The authors desire to express their appreciation to the Wisconsin Alumni Research Foundation for substantial aid in connection with this work. It is also a pleasure to acknowledge our indebtedness to the Civil Works Administration which made it possible for one of us (C. H. S.) to participate in the research.

Summary

1. The dielectric constant of the gaseous equilibrium mixture of nitrogen dioxide and nitrogen tetroxide has been measured at five temperatures between 298 and 398°A. and at seven pressures between 150 and 760 mm.

2. With the aid of density measurements already existent in the literature these data have been utilized to calculate the electric moments of the nitrogen dioxide and nitrogen tetroxide molecules.

3. The polarity of the nitrogen dioxide molecule has been found to decrease with increasing temperature over the interval studied. It is suggested that this decrease is due to the passage of greater and greater numbers of the molecules into more symmetrical higher vibrational states as the temperature is increased.

4. The dipole moment of the nitrogen tetroxide molecule does not differ greatly, if at all, from zero. Thus, there has been removed the apparent inconsistency between the results of infra-red absorption and dielectric constant studies now existent in the literature.

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

Data of State of Phosphine at Low Pressures, and from 190 to 300°A.

BY EARL A. LONG[1] AND EARL A. GULBRANSEN[1]

In conjunction with a research on low temperature heat capacities of gases by the velocity of sound method, which requires accurate corrections for gas imperfection, we have found it expedient to measure the *PVT* behavior of gases whose data of state are unknown. Although it is possible to do this accurately by measuring the velocity of sound in gases as a function of pressure,[2] we have found the methods of gas thermometry more suitable for our purposes.

This communication discusses the apparatus used and the measurements with phosphine.

Phosphine.—Phosphine was obtained from a pure sample prepared for other measurements in this Laboratory.[3] The gas was prepared by the reaction between phosphonium iodide and potassium hydroxide. A detailed description of this preparation will be given in a later communication.[4] From a consideration of the heat capacities of the solidified gas just below the melting point, the amount of solid impurity was estimated to be less than 0.004 of one mole per cent. The method of preparation precluded the presence of any impurities not soluble in the liquefied gas.

Helium.—Purified helium was taken from a supply used for liquefaction purposes in this Laboratory. The helium was passed through a charcoal trap cooled with liquid air. The charcoal had previously been degassed by evacuating to a pressure of 10^{-6} mm. at 400°.

Method and Apparatus

Our method is a modification of that of Johnston and Weimer,[5] and depends on the use of a "double" constant-volume gas thermometer wherein the properties of helium, whose behavior as a real gas is accurately established, are compared directly, in the same apparatus under identical conditions, with those of the gas whose *PVT* behavior is being investigated. The method eliminates errors due to secondary temperature standards.

The apparatus[6] is shown in Fig. 1. The thermometer bulbs A and B were surrounded with lead shot contained within a vacuum-tight copper sheath wound with an electric heater. Pressure corrections for the bulb volumes were eliminated by the compensating effect of a pressure of hydrogen in the sheath.[7] The electric heaters on the "blocks" E and F were wired for separate heating. Copper–constantan thermocouples were soldered at suitable points in the apparatus, including three thermocouples distributed along each of the German silver tubes C and D. A vacuum of better than 10^{-5} mm. provided thermal insulation of the thermometer sheath and "blocks" from the container E. The total temperature drift of the thermometer sheath was about 0.01° per hour at 200°K.

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[1] National Research Council Fellows.

[2] *Cf.* van Itterbeek and Keesom, *Comm. Phys. Lab. Univ. Leiden*, No. 209-c (1930).

[3] We are indebted to Mr. C. C. Stephenson for supplying us with this quantity of pure phosphine.

[4] Stephenson and Giauque, to be published.

[5] Johnston and Weimer, THIS JOURNAL, **56**, 625 (1934).

[6] *Cf.* also Johnston and Weimer, Ref. 5. and Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927). The latter paper describes the experimental technique employed.

[7] Since these measurements were completed, we have found this precaution unnecessary, as the correction to the bulb volume is negligible for a pressure difference of one atmosphere.

Pressure Readings and Corrections.—Two identical glass manometers of 16 mm. internal diameter were used. The pressures were determined by comparison with a standard invar steel meter bar calibrated by the United States Bureau of Standards. A Société Génévoise cathetometer was used as a comparison instrument, with a precision of 0.02 mm. Absolute measurements were obtained by maintaining a high vacuum over the upper menisci of the manometers. The usual corrections were applied as described by Giauque and Johnston.[8] To correct for the gas imperfection of helium, we used the data of Henning.[9] The corrections for thermal expansion of the thermometer bulbs and the important "dead-space" corrections for the gas in the connecting capillaries and fixed points of the manometers were applied in the usual manner.[10] A very small gravitational correction (of the order of 0.001 cm.) was also applied to the phosphine measurements to correct for the difference in height of the thermometer bulb and the fixed point of the manometer. This correction was negligible for helium. The capillary and "dead-space" volumes were less than 2% of the bulb volumes (120.90 and 124.18 cc. for helium and phosphine, respectively, at 273.1°K.). All volumes were determined by weighing displaced mercury.

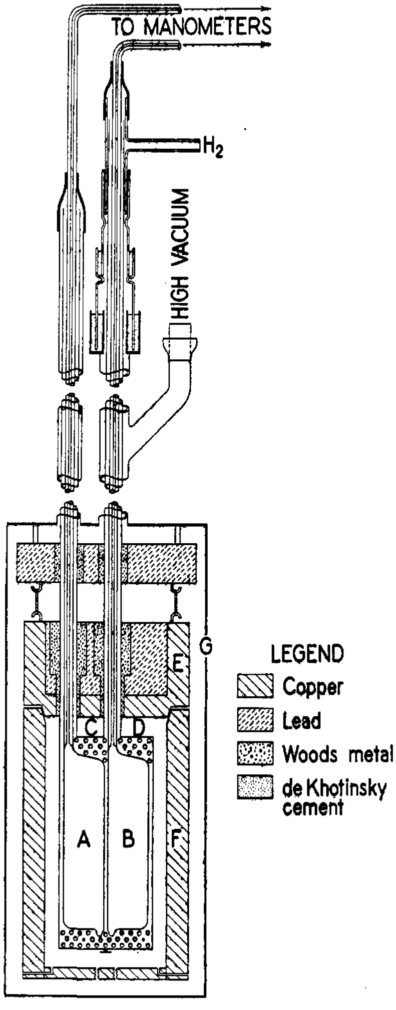

Fig. 1.—Apparatus: A, B, thermometer bulbs; C, D, German silver tubes; E, F, upper and lower blocks, equipped with electric heaters.

Ice-Point.—The ice-point measurements were taken by adjusting the apparatus temperature until the thermocouple on the bottom of the thermometer sheath read nearly zero. From previous tests of the same thermocouple with both junctions in an ice-bath, we estimate the error of this procedure to be not more than 0.003°.

In all, five ice-point pressures of helium were obtained, which varied between 74.883 and 74.895 cm., with an average deviation of 0.004 cm. from the average value of 74.885 cm. The ice-point pressures of phosphine are given in Table I. No appreciable trends of ice-point pressures with time were observed.

Results

"Full" and "half" pressure measurements were made in order to determine whether or not more than two virial coefficients were needed to express the PVT behavior of phosphine. We found no effect due to change in pressure. The possible effect of adsorption was considered at first to require another set of runs with a bulb of greatly increased surface. However, considering the agreement of our "full" and "half" pressure data, and also the results of Johnston and Weimer,[5] who found no adsorption in the case of nitric and nitrous oxides, we believe that any adsorption effect present was negligible.

The final data are given in Table I, together with the experimental values of the second virial

TABLE I

Full pressure			Half pressure		
T, °K.	P, Int. cm.	$-B$, cc.	T, °K.	P, Int. cm.	$-B$, cc.
189.91	59.318	452.3	189.99	37.096	453.5
195.99	61.290	428.2	195.13	38.113	442.3
200.42	62.766	399.6	201.20	39.356	395.6
205.07	64.291	383.9	210.07	41.140	357.9
210.55	66.063	361.9	219.12	42.952	328.5
219.05	68.740	325.5	229.91	45.102	303.3
229.10	72.053	314.4	240.51	47.185	301.1
237.72	74.858	289.7	249.95	49.111	252.6
243.12	76.636	269.6	260.11	51.132	238.1
252.19	79.575	249.8	273.10	53.754	197.0
260.14	82.121	238.4	273.10	53.754	197.0
267.17	84.424	220.4			
273.10	86.399	198.1			
273.10	86.396	198.1			
273.10	86.400	198.1			
284.52	90.086	181.6			
296.95	94.152	152.6			

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

[9] Henning, *Z. Kalte-Industrie*, 37, 169 (1930).

[10] *Cf.* Cornish and Eastman, THIS JOURNAL, 50, 643 (1928).

coefficient "B" in the equation of state of Kamerlingh Onnes.[11]

$$pVm = RT + BP \qquad (1)$$

The molal volume Vm[12] was calculated from our measured ice-point pressures by means of the accurate ice-point densities obtained by Ritchie.[13]

Equation (1) was fitted empirically to the data, giving for the second virial coefficient

$$B = 406.4 - \frac{1.0450 \times 10^5}{T} - \frac{3.02163 \times 10^7}{T^2} + \frac{1.3141 \times 10^{12}}{T^4} - \frac{2.2656 \times 10^{16}}{T^6} \qquad (2)$$

The agreement is shown graphically in Fig. 2, in which the solid curve represents Equation (2) and the experimental data are shown by circles. Since the experimental errors affect the pressure in an absolute rather than a relative sense, the full pressure runs were given greater weight in deriving Equation (2). The average error is of the order of 3 units in B, corresponding to 0.005 cm. in measured pressure.

The broken curve in Fig. 2 shows the values of B computed from Berthelot's equation

$$PV = RT\left[1 + \frac{9}{128}\frac{PTc}{PcT}\left(1 - 6\frac{Tc^2}{T^2}\right)\right] \qquad (3)$$

using the critical constants $Pc = 64$ atm. and $Tc = 324.1$°K.[14]

It is evident from Fig. 2 that, in the case of phosphine, Berthelot's equation is more accurate than might be expected, and could be used in calculations of heat capacities from velocities of sound, entropy accompanying gas imperfection, etc., without serious error.

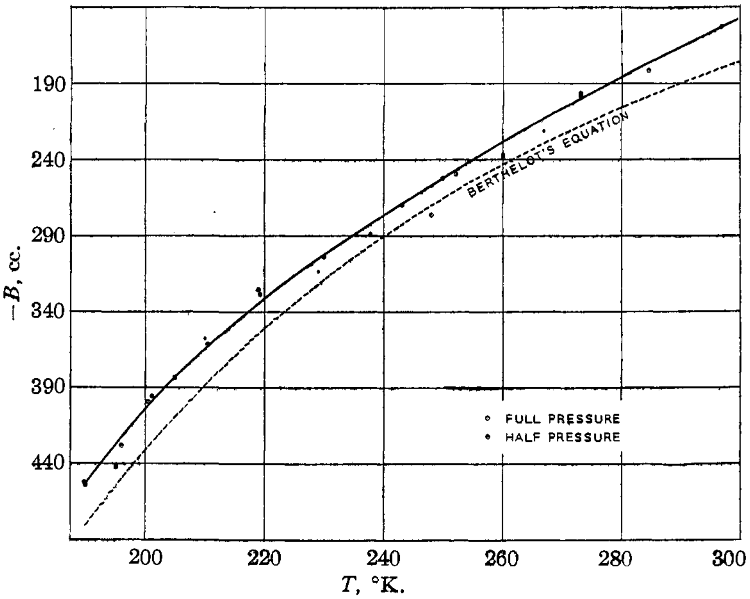

Fig. 2.—Virial coefficients of phosphine.

We express our appreciation to Professor W. F. Giauque for his generous coöperation and many helpful suggestions, and to Mr. G. F. Nelson, chief mechanician, for the skillful construction of the apparatus.

Summary

A "double" constant volume gas thermometer is described for measuring the low pressure data of state of gases at low temperatures. The method consists of a direct comparison of the properties of the gas in question with the known PVT behavior of helium.

Data of state were determined for pure phosphine from 190 to 300°K., and the experimental values of the second virial coefficient B were calculated over this temperature range. The dependence of the virial coefficient B on temperature is well represented by a power series in $1/T$. The accuracy is about 3 units in B, corresponding to 0.005 cm. in measured pressure.

The variation of the virial coefficient with temperature is shown graphically. Comparison is also made with the virial coefficients computed from Berthelot's equation, which proves to be fairly accurate both in reproducing the molal volumes and the slope of the B-T curve.

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(11) Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 71 (1901). *Cf.* also Fowler, "Statistical Mechanics," Cambridge University Press, Cambridge, England, 1929, p. 219.

(12) *Vm* is a constant in each run, since the measured pressures were corrected to the ice-point volume of the thermometer bulb.

(13) Ritchie, *Proc. Roy. Soc.* (London), **A128**, 551 (1930).

(14) "International Critical Tables," Vol. III, p. 229.