −11.20 |
| 2.89 | −14.11 | −13.64 | −13.32 |
| 5.55 | −17.06 | −17.30 | −17.38 |
| 8.30 | −20.40 | −20.21 | −20.98 |
| 10.67 | −23.51 | −23.37 | −23.67 |
| 14.11 | −28.81 | −28.87 | −30.06 |
| 16.85 | −33.61 | −34.23 | −34.96 |

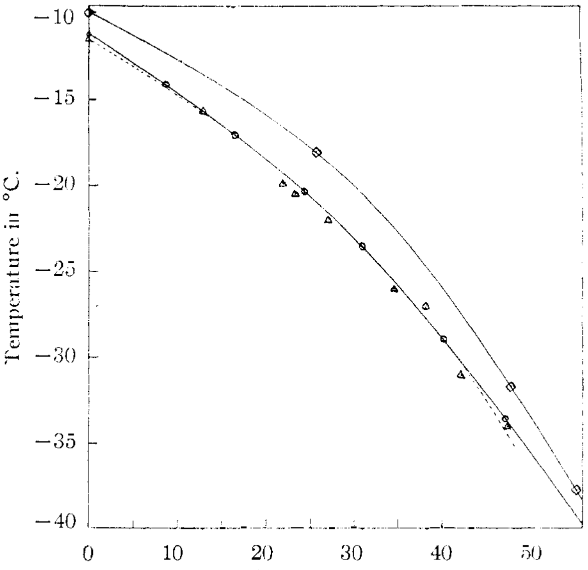

Fig. 3.—Freezing point–composition diagram for system $N_2O_3$–$N_2O_4$: -△-, data of Baume and Robert; -◇-, data of Wittorf; -⊙-, this research.

The analyses of samples taken for the various compositions was carried out according to the method of Whitnack, Holford, Gantz and Smith.[6] This method is capable of giving results accurate to 0.05% of the value reported. The results of these analyses showed that they had not reached equilibrium with the main body of material; hence, they were not representative samples. This situation was unfortunate but not serious. The compositions were calculated from the known amounts of material added to the cell and corrected for material withdrawn as samples. Results of these calculations are given in Table III. Although this

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(10) G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

TABLE III

COMPOSITION OF SAMPLES

| Wt. NO added | Wt. $N_2O_4$ removed | Wt. NO removed | Total wt. $N_2O_4$ present | NO, % |
|---|---|---|---|---|
| 1.3365 | 0 | 0 | 44.9140 | 2.89 |
| 1.2645 | 1.0956 | 0.0247 | 43.8184 | 5.55 |
| 1.3934 | 0.5239 | .0517 | 43.2945 | 8.30 |
| 1.2612 | .2734 | .0383 | 43.0211 | 10.67 |
| 1.9325 | .5126 | .0869 | 42.5085 | 14.11 |
| 1.6514 | .4689 | .1159 | 42.0396 | 16.85 |

gave no cross check of the composition as originally planned, it is estimated from small errors known to exist in the apparatus that the error in the nitric oxide concentration is of the order of 0.5% by weight of the values reported. Also, no correction was made for the evaporation into the space above the liquid (about 160 ml.), since a rough calculation showed that in the worst case the concentration error involved was only 0.3% of the value reported.

Three warming and two cooling curves were obtained with pure $N_2O_4$; the average of all the triple points was $-11.30°$, with an average deviation of 0.09°. The average freezing point was $-11.35°$, with average deviation of 0.01°; the average melting point was $-11.23°$, with average deviation of 0.04°. It is interesting to note that the value of $-11.23°$ obtained from the warming curves agrees within the experimental accuracy with that of Giauque and Kemp.[3]

## Discussion of Results

The liquid–vapor equilibrium curves show very nearly single component behavior for each composition and that their slopes are almost independent of composition; indeed, their slopes do not differ greatly from that of pure nitrogen tetroxide. Unfortunately, a quantitative reason for this somewhat surprising result cannot be given because of insufficient fundamental information concerning this complex system.

The heat of fusion of nitrogen tetroxide as determined from the phase diagrams of the data plotted either of the system $N_2O_4$–$N_2O_3$ or $N_2O_4$–NO is apparently higher than the calorimetric value given by Giauque and Kemp.[3] This means that the liquidus curve is a little more nearly horizontal than would be predicted for an ideal solution. This effect could arise from the dissociation of pure nitrogen tetroxide. However, the data by Cundall[11] indicates that the dissociation of nitrogen tetroxide at its freezing point is not enough to account quantitatively for the observed discrepancy in the heat of fusion of pure nitrogen tetroxide. The fact that nitric oxide reacts with nitrogen tetroxide (probably not to completion at the temperatures involved) does not explain the observed results because the disagreement for the system treated as $N_2O_4$–NO is in the wrong direction (*i.e.*, the heat of fusion should appear less than the calorimetric value). It is possible that, contrary to reports of previous workers, limited solid solutions are formed in this system. However, it is clear that this system needs to be studied further if it is to be understood completely.

It was found that a better least squares fit for the vapor pressure data was obtained for the liquid–vapor curves than for the liquid–solid–vapor curve. Since the same liquid–solid–vapor curve was obtained for all compositions, as the concentration of NO increased more points were obtained in the lower regions of the curve than in the upper. This situation resulted in the points in the lower regions carrying too much weight in determining the least squares fit. The fit of the curve, therefore, is quite good in the lower regions, and rather poor in the upper regions. As a consequence pressures predicted from the equation have an error of about 3% or less in 68% of the cases. The points were more or less uniformly distributed along the liquid–vapor curves, so no regions exerted undue influence on their shapes.

As previously mentioned, slight curvature was present in the liquid–vapor curves for compositions less than 8% NO. Two attempts were made to indicate this curvature in the least squares fit. However, the curvature was slight and over such a short range that a curve fitted to the data did not show a significantly better fit than the over-all straight line through all of the data points.

**Acknowledgment.**—The authors wish to express their appreciation for the assistance of Gerald C. Whitnack and Clifford Holford of the Analytical Branch in the analyses of the samples; to Martha Kenyon and Helen Morrin of the Mathematics Division for the least squared fit equations for the vapor pressure curves of the mixtures; and to Floyd Swanson of the Chemistry Division shop for assistance in the construction of parts of the apparatus.

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[11] J. T. Cundall, *J. Chem. Soc.*, **59**, 1076 (1891).