of the reaction vessel, without illumination. That the steady state in the light is identical with the thermal equilibrium, is shown by the fact that

no shift occurs in the dark after illumination, or in the light after attaining equilibrium in the dark.

BERKELEY, CAL.   RECEIVED NOVEMBER 29, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Low Pressure Data of State of Nitric Oxide and of Nitrous Oxide between their Boiling Points and Room Temperature

BY HERRICK L. JOHNSTON AND HARRY R. WEIMER

Comparatively little has been published on the $P-V-T$ relationships in real gases below the ice point. Such data as do exist relate, for the most part, to the few gases commonly employed in gas thermometry and to high pressure isothermals of industrially important gases. In conjunction with a program of accurate low temperature heat capacity measurements of gases by the velocity of sound method, now in progress in this Laboratory, it has been found necessary to determine for ourselves the necessary corrections for gas imperfection. The present paper gives a description of the apparatus and procedure used, followed by the results obtained with nitric oxide and with nitrous oxide.

Preparation and Purification of the Gases

Nitric Oxide.—We prepared nitric oxide by the procedure followed by Johnston and Giauque[1] which combines the chemical process of Winkler[2] with the highly efficient distillation and sublimation process of Gray.[3] We employed "reagent quality" or high grade "c. p." chemicals as reagents. The capacity of our preparation and purification system was about one-fourth that of Johnston and Giauque but in other respects it was identical in construction and we employed the same technique in its operation. Hence we think it reasonable that the quality of our nitric oxide was approximately the same as that of those authors (i. e., the mole fraction of impurity less than 0.00001).

Nitrous Oxide.—We prepared nitrous oxide by the method of Gehlen,[4] which consists in the addition of sulfuric acid to a slightly alkaline aqueous solution of the normal potassium salt of nitrosylsulfuric acid. A consideration of the facts presented in Gehlen's paper, in conjunction with a careful search of the literature, convinced us that this method yields a product of higher purity than is given by the methods more commonly in use. Our preparation line, which was made of Pyrex glass with fused joints and was previously flushed and evacuated, consisted of a five-liter generating flask con-

taining a saturated solution of potassium nitrosylsulfite into which 50% sulfuric acid was added, dropwise, and the following units for the preliminary purification: a trap cooled with dry ice–ether, a bead tower with 50% potassium hydroxide, a bead tower with 90% sulfuric acid, a second dry ice–ether trap, a storage bulb in which the liquid was condensed, by means of liquid air, to a colorless liquid, and a freshly charged phosphorus pentoxide drying column. The final stage of purification was carried out by circulating the product, four times, through the identical distillation and sublimation cycle employed with the nitric oxide.

The potassium nitrosylsulfite was prepared by introducing nitric oxide, produced in the manner described earlier except for the physical purification which was omitted, into a 40% solution of potassium sulfite which was, likewise, 5% in potassium hydroxide. The crystals obtained by this process were washed with a 5% potassium hydroxide solution and were, eventually, redissolved to form the charge for the generating flask.

As with the nitric oxide, only "reagent quality" or "c. p." chemicals were employed; the distilled water used to make up solutions (or the solutions themselves) was boiled to exclude air and we followed the same general technique described by Johnston and Giauque.[1]

While we had available no convenient method of estimating small traces of impurity we think it probable that the final product was comparable, in purity, with the nitric oxide.

Hydrogen, used to calibrate the resistance thermometer, was taken from a commercial tank of electrolytic hydrogen and was purified by slow passage through high grade charcoal cooled with liquid air. The charcoal was previously degassed with a stream of hydrogen at a temperature a little below red heat.

Method and Apparatus

Our method is based on the use of the constant volume gas thermometer wherein the same equipment is used for both hydrogen, whose properties as a real gas are known, and the gases of interest whose $P-V-T$ properties we desired to ascertain. The calibration of a sensitive electrical resistance thermometer was secured when hydrogen was used in the apparatus, thereby establishing the true temperature when the nitrous and nitric oxides were under measurement.

Figure 1 is a diagram of the apparatus, which is modeled after the constant volume gas thermometer of Giauque

(1) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(2) Winkler, Ber., **34**, 1408 (1901).

(3) Gray, J. Chem. Soc., **87**, 1601 (1905).

(4) Gehlen, Ber., **65**, 1131 (1932).

Buffington and Schulze.[5] The thermometer bulb "B" is surrounded with lead shot and enclosed in a vacuum-tight copper sheath on whose outer surface the resistance thermometer, double silk insulated No. 40 B. and S. gage copper wire, is wound tightly, and varnished with bakelite. Hydrogen at a pressure close to that within the bulb is admitted through the German silver tube "G" to
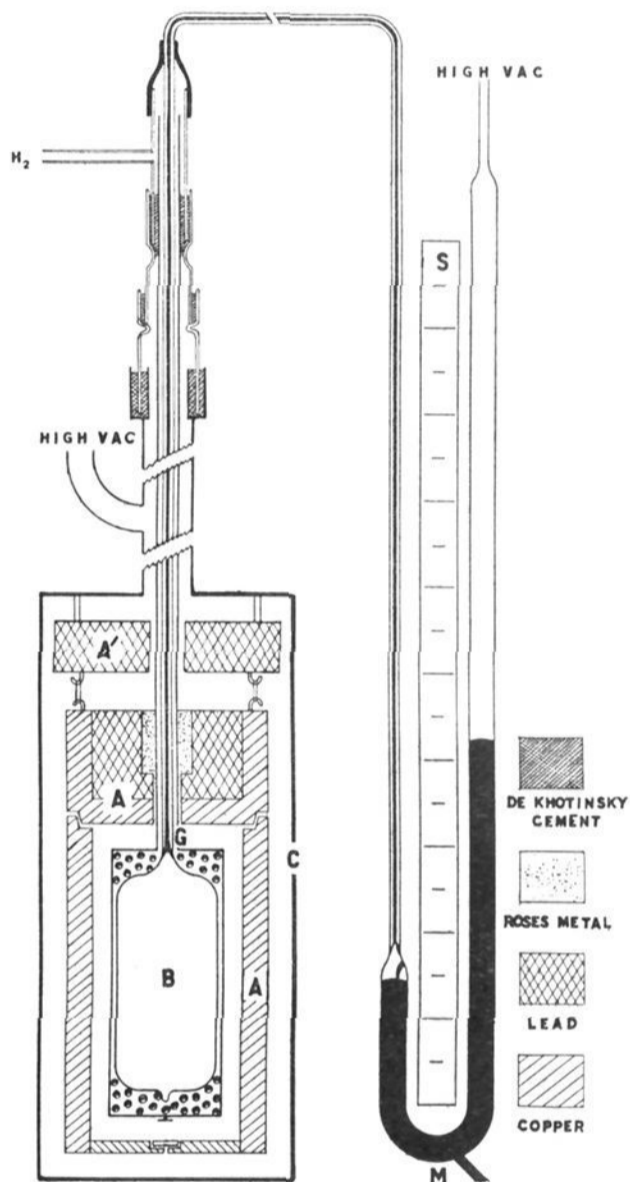

Fig. 1.—Diagram of the apparatus: A, A, upper and lower blocks; A', auxiliary block; B, Pyrex thermometer bulb surrounded with shot and sealed in a gas-tight copper sheath; G, thin-walled German silver tube; C, vacuum-tight outer container which is immersed in a cryostat bath; M, large bore mercury manometer connected to B through a capillary of approximately millimeter bore; S, standard meter bar.

the space between the copper sheath and the outer surface of "B." A vacuum of 10^{-5} mm. or better, isolates the thermometer sheath from the "blocks" and the "blocks" from the outer container. Heating circuits were so arranged that the blocks could be heated separately. A *standard copper–constantan thermocouple* was also soldered to the bottom of the copper thermometer sheath and several thermocouples for control purposes were distributed at suitable points in the apparatus, including

upper, middle and bottom segments of the German silver tube "G."

Resistance Thermometer Calibration.—The sensitive resistance thermometer[6] was calibrated, in place, by means of pressure readings taken with pure hydrogen in the thermometer. Two sets of readings, with calibration points selected at approximately ten-degree intervals between 110 and 320°K., were taken for this purpose. The corrected results[7] were in good agreement and, with few exceptions, the individual calibrations fitted a smooth calibration curve (on which the data were plotted as deviations from a linear equation) to within 0.01°, or better. This smooth curve was used as the basis of the final temperature scale which was further smoothed to first and second differences by an analytical procedure.

The ice point readings, necessary as a basis for the gas thermometer scale, were taken when the entire apparatus had come to thermal equilibrium with an ice-bath and were based on the temperatures given by the standard thermocouple. Five readings were taken,[8] which varied between 812.01 and 812.12 mm. in the extremes with an average deviation, from the mean, of 0.04 mm. (equivalent to 0.013° at the ice point). There appeared to be a slight trend toward a lower pressure as between the first and second series of runs, but this was barely beyond the limits of reproducibility of the standard thermocouple and no further change was observed in the final reading. The arithmetical average of the five readings, which was 812.06 mm., was taken as the ice point pressure.

Pressure Readings.—Pressures were read on a standard meter bar of steel graduated in millimeters and calibrated at centimeter intervals, by the United States Bureau of Standards. A Société Génevoise cathetometer, whose telescopes were equipped with moving cross hairs for interpolation, was used as the comparison instrument. The measurements were obtained with a normal precision of 0.02 mm. Corrections for temperatures of mercury and of meter bar, for standard gravity and for meniscus height, were applied as described in a previous paper.[9] A correction was also applied for the very slight pressure gradient due to the difference in height of the thermometer bulb and the lower meniscus. This correction amounted for nitrous and nitric oxides at the higher pressures to about 0.01 mm. but was negligible for hydrogen.

Dead Space Corrections.—The thermometer bulb was made especially large in order to diminish the importance of "dead space" corrections for the capillary and for the portion of the manometer above the mercury surface. Two thermometer bulbs, described as No. 1 and No. 2, were employed in the course of the measurements in order to detect and, if necessary, correct for the effects of adsorption at low temperatures. Bulb 2 was made, as

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(5) Giauque, Buffington and Schulze, THIS JOURNAL, **50**, 101 (1928). *Cf.* this paper for details of manipulation.

(6) With a dR/dT of approximately 1.9 ohms per degree and a precision of approximately ± 0.001 ohm.

(7) The experimental corrections were the same as those discussed later, for the other gases. The corrections for gas imperfection of hydrogen were taken from the work of Cath and Onnes [*Comm. Phys. Lab. Leiden*, No. 156, p. 26 (1922)] and were employed in the manner used by Cornish and Eastman [THIS JOURNAL, **50**, 643 (1928)].

(8) One taken before and one after each of the two series of runs and the fifth after the apparatus was allowed to stand for several days.

(9) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

nearly as possible, equal in dimensions to Bulb 1 but was filled with approximately two hundred thin-walled Pyrex tubes which greatly increased the glass surface exposed to the gases without greatly diminishing the volume. Table I gives the extent of exposed surfaces in the two bulbs together with the free volumes in the bulbs and the dead space volumes in the capillary and manometer end divided with respect to the temperatures to which the several regions in the dead space were exposed.

TABLE I

INNER SURFACES AND VOLUMES OF THE THERMOMETER BULBS AND THE DEAD SPACE VOLUMES

	Bulb 1	Bulb 2
Total exposed surface, sq. cm.	400	3740
Free bulb volume, cc.	310.88	291.58
Dead space volume, cc.		
Upper block region	0.076	0.091
Auxiliary block region	.038	.046
Bottom third G. S. tube (above blocks)		.206	.250
Middle third G. S. tube (above blocks)	.206	.250
Top third G. S. tube (above blocks)	.215	.251
Capillary exposed to room temp.	.617	.618
Capillary (in manometer case) and manometer dead end	2.497	2.497

These volumes, which relate to a temperature of 273.1°, were determined by weighing displaced mercury. In computing the gas thermometer data the volume of the thermometer bulb was corrected for the thermal expansion of Pyrex glass.[10]

Corrections for the portion of the gas present in the dead space were made in the usual manner, with the several regions at their appropriate temperatures treated separately. The total dead space correction, applied to the pressure, amounted to about 0.1 of 1 per cent. at the ice point and, with the correction for thermal contraction of the thermometer bulb included, to about 1% at 120°K.

The Data

In all, four sets of measurements were taken with each gas. "Full pressure" measurements (approximately 900 mm. at the ice point) were taken with each thermometer bulb in order to detect the influence of possible adsorption. "Half pressure" measurements (approximately 500 mm. at the ice point) were taken to determine the possible need of more than first and second virial coefficients in the analytical expression of the results. As the data themselves indicate, within the limits of our experimental error neither the changes in surface nor in pressure produced a difference in the results.

The corrected data are recorded in Tables II to V, inclusive, together with the experimental

(10) Buffington and Latimer, THIS JOURNAL, **48**, 2305 (1926).

values of the second virial coefficient "B" in the equation

$$PV_m = RT + BP + \ldots \quad (4)$$

TABLE II

TABULATED RESULTS WITH NO IN THERMOMETER BULB 1

T, °K.	Full pressure Corr. P, mm.	−B, cc.	T, °K.	Half pressure Corr. P, mm.	−B, cc.
121.72	421.18	224.4	125.51	218.88	209.5
135.08	469.27	150.9	129.93	226.82	172.9
141.30	491.13	141.7	134.97	235.77	149.9
146.91	511.23	120.6	140.03	244.68	139.6
153.06	533.01	107.9	145.22	253.88	121.0
160.12	557.91	97.8	149.87	262.06	113.2
172.21	600.56	82.2	160.10	280.07	98.9
180.37	629.35	72.7	169.98	297.42	90.7
189.90	662.58	63.9	180.17	315.37	77.0
200.47	700.12	56.5	197.57	346.00	59.5
201.09	702.30	56.1	203.59	356.66	47.6
210.70	736.11	50.1	209.79	367.53	46.9
219.97	768.67	46.0	220.18	385.76	43.8
230.64	806.17	41.3	230.26	403.49	38.1
240.48	840.81	36.0	239.46	419.67	32.9
250.28	875.24	32.8	256.86	450.20	30.3
260.25	910.30	28.9	265.63	465.58	28.8
274.00	958.72	22.8	274.10	480.55	21.5
274.09	959.08	21.9	274.12	480.57	21.8
			274.27	480.91	18.2
			280.54	491.84	20.3
			289.85	508.25	14.3
			299.26	524.81	10.2
			307.98	540.03	15.7

TABLE III

TABULATED RESULTS WITH NO IN THERMOMETER BULB 2

T, °K.	Full pressure Corr. P, mm.	−B, cc.	T, °K.	Half pressure Corr. P, mm.	−B, cc.
124.95	389.11	199.3	124.99	264.84	200.7
129.79	404.65	176.1	129.88	275.49	169.9
135.16	421.95	149.7	135.05	286.69	145.9
144.32	451.13	123.8	141.85	301.35	124.0
149.76	468.41	112.1	149.74	318.26	110.4
159.74	500.04	95.6	169.93	361.53	81.3
169.53	531.00	83.8	189.86	404.21	60.9
179.82	563.52	73.5	210.65	448.65	49.3
190.05	595.90	62.6	229.88	489.84	35.4
200.01	627.36	55.8	249.93	532.71	27.7
209.91	658.57	50.8	273.04	582.07	22.3
220.12	690.80	45.0	273.09	582.22	20.2
230.39	723.17	36.0			
240.06	753.75	35.2			
249.98	785.06	31.2			
259.94	816.49	27.4			
273.13	858.08	23.8			
273.15	858.17	23.2			

The molal volume V_m (a constant in each set of runs since we always corrected our pressures to the ice point volume of the thermometer bulb) was computed from the measurements made at or

TABLE IV

TABULATED RESULTS WITH N₂O IN THERMOMETER BULB 1

Full pressure			Half pressure		
T, °K.	P, mm.	Corr. −B, cc.	T, °K.	P, mm.	Corr. −B, cc.
198.68	623.52	349.4	200.19	383.52	349.7
204.89	643.77	325.9	210.05	402.84	315.1
213.80	672.65	299.8	220.11	422.55	283.1
220.02	692.86	281.5	233.59	448.84	253.1
230.10	725.47	257.8	240.53	462.39	238.1
240.07	757.74	235.5	250.25	481.33	221.1
250.16	790.32	217.2	260.41	501.14	203.9
261.71	827.60	198.8	273.09	525.84	184.6
273.13	864.38	183.6	273.11	525.91	184.2
273.14	864.46	182.5	273.12	526.03	178.6
273.15	864.48	182.8	280.77	540.73	179.1
280.67	888.61	174.8	290.33	559.29	167.2
290.29	919.62	163.5	298.51	575.28	157.4
296.43	939.47	155.3			

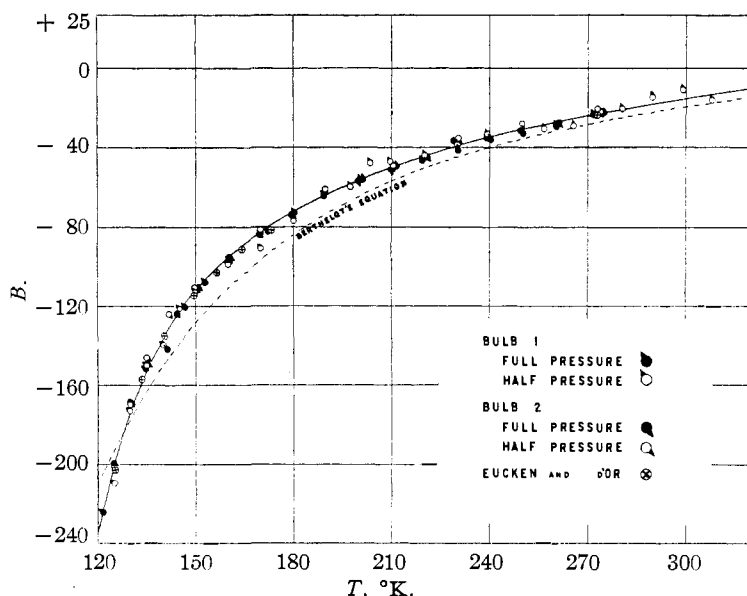near the ice point with the aid of the accurate ice point densities determined by Batuecas.[11]

Fig. 2.—Virial coefficients of nitric oxide.

Discussion of the Data

We find that, for both gases, the data are well represented empirically by equation (4), with

$B = 20 + 5881.5/T − 5.7639 \times 10^6/T^2 +$
$\quad 8.4301 \times 10^{10}/T^4 − 9.2783 \times 10^{14}/T^6$ cc./mole   (5)

for NO, and

$B = 32 − 5611.5/T + 3.9424 \times 10^6/T^2 −$
$\quad 3.9145 \times 10^{11}/T^4 + 3.0747 \times 10^{15}/T^6$ (6)

for N₂O. The agreement is shown in Figs. 2 and 3 in which the solid lines are constructed from equations (5) and (6) while the experimental

(11) Batuecas, *J. chim. phys.*, **22**, 101 (1925); *ibid.*, **28**, 572 (1931).

TABLE V

TABULATED RESULTS WITH N₂O IN THERMOMETER BULB 2

Full pressure			Half pressure		
T, °K.	P, mm.	Corr. −B, cc.	T, °K.	P, mm.	Corr. −B, cc.
198.14	616.63	352.1	196.87	392.49	359.4
204.07	635.74	331.6	199.82	398.50	349.3
209.88	654.46	312.7	204.87	408.74	336.4
215.63	673.01	294.2	213.60	426.67	298.8
220.11	687.41	282.1	224.96	449.87	263.5
229.77	718.57	254.6	249.93	500.57	215.9
240.20	751.84	237.2	273.08	547.50	183.8
249.69	782.36	216.5	273.09	547.50	184.9
260.05	815.53	199.2			
273.14	857.29	182.7			
273.15	857.34	182.3			

values, taken from Tables II to V inclusive, are represented by circles.[12]

The broken lines in the figures represent the values of B calculated from Berthelot's[13] equation

$$PV = RT\left[1 + \frac{9\,PT_c}{128\,P_cT}\left(1 − 6\,\frac{Tc^2}{T^2}\right)\right]$$
(7)

with the critical constants T_c = 180.2°K. and P_c = 64.6 atm. for NO[14] and T = 309.6°K. and P_c = 71.7 atm. for N₂O.[15] This comparison is of interest since Berthelot's equation has been extensively used, by various authors, to correct for gas imperfection at low temperatures. It is clear, from the figures, that for both NO and N₂O the molar gas *volumes* are given with fair accuracy throughout the whole temperature interval. Hence, for these gases at least, the use of equation (7) has been justified in those calculations, such as the entropy accompanying gas imperfection,[16] molar heats of vaporization by the Clapeyron equation,[17] etc., which utilize only the *molal volume* of the gases concerned. The *slope* of the B-T curve is also well reproduced, by Berthelot's equation

(12) The black circles, which represent "full pressure" runs, are entitled to the greater weight since the chief sources of experimental error influence P by absolute rather than relative amounts.

(13) D. Berthelot, *J. Phys.*, [3] **8**, 263 (1899).

(14) Adwentowski, *Anz. Akad. Wiss. Krakau*, 142 (1909).

(15) Cardoso and Arni, *J. chim. phys.*, **10**, 504 (1912).

(16) *Cf.* the papers of Giauque and co-workers on the comparison of spectroscopic entropies with those obtained calorimetrically.

(17) Out of curiosity we have recalculated the molal heat of vaporization of nitric oxide, computed from the vapor pressure data of Johnston and Giauque (Ref. 1), with the gas volume obtained from our experimental value of B at the boiling point. This recalculation gives ΔH = 3309 cal./mole which compares with 3316 cal./mole obtained with the use of Berthelot's equation and with the accurate calorimetric value of 3293 (±3) cal./mole.

for N_2O but, for NO, is not well represented at low temperatures. Thus, in calculations which require $\partial V/\partial T$ and, especially, $\partial^2 V/\partial T^2$, such as heat capacity determinations by the velocity of sound method, some caution must be exercised in the use of Berthelot's or any similar equation in the absence of experimental data.

The only low temperature experimental work in the literature, for either of these gases, is that of Eucken and d'Or[18] on nitric oxide, which we include among the experimental data in Fig. 2. It was our original feeling that the data of these authors may have been influenced by adsorption on the walls of the thermometer bulb at the lowest temperatures and the use of our Bulb 2, with the large surface increase, was designed to correct for that. But our results show, effectively, that adsorption does not play a noticeable part. Within the limits of experimental error (normally, about two units in B in our own data) we are in complete agreement with Eucken and d'Or.

However, as an empirical representation of the data, our own equation (5) is an improvement over their equation II

$$B = 16.0 - (29 \times 10^5/T^2) - 23 \times 10^{-7} e^{2000/T} \quad (8)$$

in which the last term is designed to account for assumed association (into N_2O_2) in the gas phase, with a molar heat of association of approximately 4000 calories, but which fails to reproduce some of their own experimental values by as much as ten units in . Nitric oxide is known to be highly associated in the liquid phase and it is not impossible that the rapid change in slope of the $(B-T)$ curve near the boiling point (121.36°K.) has its origin in some association in the vapor, as Eucken and d'Or assume. However, since an expression of the form of equation (8) is not needed to represent the empirical data, and indeed is inferior to equation (5), we believe that evidence for the association in the vapor phase, if it exists,[19] must

(18) A. Eucken and L. d'Or, Nachrichten von der Gesellschaft der Wissen., Göttingen, Math.-physik. Klasse, 107 (1932)

(19) The unusually steep rise in the heat capacity curve of liquid nitric oxide (Ref. 1) indicates that dissociation of the polymerized molecules is already proceeding rapidly in the liquid phase just below the boiling point This renders it unlikely (although we cannot say impossible) that any appreciable trace of association yet remains in the gas phase, because of the much lower concentration of the molecules in the latter

be sought outside of low pressure $P-V-T$ data.[20]
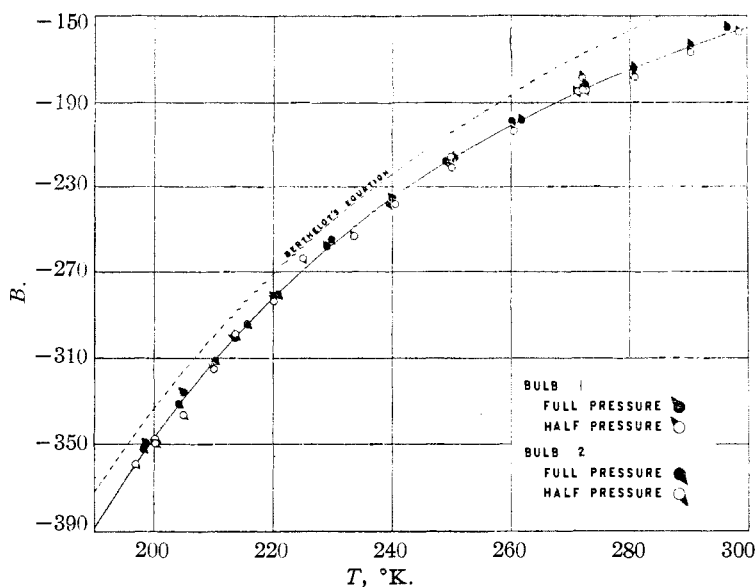
Fig. 3.—Virial coefficients of nitrous oxide.

Summary

An apparatus is described for measuring the low pressure data of state for gases between their boiling points and room temperature. The method is essentially an intercomparison with the known $P-V-T$ relationships for hydrogen,

(20) Briner, Biedermann and Rothen, Helv. Chim. Acta, 8, 923 (1925), have measured the compressibility of NO up to pressures of 160 atmospheres and down to a temperature of 193°K., for the express purpose of detecting possible association in the gaseous phase. By comparison with the compressibility isothermals for carbon dioxide, for air and for ethylene, at corresponding temperatures (same fraction of the critical temperatures), they conclude that NO is not associated. However, these authors were undoubtedly concerned with a larger degree of polymerization than is involved here and their results do not rule out a possible small association sufficient to fit in with the suggestion of Eucken. Thus 0.4 of 1% association at 120°K. and one-half atmosphere would account for 40 units decrease in B, which is about the extent of the abnormality of our experimental curve at that temperature (Fig. 2). If, with Eucken, we make the assumption that the molal heat of polymerization is approximately 4000 calories, a simple calculation gives 0.2 of 1% association at 193°K. and 160 atmospheres. This amount of association would affect the value of PV under the latter conditions by only 0.1 of 1%, which is without significance in the considerations of Briner, Biedermann and Rothen.

through the medium of a constant volume gas thermometer. The usual experimental corrections, appropriate to careful work in gas thermometry, are applied.

Data of state were determined, for pure NO, between 122 and 308°K. and, for pure N_2O between 197 and 298°K., and the second virial coefficients were computed, for each gas, over the experimental range of the observations. These are well represented by power series in $(1/T)$ (equations 5 and 6, respectively). The accuracy of the data is, normally, about two units in the second virial coefficient.

The values of the virial coefficients are shown graphically as functions of temperature, where comparison is also made with the virial coefficient calculated from Berthelot's equation. For both NO and N_2O Berthelot's equation reproduces molar volumes with a fair degree of accuracy but fails to reproduce the temperature derivatives of the volume, in NO, at temperatures near the boiling point, where the $(B-T)$ curve changes slope rapidly.

The equation of Eucken and d'Or, which is based on an assumed partial association to N_2O_2 in the gaseous phase, is discussed and it is concluded that evidence for association, if it exists, must be found in some source outside of $P-V-T$ data.

Johnston and Giauque's value for the molal heat of vaporization of nitric oxide, from vapor pressure data, has been recalculated with the aid of the improved equation of state. The recalculation improves the already good agreement with their reliable calorimetric value.

COLUMBUS, OHIO   RECEIVED DECEMBER 1, 1933

The Photolysis of Nitrogen Oxides: N2O5, N2O4 and NO2

BY HARRISON H. HOLMES AND FARRINGTON DANIELS

Improvements in photochemical technique and increased importance of the nitrogen oxides in chemical kinetics have made desirable an amplification of the early work on the photolysis of nitrogen pentoxide.[1,2] Although the careful work of Baxter and Dickinson[3] on nitrogen pentoxide and of Norrish,[4] and Dickinson and Baxter[5] on nitrogen dioxide established the nature of some of the reactions, a wider range of observations was needed, particularly at shorter wave lengths. The photolysis of nitrogen tetroxide and of uncatalyzed nitrogen pentoxide had not yet been investigated. A knowledge of the influence of foreign gases and solvents was important, also. For these reasons the present investigation was undertaken.

Under many experimental conditions these three oxides are mixed together, and photolysis is complicated, but in the present investigation the individual behavior of each has been determined by suitably changing the wave length, the temperature and the pressure.

Experimental Procedure

The monochromator and lamp, described previously,[6] provided monochromatic radiation of high intensity and purity, using a slit width of 0.6 mm.

The thermopile, 8 × 40 mm. in area, measured all the light passing through the cell. It was calibrated at 0 and 25° against U. S. Bureau of Standards radiation lamp C-132 with the aid of a 1000-watt secondary standard.[7] Deflections were 3.3% higher at 0° than at 25°. Quantum yields of 0.597 and 0.556 were obtained at 436 mμ for the photolysis of uranyl oxalate whereas Leighton and Forbes[8] found 0.610, 0.555 and 0.585. In the opinion of the authors all important measurements should be cross-checked under actual working conditions against this standard work of Leighton and Forbes.

The rectangular quartz reaction cell, 4.6 × 1.2 × 2.75 cm., was similar to one described before.[9] Pressure measurements were made in it with a reproducibility of 0.2 mm. using a diaphragm, mercury manometer and cathetometer, while the gases were sealed off in contact only with quartz. The beam of light, rendered parallel by a quartz lens, nearly filled the cell without touching the sides. A block of polished, crystalline quartz mounted by the side of the cell served as a blank in determining the incident energy. The thermostat containing the cell and thermopile was constant within less than 0.05°.

The nitrogen oxides were prepared by standard methods

(1) Daniels and Johnston, THIS JOURNAL, 48, 72 (1921).
(2) A further unpublished research was carried out in this Laboratory by Waldemar Vanselow.
(3) Baxter and Dickinson, THIS JOURNAL, 51, 109 (1929).
(4) Norrish, J. Chem. Soc., 761 (1927); 1158, 1604, 1611 (1929).
(5) Dickinson and Baxter, THIS JOURNAL, 50, 774 (1928).

(6) Heidt and Daniels, ibid., 54, 2381, 2384 (1932).
(7) Forbes, J. Phys. Chem., 32, 490 (1925).
(8) Leighton and Forbes, THIS JOURNAL, 52, 3139 (1930).
(9) Damon and Daniels, ibid., 55, 2363 (1933).