TABLE II.

The Transference Number of Potassium Ion in Potassium Chloride Solutions at 25°.

Concentration range.	Mean concentration.	Transference number.
1.0 –0.1	0.3162	0.496
0.5 –0.05	0.1581	0.498
0.1 –0.01	0.03162	0.496
0.05–0.005	0.01581	0.494

Summary.

The work of MacInnes and Parker on the activity values and transference numbers of potassium chloride solutions is extended to one molal concentration.

The potential of the normal calomel electrode is calculated to be —0.2826 volt, agreeing quite well with Lewis, Sebastian and Brighton's value (—0.2824 volt), when corrected for the liquid junction potential between 0.1 and 1.0 *N* potassium chloride solutions.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]

PRESSURE MEASUREMENTS OF CORROSIVE GASES. THE VAPOR PRESSURE OF NITROGEN PENTOXIDE.[1]

BY FARRINGTON DANIELS AND ARTHUR C. BRIGHT.

Received March 20, 1920.

Pressure measurements of the higher oxides of nitrogen and nitric acid are difficult because these substances attack materials on which the chemist usually relies, including rubber tubing, mercury and stopcock grease. Since such measurements are necessary for the proper study of nitrogen fixation processes, an apparatus made entirely of glass has been devised which is capable of measuring gas pressures conveniently and accurately over a wide range of conditions. With it the vapor pressure of nitrogen pentoxide has been determined. Further related researches are also in progress.

Description of the Apparatus.

The vapor pressure apparatus in its final form is shown in Fig. 1. Its unique feature consists of the glass diaphragm, movement of which makes or breaks an electrical circuit and permits balancing of an air pressure against the unknown pressure. The air pressure is read directly on a mercury manometer as shown.

The method of making the glass diaphragm is shown in Fig. 2. A small bulb of glass, with a thin end, is blown as shown in the first illustration. This is flattened by plunging the end into a flame, momentarily, while rotating. A little practice is necessary to judge properly the ex-

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[1] Published by permission of Mr. George J. Roberts, special Assistant to the Chief of Ordnance, U. S. A. and Dr. Mellow Whitney, Chief, Bureau of Soils.

tent of the flattening process and to give sufficient annealing without destroying the shape. Previous to flattening, the whole bulb and a short length of the stem are carefully platinized with several applications of a very thin platinizing solution and heated to dull redness after each application. A glass arm, with rounded end platinized, is fused on as shown in the third illustration, and adjusted so that after cooling it presses gently against the center of the diaphragm. After twisting platinum wires tightly around the base of the bulb and around the platinized arm, the whole is mounted in a glass shell and fused to the vessel which is to contain the material to be tested. The assembled apparatus is shown at C in Fig. 1.

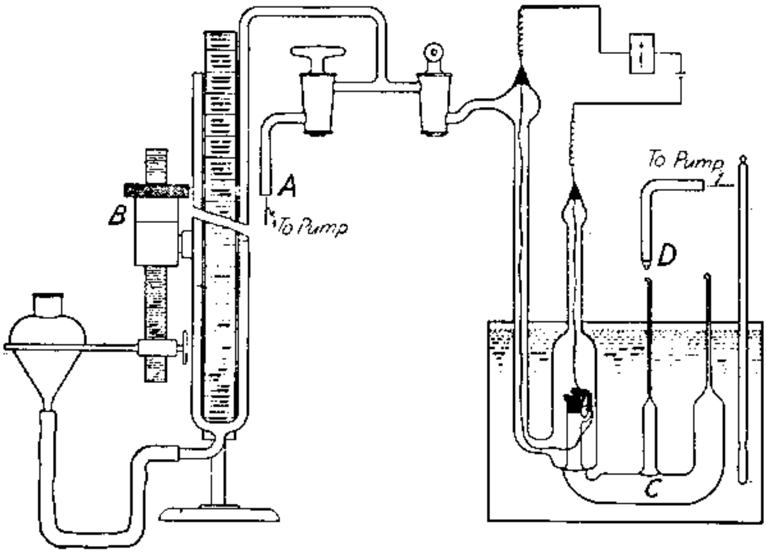

Fig. 1.—Vapor pressure apparatus.

The dimensions of the glass diaphragms varied somewhat but averaged about one cm. in diameter and between 0.1 and 0.2 mm. in thickness. All those which did not make and break electrical contact with a pressure difference of a millimeter of mercury or less were rejected. The most sensitive ones likewise were not used in the present research because the chance of breakage was too great. No difficulty was encountered from this source if the inner compartment was never evacuated without first evacuating the outer one. All the diaphragms used withstood a pressure of more than an atmosphere outward and most of them were capable of withstanding one atmosphere inward. They gave the same zero reading at all temperatures over a range of 75°, even after withstanding pressure differences of an atmosphere. The diaphragms actually used were sensitive to a fraction of a millimeter and accurate to a millimeter.

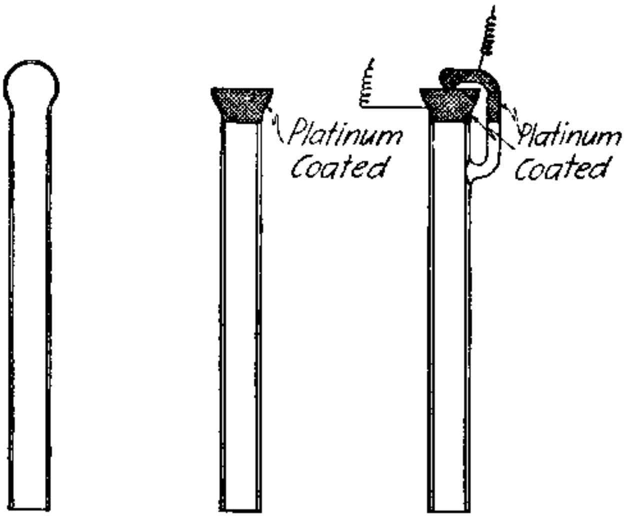

Fig. 2.—Glass diaphram.

The electrical circuit comprised a small portable galvanometer and a low voltage cell (silver and platinum in an electrolyte) which gave proper deflections, or a dry cell with a high resistance in series. It was essential to have the voltage so low that there was no sparking between the platinized surfaces. Electrical connection was made through the glass shell by short pieces of platinum wire, welded to copper wires. It was necessary to prepare the platinized surfaces with great care and to keep them scrupulously clean.

Several all-glass manometers are described in the literature,[1] most of which depend on the movement of glass indicators or spirals. It is thought that the one described here is to be preferred because of its simplicity and its freedom from optical systems. This apparatus may be used in high pressure bombs or in high temperature furnaces (if made of quartz) where the visual observation required by all other types is more difficult.

Preparation of Nitrogen Pentoxide.

The nitrogen pentoxide was prepared by dehydration of nitric acid with phosphorus pentoxide by the Berthelot-Weber[2] method and purified by sublimation in ozone as recommended by Russ and Pokorny.[3] Conc. nitric acid was distilled from an excess of sulfuric acid. About 25 cc. of this 100% acid was placed in a glass-stoppered washing bottle with the inlet sealed off, and mixed with small portions of phosphorus pentoxide until a thick paste resulted. This operation was carried out carefully with cooling, in ice and salt, to prevent decomposition of the nitrogen pentoxide from local heating. Distillation was carried out in the apparatus shown in Fig. 3, in which the whole system was subjected to intermittent evacuation, not rapid enough to cause excessive foaming. With the first bottle at +35° to +40° and the condensing U-tube at about —20° it was possible in a couple of hours to condense out 5 to 10 g. of the crude nitrogen

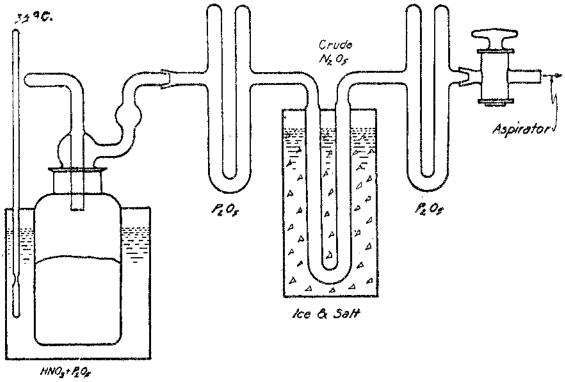

Fig. 3.—Preparation of crude nitrogen pentoxide.

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[1] Ladenburg and Lehman, *Verh. deut. physik. Ges.*, **8**, 20 (1906); Johnson, *Z. physik. Chem.*, **61**, 457 (1907); Bodenstein, *Z. Elektrochem.*, **15**, 244 (1909); Preuner, *Z. physik. Chem.*, **81**, 129 (1913); Gibson, *Proc. Roy. Soc. (Edinburgh)*, **33**, 1 (1913); Baumé and Robert, *Compt. rend.*, **168**, 1199 (1919).

[2] Weber, *J. prakt. Chem.*, **6**, 342 (1873); Berthelot, *Ann. chim. phys.*, **6**, 202 (1875).

[3] *Monatsh.*, **34**, 1051 (1913).

pentoxide, stained yellow from its partial decomposition into nitrogen peroxide.

The crude product, protected with its drying tubes of phosphorus pentoxide, was next purified by sublimation in a stream of ozonized air which had passed through an ozonizer of the Berthelot type, and condensed in the vapor-pressure apparatus or other receiver, in the manner shown in Fig. 4. The decomposition of nitrogen pentoxide gas into brown fumes of nitrogen tetroxide (and nitrogen peroxide) and oxygen was prevented by an excess of ozone, and pure white crystals could be condensed out under these conditions. Before sublimation all the brown gas was swept out of the apparatus with ozonized air while the crystal tube was still surrounded by ice and salt and the receiver was at room temperature. The receiver was then packed in ice and salt and the crude crystals raised to about 20°, or higher, if the stream of ozone was sufficiently concentrated to prevent all decomposition.

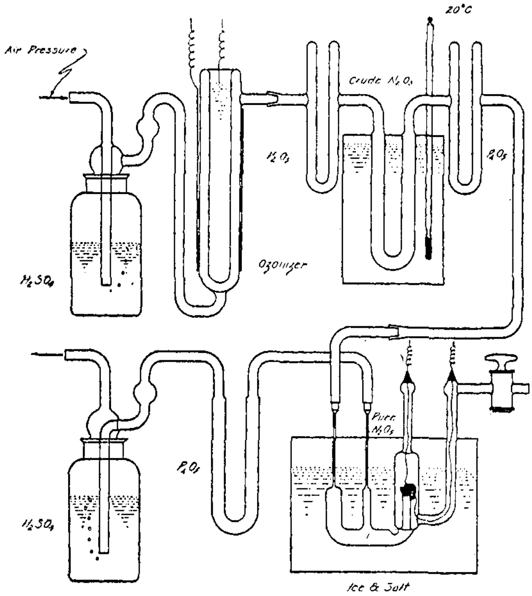

Fig. 4.—Preparation of nitrogen pentoxide.

All connections were made with ground-glass joints or with small tubes fitting tightly into larger ones and rendered gas-tight with de Khotinsky cement. The latter was rapidly attacked, however, if appreciable areas were exposed. It was absolutely necessary to exclude every trace of moisture and all leaks had to be guarded against. During the sublimation in ozone, in which operation the greatest care is required, the pressure of the system was always greater than that of the atmosphere so that moist air could not get in.

Some of the nitrogen pentoxide was lost, inasmuch as its vapor pressure at —21° is 7 mm., but this loss was comparatively small since the concentration of the entering gas corresponds to its vapor pressure of 279 mm. at +20°. Russ and Pokorny[1] recommend the use of solid carbon dioxide for the refrigerating agent and oxygen instead of air to give a higher concentration of ozone. This makes the preparation more diffi-

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[1] *Loc. cit.*

cult, but it is necessary in their method, which combines the 2 operations shown in Fig. 3 and Fig. 4 into one operation. The reason for this lies in the fact that the driving out of the nitrogen pentoxide from the semi-solid mass of nitric acid and phosphorus pentoxide, according to their procedure, is a very slow process, and does not permit the attainment of vapor-pressure equilibrium except in a very slow stream of ozone.

Experimental Procedure.

A serious difficulty in the way of accurate determinations of the vapor pressure of nitrogen pentoxide, aside from chemical action on apparatus ordinarily used for such work, lies in the fact that it decomposes rapidly in the gaseous state, giving an abnormally high, and constantly increasing, pressure. In the present research a simple, static method was used in which the rate of decomposition at each temperature was determined and corrected for.

After condensing out about 5 g. of the pure nitrogen pentoxide as shown in Fig. 4, the capillaries were sealed off and the apparatus transferred to a thermostat which was constant to a few hundredths of a degree. Since decomposition was greatly accelerated by light the thermostat was placed in a photographic dark room and connected with the rest of the apparatus shown in Fig. 1, through holes in the wall. After evacuating with a Nelson pump through Stopcock A, Tube D, containing a short collar of glass, was slipped over the end of one of the capillaries and made gas-tight with a little de Khotinsky cement. The pump was started and the tip of the capillary broken off inside the rubber tubing with the help of a pair of forceps. A file scratch previously made facilitated the operation. In this way it was possible to make many successive evacuations with the same crop of crystals without access of the atmosphere at any time.

When the evacuation had continued long enough the capillary was sealed off while the apparatus was in the thermostat. It was necessary to have the capillaries very small so that the volume of gas heated in the process of sealing them off was negligible. In making a pressure reading, air was admitted slowly through Stopcock A, (Fig. 1) until the electrical circuit was broken. The levelling bulb was lowered first by hand and then with the help of the micrometer screw, B, until a throw of the galvanometer was registered. The difference in level between the 2 columns of mercury when electrical connections was just *made* was always taken as the manometer reading. In case the pressure to be measured was greater than an atmosphere it was necessary to force air under pressure through A.

A typical numerical example shows the method of obtaining the desired pressure values.

Manometer reading with inner compartment open to the atmosphere = 37.0 mm. (zero reading).

Manometer reading when material is sealed off = 661.0 mm.

Barometer = 748.4 mm.

748.4 — 37.0 — 661.0 = 50.4 mm. (pressure inside the diaphragm at the temperature of the thermostat).

All the readings of the barometer and manometer were reduced to zero centigrade.

In any static method for determining vapor pressures it is absolutely essential to remove every trace of impurity, for each foreign gas registers its own partial pressure, and the sum of all the pressures is the quantity measured in the experiment. This source of error was eliminated by continued evacuation and evaporation of a large portion of the crystals, in which operation any gas other than nitrogen pentoxide was swept out. In the preliminary experiments there was no criterion for sufficient evacuation except constancy of results after repeated experiments. The time-pressure curves for one temperature were all parallel, but each new one was lower by several millimeters than the preceding curve, until the constant value was reached, after which further evacuation gave no change. It became evident that it was necessary to evaporate a large portion of the crystals, nearly half, before the true vapor pressure could be obtained. The ultimate procedure then consisted in evacuation at or near room temperature until all the crystals had fallen to the bottom of the apparatus, since the proper value was never obtained while crystals were still clinging to the glass walls. A necessary criterion of sufficient evacuation was the "rattling" of the crystals on shaking. In the final experiments, further evacuations rarely showed any lowering of the vapor pressure. After once obtaining the pure material in this way, only a short evacuation was needed after each experiment before starting a new one with the same crop of crystals.

Results.

An examination of the time-pressure curves shown in Fig. 5 is interesting. During the first minute or two after sealing off, the pressure rose rapidly, particularly at the higher temperatures. This rapid rise was due chiefly to the attainment of thermal equilibrium, for although the apparatus was immersed in the thermostat water, the thermal conduction through the glass and the crystals was not sufficient to counterbalance the cooling due to the vaporization of the crystals. The slope of the first part of the curve has no particular significance since it depended on several variables such as the ratio of the quantity of crystals to the total volume 20 cc. and their geometrical arrangement, as well as on the speed of evacuation. The steepest slope possible was desired so that the significant part of the curve, the more horizontal part, due to the decomposition of gaseous nitrogen pentoxide, would be quickly reached. The shorter this indefinite region the more accurate is the extrapolation to zero time. The extrapolated value gives the true vapor pressure without decomposition.

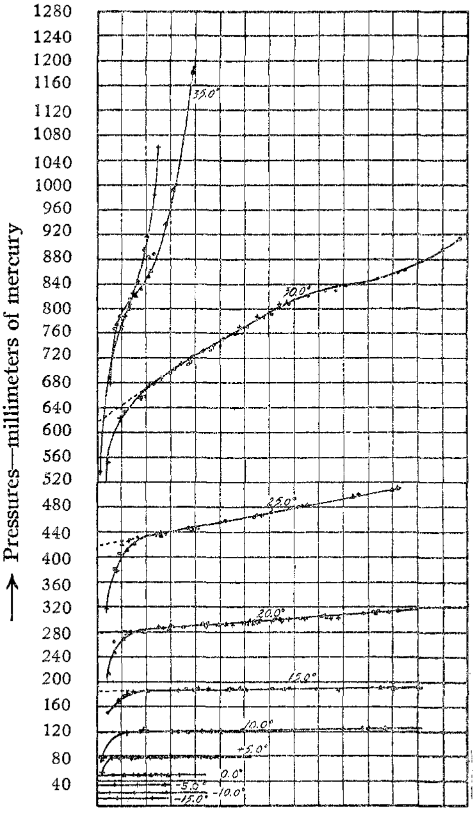

Fig. 5.—Decomposition of nitrogen pentoxide with solid phase present.

At the higher temperatures the extrapolation becomes less accurate for 3 reasons: first, the decomposition slope becomes so steep that it is difficult to tell just where it begins and where the slope, due to the attainment of thermal equilibrium, ends; second, the cooling effect from the evaporation of crystals is greater because of the higher vapor pressures, so that the extrapolation has to extend over a longer time interval; third, the decomposition curve is not a straight line.

At the higher temperatures the decomposition curve is not straight for the following reasons. The rate of decomposition of gaseous nitrogen pentoxide depends on its concentration, but this is constant in the presence of the solid phase when the temperature is constant. Accordingly, the decomposition would be represented on the time-pressure diagram as straight lines, except for the fact that as the reaction

$$\begin{array}{c} 2N_2O_5 \longrightarrow 2N_2O_4 + O_2, \\ \downarrow\uparrow \\ 4\ NO_2 \end{array}$$

proceeds, the partial pressure of the nitrogen tetroxide and peroxide becomes greater, and a shifting of the equilibrium toward nitrogen tetroxide (smaller volume) results. The pressure increase due to the decomposition of a definite number of molecules of nitrogen pentoxide becomes, then, continually smaller. If the experiments were carried out over a sufficiently long time an abrupt change would occur when the partial pressure of the nitrogen tetroxide reached a sufficiently high value to give condensation.

At the lower temperature the partial pressure of the nitrogen tetroxide and dioxide is so small even after an hour, that the change due to the equilibrium shift is negligible. Even at 25° and 30°, although a correction for this effect, after an hour amounts to several millimeters, its influence on the extrapolation is not sufficiently great to warrant a correction for it in obtaining the vapor pressures. The rate of decomposition of nitrogen pentoxide will be discussed fully in a later paper.

On the 30.0° curve a change in the slope occurs after about 45 minutes, which is coincident with the first appearance of melting. It is not a true melting, but a phenomenon complicated by the dissolving of nitrogen tetroxide in the surface of the crystals.

The 35.0° curve is of small value in estimating the vapor pressure because the contamination with nitrogen tetroxide and the appearance of melting occurs in the first few minutes. Furthermore, the decomposition curve is so steep that it cannot be distinguished from the curve showing the attainment of thermal equilibrium.

Extrapolation back to zero time for the true vapor pressures, is not entirely legitimate for in so doing it is assumed that the vapor pressure equilibrium is reached immediately after sealing off the capillary, whereas the experiments show that such is not the case. No exact mathematical correction can be made for this error, but it is entirely negligible at the lower temperatures, and even at the higher temperatures remains less than the other errors of extrapolation.

Most of the curves are the average of 3 independent experiments as shown by the representation of points as +, O and ⊙. Each series of these marks represents a fresh evacuation, and many of them were obtained with different crops of crystals. Three different diaphragms were used in the experiments, each with different dimensions and a different zero point.

The true vapor pressures (without decomposition) obtained by extrapolation to zero time are shown in the second column of Table I. In Fig. 6, which gives the vapor pressure-temperature curve they are represented by circles. They check closely with results of Russ and Pokorny,[1] shown in Col. 3, and represented by triangles on the curve. These investigators used a dynamic method, which was not suitable above 8.5° on account of the decomposition of nitrogen pentoxide.

Russ and Pokorny[1] used, for temperatures between 0° and 17.5°, a static method in which ozone prevented the decomposition. These results are shown by crosses in Fig. 6. They are several millimeters higher than the other results. In discussing the discrepancy between their two

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[1] *Monatsh.*, **34**, 1027 (1913).

methods, Russ and Pokorny placed reliance in the dynamic method and concluded that the crystals used in their static method were contaminated with traces of nitric acid. The experience gained in the present research supports this conclusion and shows further that the last traces of foreign gases can be eliminated only by long evacuation and evaporation of a large portion of the crystals.

Using the results obtained by their dynamic method, Russ and Pokorny derived the following equation, based on the Nernst vapor pressure formula, to show the relation between temperature and the vapor pressure of nitrogen pentoxide.

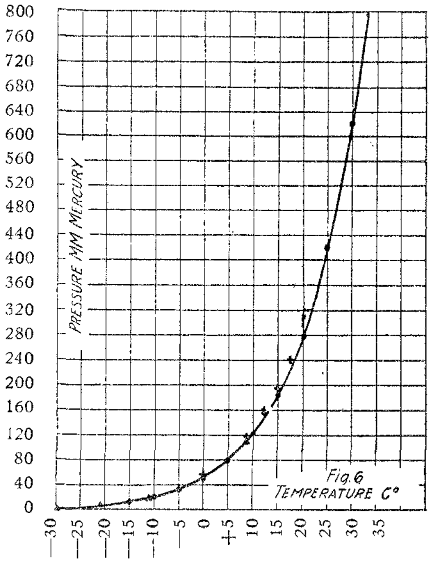

Fig. 6.—Vapor pressure of nitrogen pentoxide.

$$\text{Log } P = \frac{-3161.2}{T} + 1.75 \log T - 0.00606\, T + 10.679.$$

The values calculated from this equation are shown in Col. 4 of Table I. For pressures below a quarter of an atmosphere it is very satisfactory, but it is only approximate for higher pressures.

For a whole range of vapor pressures up to one atmosphere the following *empirical* equation is superior:

$$\text{Log } P_{\text{mm.}} = \frac{1244}{T} + 34.1 \log T - 85.929.$$

The figures given in Col. 5 of Table I are calculated from it.

The vapor pressure reaches an atmosphere at 32.5°, as shown by a short extrapolation of the curve. The melting point lies above the sublimation point, as stated by Russ and Pokorny.[1] Liquid nitrogen pentoxide, referred to in the older literature, must have been contaminated with moisture from the atmosphere. The solid nitrogen pentoxide forms clear and perfect hexagonal prisms, growing to a length of several millimeters on long standing at 0°.

The heats of sublimation as calculated by the Clausius-Clapeyron equation $\left(L = 2.303\, R \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1}\right)$ are given in Table II. P_1 and P_2 in each case represent the vapor pressure at 5° above and 5° below the temperature for which the heat of sublimation, L, is calculated. The

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[1] *Loc. cit.*

TABLE I.—VAPOR PRESSURE OF NITROGEN PENTOXIDE.

1. Temp. ° A.	2. Observed. Daniels & Bright. Static method. Mm.	3. Observed. Russ & Pokorny. Dynamic method. Mm.	4. Calculated. Russ & Pokorny. Log P = —3161.2/T + 1.75 log T — 0.00606 T + 10.679. Mm.	5. Calculated. Daniels & Bright. Log P = 1244/T + 34.1 log T — 85.929. Mm.
243.0	...	2.3	2.3	3.5
246.5	...	3.3	3.4	4.8
252.0	...	6.3	6.5	7.8
258.0	13	...	12.4	13.5
262.3	...	18.6	18.7	19.7
263.0	21	...	19.9	21.0
268.0	32	...	32.3	32.5
273.0	51	51.5	51.1	50.2
278.0	79	...	79.7	77.3
281.7	...	111.2	109.4	106
283.0	118	...	121.5	118
283.5	...	132	126.7	125
288.0	183	...	183	181
293.0	279	...	270	275
298.0	420	...	399	414
303.0	620	...	566	622
305.5	760	...	674	762

results at the lower temperatures are not accurate because the experimental error of one mm. is large compared with the total vapor pressure. At the higher temperatures, also the results are less accurate on account of the large error of extrapolation of the decomposition curves. It is evident from the table that the heat of sublimation, as calculated, increases with the temperature, but the experimental error is magnified to such an extent in the calculations that the exact value of the temperature coefficient is in doubt.

TABLE II.

Temperature. ° A.	Heat of sublimation. Calories.
263	12,360
268	12,640
273	12,760
278	13,110
283	13,360
288	14,160
293	14,140
298	14,040
305.5 (extrapolated)	14,970

The results agree within the limit of experimental error with those calculated from the results of Russ and Pokorny.[1] Berthelot[2] found the heat of sublimation of nitrogen pentoxide at 10° to be 13,100 calories by calorimetric experiments. This checks satisfactorily with the value 13,360 calories, as shown in the table.

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[1] *Loc. cit.*

[2] *Ann. chim. phys.*, 6, 151 (1875).

Summary.

1. A new all-glass manometer has been devised in which a platinized glass diaphragm is arranged to close an electrical indicating circuit. A measured air pressure was thus balanced against the unknown pressure, without the aid of optical systems.

2. A convenient method for preparing pure nitrogen pentoxide has been described.

3. The vapor pressures of nitrogen pentoxide have been determined by a static method in which corrections were made for the decomposition occurring in the gaseous phase. The results agree at the lower temperatures with those of Russ and Pokorny obtained by a different method, and extend to higher temperatures than they were able to employ. The vapor pressures of nitrogen pentoxide are conveniently given by the empirical formula:

$$\text{Log } P_{\text{mm.}} = \frac{1244}{T} + 34.1 \log T - 85.929.$$

4. The sublimation point and heats of sublimation of solid nitrogen pentoxide have been calculated.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 334.]

ADDITION COMPOUNDS OF AMMONIA WITH THE AMMONIUM HALIDES.

BY JAMES KENDALL AND J. G. DAVIDSON.

Received March 23, 1920.

The fact has long been noted in the literature[1] that the majority of the salts of ammonium are exceptionally soluble in anhydrous liquid ammonia, and a great deal of work has been done in the examination of the nature of such solutions. The most familiar case is that of ammonium nitrate, which absorbs ammonia readily at ordinary temperatures to form a mobile liquid known as Divers' solution.[2] Conflicting conclusions have been drawn regarding this system by different investigators. Raoult[3] deduced the existence of compounds of the formulas $NH_4NO_3, 2NH_3$, and $NH_4NO_3.NH_3$; Troost[4] claimed to have obtained 2 different compounds; $2NH_4NO_3.3NH_3$, and $NH_4NO_3.3NH_3$; while Kuriloff,[5] who first established the complete freezing point diagram, isolated only the latter compound—$NH_4NO_3,3NH_3$—which showed a m. p. of $-40°$.

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[1] See Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898).

[2] Divers, *Proc. Roy. Soc.*, **21A**, 109 (1873).

[3] Raoult, *Compt. rend.*, **76**, 1261 (1873).

[4] Troost, *ibid.*, **94**, 789 (1882).

[5] Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).