

Discussion of Results

The molal heat capacities of the solid forms show abnormalities in that the values for *n*-amyl bromide are only slightly lower than those for *n*-hexyl bromide, whereas the values for *n*-butyl bromide are from five to six calories below those for *n*-hexyl bromide. However, the values for the liquid form show a constant difference of approximately six calories between *n*-butyl bromide and *n*-amyl bromide, and *n*-amyl bromide and *n*-hexyl bromide. In each case the curves show nearly constant values up to 40 to 60° above the melting point. This is thought to be due to the breaking down of an association of the molecules. The entropies as calculated show a difference of 19.1 entropy units between *n*-butyl bromide and *n*-amyl bromide and a difference of 11.0 entropy units between *n*-amyl and *n*-hexyl bromide. This variation in difference is due to the abnormally high values for solid *n*-amyl bromide.

The author wishes to express appreciation to Dr. D. H. Andrews for his advice during the course of the research.

Summary

1. An apparatus for the determination of heat capacities by two methods has been built and calibrated and a further comparison of the continuous and discontinuous methods has been made.
2. The heat capacities, heats of fusion, and melting points of *n*-butyl bromide, *n*-amyl bromide and *n*-hexyl bromide have been determined.
3. The entropies have also been calculated.

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THERMAL ENERGY STUDIES. V. THE HEAT CAPACITY OF NITROGEN PENTOXIDE AT LOW TEMPERATURES¹

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Nitrogen pentoxide is a very interesting compound as material for a study of thermal energy² because so much work has been devoted to measuring its rate of spontaneous dissociation under various conditions.³ Presumably the thermal energy plays an important part in bringing about

¹ From the dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² R. H. Smith and D. H. Andrews, "Thermal Energy Studies. I," THIS JOURNAL, **53**, 3644 (1931).

³ For a survey of the literature up to 1930 see J. H. Hibben, *J. Phys. Chem.*, **34**, 1387 (1930). For work during the past year, F. O. Rice, "Annual Survey of American Chemistry for 1930," The Chemical Catalog Co., Inc., New York, 1931, p. 25.

this dissociation and a knowledge of the variation of thermal energy with temperature should prove valuable in making calculations of the reaction kinetics for this substance. Moreover, a knowledge of the entropy and free energy should be useful in rounding out our thermodynamic knowledge of nitrogen and its compounds.

With this in mind, measurements of the specific heat of nitrogen pentoxide were undertaken in the temperature range 90 to 250°K., as high a temperature as could be reached without running into difficulties due to decomposition. Because of the instability of this compound and its corrosive action, the ordinary methods of calorimetry appeared to be rather unsuitable, so a special type of apparatus was developed, which would require only a small amount of substance contained in a glass capsule. After being brought to a definite temperature, the capsule was dropped into liquid oxygen and the resultant evaporated oxygen was measured, according to the general procedure first employed by Dewar.⁴ In this way it was possible to calculate the heat capacity and from that the entropy and free energy. The only previous value for the heat capacity in the literature is that of Russ and Pokorny,⁵ a mean value of 25.9 cal./mole between -80 and +5°.

Apparatus

The apparatus shown in Fig. 1 may be divided in two parts, (A) the vaporization system and (B) the gas measuring system. The essential parts of the vaporization system are the large glass Dewar flask (A1), the copper Dewar (A2), the heating unit (A6) and the solenoid (A9) for raising and lowering the dropping bulb. The inner tube of the glass Dewar was of 4 cm. inside diameter and 83 cm. in length to the top of the ground-glass stopper (A3). The liquid oxygen into which the bulb was dropped was placed in this tube. This Dewar was evacuated to 10^{-5} mm. through the line (A4). The ground-glass stopper contained three entrance tubes: the center one for two silk threads, one leading from the solenoid plunger to the dropping bulb and the other from the stopcock above by which the trap-doors of the heating unit were operated. The other two were for the heating wires and thermocouple sealed in with Picein cement. The small tees on the side of these tubes contained a wire to which the silk threads supporting the heating unit were fastened.

The heating unit shown in Fig. 2 was made of copper about 0.15 cm. thick. The unit was 10 cm. in length inside and of 2.2 cm. inside diameter. The thermocouple junction was soldered inside. The isometric drawing shows the method of operating the trap doors by the stopcock. The heating coil was made of B. and S. No. 30 constantan silk-insulated wire; a sheet of mica was placed between the coil and the copper and the coil was coated with bakelite varnish. A dropping bulb is shown in position in the heater. These were about 9 cm. over all in length, the bulb portion being 1.5 cm. inside diameter and 2.0 cm. in length for the cylindrical part. One usually weighed about 13-14 g. when filled, which was sufficient to overcome the buoyancy effect of the liquid oxygen.

At the bottom of the glass Dewar was placed a cylindrical basket (A7) 10 cm. in

⁴ "Collected Papers," Cambridge, England, 1927, p. 1399.

⁵ F. Russ and E. Pokorny, *Monatsh.*, **34**, 1027 (1913).

length, made of copper screening. This served to bring about thermal equilibrium in the liquid oxygen and to keep the dropping bulb from striking the glass walls.

The long glass tube (A8) served as a track for the solenoid. The iron plunger weighed about 20 g., which was not enough to overcome thread friction and raise the bulb quickly, should the circuit break.

The copper Dewar was constructed of No. 18 gage copper, all joints riveted and soldered. It was 12 cm. in inside diameter, 15 cm. outside diameter, 67.5 cm. deep inside and was packed in felt. It was evacuated to 10^{-3} mm. and filled with liquid oxygen, which evaporated at the rate of about 1 liter per hour. By means of this Dewar, the adiabatic state was maintained in the vaporization chamber except for heat conduction down the gas column above the chamber.

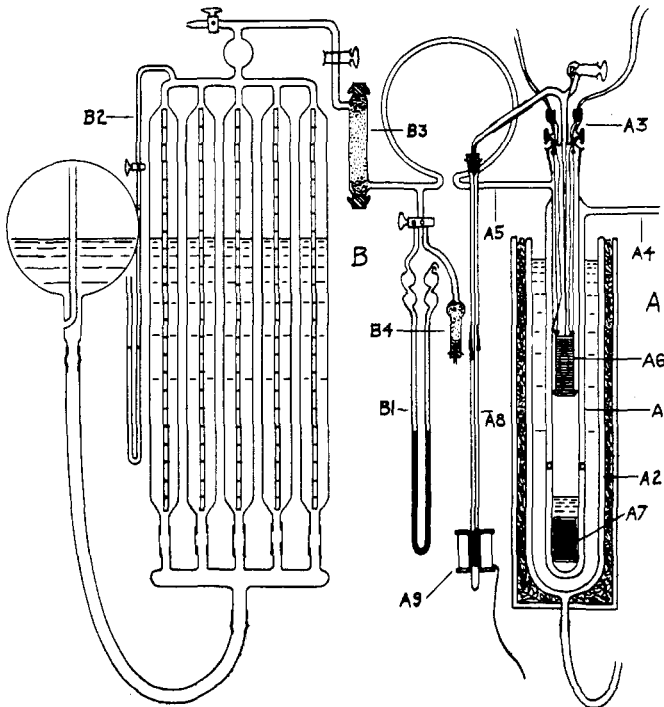


Fig. 1.—Assembly of apparatus.

The gas measuring system consisted of five burets, a mercury manometer (B1), a water manometer (B2) and the water leveling bulb. The burets were 75 cm. in length and 5 cm. in diameter, having a total volume of 8 liters. They were graduated to 5 cc. and the water meniscus could be read within 2 cc.; the tubes at the bottom of the burets being 1.5 cm. inside diameter and the manifold and rubber tubing having a cross-section five times one of these, allowed the water to be drawn from the burets quickly. The leveling bulb had an inside entrance tube which served to keep the water clean and to maintain a hydrostatic head in the burets by holding the thumb over the entrance tube. This was necessary when the gas came over rapidly, that is, when the dropping bulb was lowered into the liquid oxygen.

The mercury manometer was only employed when the gas came over rapidly. The leveling bulb was lowered just fast enough or sufficient hydrostatic pull maintained

to keep the mercury as level as possible. The gas delivery line was 0.8 cm. inside diameter; the large bend relieved the system of strains during any vibration. The water manometer was used to maintain atmospheric pressure in the apparatus when the gas came over slowly. The calcium chloride tube (B3) prevented moisture from distilling into the vaporization chamber, and the tube (B4) kept out atmospheric moisture when it was necessary to open the inner Dewar to the air.

The temperature measuring system consisted of a copper-constantan thermocouple, a type K Leeds and Northrup potentiometer, an Eppley standard cell, a variable resistance, a 6-volt storage battery and a Leeds and Northrup ballistic galvanometer.

The thermocouple was made of B. and S. No. 36 copper and No. 30 constantan. The heating circuit operated on 110 volts d. c. with carbon lamps in series. The microvolt-temperature scale employed was that compiled experimentally by J. C. Southard and D. H. Andrews.⁶

Experimental Procedure

Having placed the liquid oxygen in the inner Dewar to a depth of about 22 cm. (which was enough for fourteen determinations over a period of forty hours), the dropping bulb (previously tied to the thread) containing the pentoxide was transferred to it as quickly as possible (to prevent condensation of moisture on the bulb and to keep the pentoxide from warming up), and the solenoid adjusted for the dropping distance. The outer Dewar was now raised and the system allowed to cool to equilibrium temperature, about 120°K., which required about six hours. During this time the large stopcock on the gas delivery line was kept closed and pressure relieved to the atmosphere through the stopcock above the mercury manometer.

When the apparatus had cooled down, the pentoxide was raised into the heating unit and the trap doors closed. As soon as the temperature of the unit became fairly constant, the water was raised in the burets, the air escaping through the small stopcock above the burets.

Then this stopcock was closed, the two-way stopcock closed, and the large one on the delivery line opened immediately. The time was taken when the two-way stopcock was closed, and volume readings were taken every five minutes. To read all five burets at once, a thread was stretched along the meniscus line. Room temperatures were taken at each volume reading on a thermometer placed between the burets. Barometric readings were taken at the beginning and end of each determination.

Heat was not applied to the heating unit at equilibrium temperature. On all other determinations, when heat was applied, the temperature was kept constant by setting the potentiometer on a given microvolt reading and closing the heating circuit often enough to keep the galvanometer deflection zero.

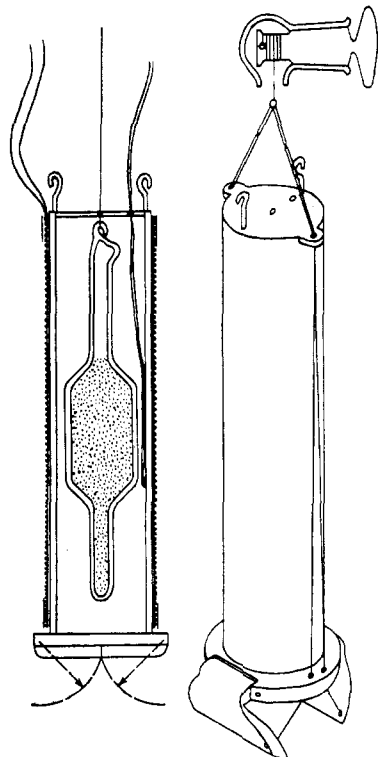


Fig. 2.—Heating unit.

⁶ J. C. Southard and D. H. Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

After three or four points had been obtained on the initial evaporation curve, the water manometer was closed, the mercury manometer opened and a hydrostatic pull of a few inches maintained in the burets. The trap doors were opened, the bulb was dropped and the doors were closed immediately. As soon as the gas had ceased coming over rapidly, the water manometer was opened and when it was level, the mercury manometer closed. Readings were taken until the rate of evaporation became constant again. Then the bulb was raised and the procedure repeated at a higher temperature.

At the end of the run, which consisted of fourteen determinations, the bulb and pentoxide were weighed in a freezing mixture of salt and ice at -15° , made up in a small Dewar covered with a rubber stopper. The weight of this mixture was obtained immediately before weighing it with the bulb and pentoxide. The pentoxide was now allowed to escape and the bulb weighed, giving the weight of the pentoxide.

Preparation of Materials

The nitrogen pentoxide was prepared by dehydrating 100% nitric acid with purified phosphorus pentoxide. The 100% nitric acid⁷ was made by mixing four parts of sulfuric acid (sp. gr. 1.84) with one part of nitric acid (sp. gr. 1.42) and distilling the nitric acid under vacuum into a receiver cooled with solid carbon dioxide. The phosphorus pentoxide was purified⁸ by distillation in a stream of oxygen. The nitrogen pentoxide was purified by several distillations in vacuum through phosphorus pentoxide with intermittent pumping out of the system.

The dropping bulb was sealed into the system at the beginning and was protected on both sides by phosphorus pentoxide as shown in Fig. 3. To fill it, the line leading from the pentoxide reservoir to the pump was sealed off at A. Then the lower part of the bulb was cooled with liquid oxygen and the pentoxide pulled over by the pump. The liquid oxygen was gradually raised until the bulb was filled. At the end of the distillation, which required about twenty-five minutes, the line was sealed off at B. Air was now admitted to the bulb and it was sealed off at C. The air allowed a neat seal to be made at C and E and increased heat conduction which was advantageous in obtaining thermal equilibrium. After tying a silk thread to the bulb at the small loophole, it was sealed off at D. Supporting the bulb by the U-tube extension, it was inverted in the liquid oxygen and sealed off at E.

The liquid oxygen was purchased from the Air Reduction Sales Company of Baltimore. This was about 99.5% oxygen. The boiling point of the liquid was determined before placing it in the vaporization chamber.

The dropping bulbs were made of Pyrex glass.

The sodium chloride employed was "Baker's Analyzed." This was powdered before placing in the bulb.

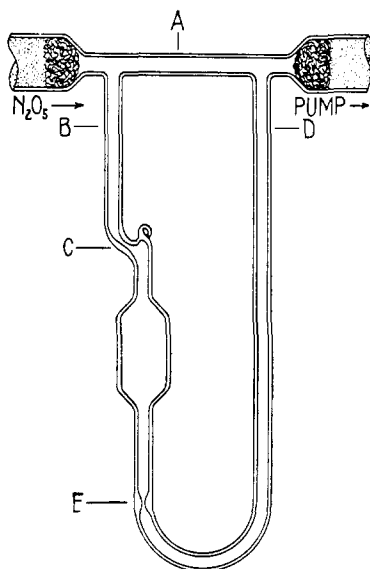


Fig. 3.—Arrangement of dropping-bulb in N_2O_5 distillation apparatus.

⁷ F. O. Rice and D. Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

⁸ G. I. Finch and R. P. Fraser, *J. Chem. Soc.*, 117 (1926).

Results and Calculations

Five experiments were carried out: three on Pyrex glass, one on nitrogen pentoxide and one on sodium chloride, to find the efficiency of the apparatus. Each experiment consisted of six to fourteen determinations, and a determination consisted of dropping the bulb at a given temperature difference and obtaining a steady state of evaporation before and after.

For the reason of space economy the direct laboratory results are not included in this paper. The experiments are numbered 1 to 5 in the order given above, and the determinations numbered in the order performed. The direct results, however, are given for one determination in Table I, namely, Determination No. 4, Experiment 4 on nitrogen pentoxide. The weight and boiling point data given at the top of the table were the same for each determination under a given experiment. The first column gives the time at each reading. The observed volumes of oxygen plus water vapor are given in the second column. Column three gives the room temperature, and column four the corrected barometric pressure. The temperature of the heating unit in microvolts and the corresponding degrees absolute are recorded in the last two columns. The time at which the bulb was dropped is given at the bottom of the table. A parenthesis indicates an interpolated value.

TABLE I

EXPERIMENT 4, NITROGEN PENTOXIDE. DATE, APRIL 14, 1930

Weight of nitrogen pentoxide, 5.376 g.; weight of glass bulb, 8.334 g.; boiling point of liquid oxygen, 5218μ V or 90.009°K .

Determination No. 4

Time, min.	Volume, cc.	Room temp., $^{\circ}\text{C}$.	Bar. press. (corr.), mm.	Heating unit, μ	Temp., $^{\circ}\text{K}$.
0	0	..	(754.8)	3928	150.296
15	133	24.8	(755.0)	3928	150.296
20	177	24.8	(755.1)	3928	150.296
25	219	24.8	(755.2)	3928	150.296
30	1767	25.0	(755.2)	3928	150.296
35	1839	25.0	(755.3)	3928	150.296
40	1913	25.0	(755.4)	3928	150.296
45	1984	25.0	(755.5)	3928	150.296
50	2050	25.0	(755.6)	3928	150.296
55	2117	25.0	(755.6)	3928	150.296
60	2183	25.0	(755.7)	3928	150.296
65	2247	25.0	(755.8)	3928	150.296
70	2314	25.0	(755.9)	3928	150.296
75	2373	25.0	(755.9)	3928	150.296
80	2443	25.0	(756.0)	3928	150.296
105	756.4

Time when bulb was dropped, 27 min.

To calculate the heat capacity, it was first necessary to obtain the volume of oxygen evaporated by the bulb and its contents for each temperature difference, *i. e.*, for each determination. These volumes, ΔV , were obtained graphically as shown in Fig. 4 for the results given in Table I, the volumes of oxygen first having been calculated to standard conditions. AB is the initial evaporation curve, BE the jump at the time the bulb was dropped and EFG the final evaporation curve. DC represents the time when the bulb was dropped. It is noted that the final rate is decreasing in the region EF and becomes constant in FG or nearly paralleled to AB. To obtain ΔV , AB was produced forward and FG backward, intersecting the "dropping time" at D and C. The distance DC gives the volume ΔV .

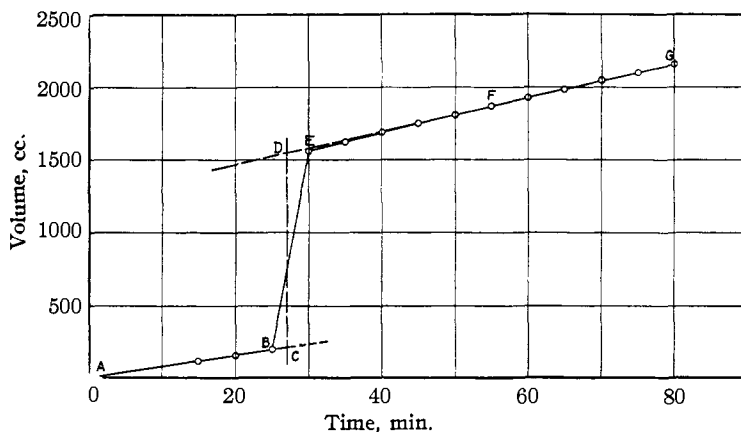


Fig. 4.—Volume-time curve for determination No. 4 on N_2O_5 .

A longer time was required at low temperature differences than at high temperature differences for the final evaporation curve to become constant. In some cases at high temperatures the final curve was constant throughout, and in others it showed an increasing slope, in which case the lesser slope was produced.

In obtaining the values of the temperature differences, ΔT , for the determinations in which heat was not applied to the heating unit, a time lag of one to two minutes was assumed between the temperature of the unit and that of the sample.

The weights of the samples, the boiling points of the liquid oxygen and the values of ΔV and the corresponding ΔT are given for all five experiments in Table II.

In Fig. 5 the values of ΔV are plotted against ΔT for the three experiments on glass and the experiment on the nitrogen pentoxide. The values ΔV for glass as given in the table have not been directly plotted, but,

TABLE II
 VALUES OF ΔV AND ΔT

Expt. 1, Pyrex glass			Expt. 2, Pyrex glass		Expt. 3, Pyrex glass	
Weight, g.....	13.226		13.226		17.723	
B. p. oxygen, °K.	90.236		90.122		90.179	
Detn.	ΔV	ΔT	ΔV	ΔT	ΔV	ΔT
1	733	49.391	1104	70.161	1305	60.038
2	445	35.253	477	40.013	1043	49.843
3	292	28.275	834	60.095	807	39.956
4	304	27.473	1312	79.836	613	33.215
5	1154	74.576	1488	90.161	1552	69.749
6	1826	99.962	2018	109.962	2318	94.935
7			2265	119.828	4107	144.738
8			2555	129.985		
9			2879	139.835		
10			3193	149.973		
11			3497	159.825		
Expt. 4, N_2O_5			Expt. 5, NaCl			
Wt. sample, g.....	5.376		6.908			
Wt. glass, g.....	8.334		7.255			
B. p. oxygen, °K.....	90.009		90.236			
Detn.	ΔV	ΔT	ΔV	ΔT		
1	630	31.482	785	35.393		
2	806	40.126	870	39.899		
3	1072	50.013	1095	49.786		
4	1333	60.287	1397	59.981		
5	1615	69.919	1684	69.692		
6	1886	79.949	1955	79.722		
7	2257	90.274	2450	94.878		
8	2588	100.189	2923	109.848		
9	2952	110.075	3398	124.681		
10	3265	119.941	3941	139.721		
11	3590	130.098	4255	149.859		
12	4033	139.948	4574	159.711		
13	4410	150.086				
14	4738	159.938				

instead, the fraction of these volumes that would be evaporated by the weight of glass making up the pentoxide bulb.

For the curve on glass, the points obtained from Experiment 3 have been chosen in preference to the ones from Experiments 1 and 2. This preference is based on the fact (1) that the final evaporation curves in Experiment 3 extended over a longer time, allowing the region of constancy to be more clearly defined, which was more nearly paralleled with the original rate, and (2) that thermal equilibrium could be obtained more quickly with the capillary sample.⁹ In general, the shape of the evapora-

⁹ The dropping bulb used in Experiments 1 and 2 was filled with ground glass to overcome buoyancy, but in Experiment 3 it was made of a heavy piece of capillary, empty and sealed off. This offered better heat conduction.

tion curves for Experiment 3 were similar to the ones found for the pentoxide and the salt.

To obtain the $\Delta V/\Delta T$ curve for nitrogen pentoxide, the difference between these two curves was taken at every ten-degree temperature difference and plotted likewise. The average slope of this curve for every ten-degrees was found by taking the difference in volume between two ten-degree intersections. Dividing this difference by ten gave the average

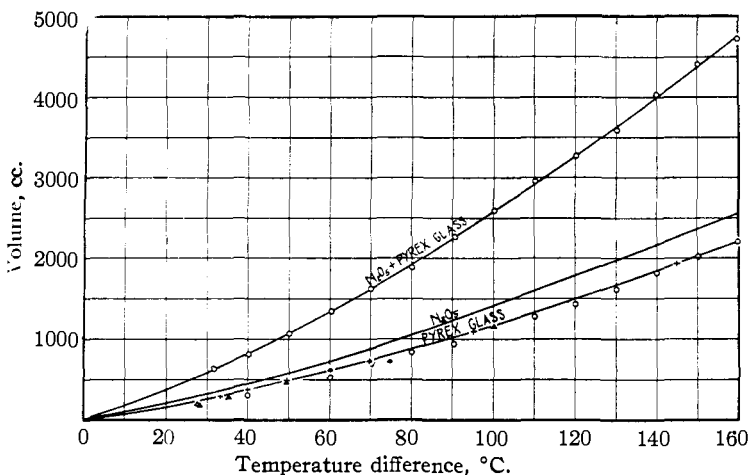


Fig. 5.— $\Delta V-\Delta T$ curve for N_2O_5 .

number of cubic centimeters of oxygen evaporated by the pentoxide per one degree over the ten-degree interval. Multiplying this value by the factor

$$\left[\frac{\frac{1}{22400} \times 1634}{W} \right] M$$

gave the heat capacity, where 1634 is the heat of vaporization of oxygen at its normal boiling point $90.1^\circ K.$, W the weight of the pentoxide sample and M the molecular weight of the pentoxide.

The resulting values are given in Table III, column two, and plotted against the absolute temperature in Fig. 6, being represented by the solid circular points designated N_2O_5 . The results as obtained for sodium chloride are recorded in the third column and are also represented by solid circles in Fig. 6.

The circular points under $NaCl$ in Fig. 6 represent values obtained by Nernst¹⁰ for sodium chloride.

The values obtained in this work for salt deviate from the Nernst values by a maximum of about 5%, being less than the Nernst values at low

¹⁰ Nernst, *Ann. Physik*, **36**, 395 (1911).

TABLE III
 C_p , CAL./MOLE, FOR NITROGEN PENTOXIDE AND SODIUM CHLORIDE AS CALCULATED
 FROM THE $\Delta V/\Delta T$ SLOPES

T , °K.	N_2O_5	NaCl	N_2O_5 (corr.)
95	14.65	8.15	14.27
105	15.38	8.33	15.96
115	16.85	8.45	18.40
125	18.30	9.00	18.99
135	19.35	9.57	18.99
145	21.10	9.94	21.69
155	22.70	10.62	22.03
165	24.90	11.05	23.20
175	26.50	11.39	25.50
185	26.80	11.39	25.05
195	26.95	11.39	26.12
205	27.10	11.39	26.02
215	28.12	11.39	27.38
225	28.40	11.39	28.30
235	28.40	11.42	29.54
245	28.58	11.42	29.79

temperatures and greater at high temperatures. The same kind of deviation is observed for the pentoxide values. It was possible, therefore, to correct the values for the pentoxide from the values for salt by an equa-

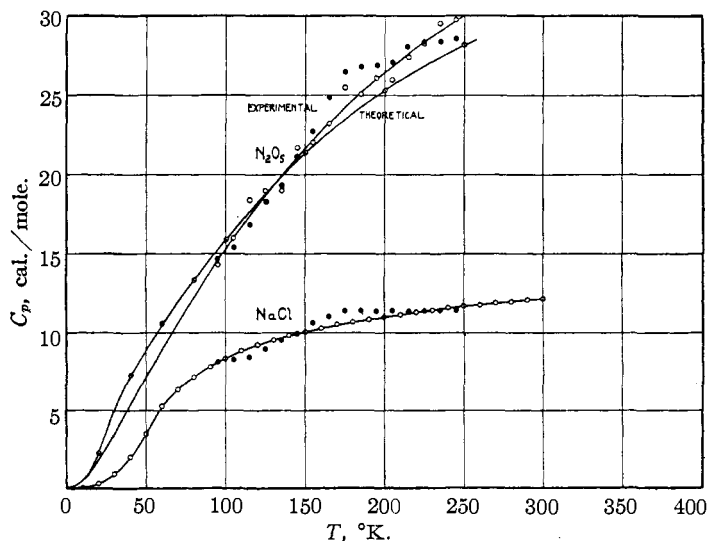


Fig. 6.—Heat capacity of nitrogen pentoxide and sodium chloride.

tion relating the measured (apparent) specific heats, the actual specific heats and the weights of the samples of pentoxide, salt and glass and a value for the heat loss or gain due to radiation, etc. This correction re-

duced the maximum error in the pentoxide values to about 2%. The corrected heat capacity values so obtained for the nitrogen pentoxide are given in the fourth column of Table III and are represented by the circular points under N_2O_5 in Fig. 6. The values obtained along a line passing through these points and extrapolated to zero are given in Table IV as the heat capacity of nitrogen pentoxide between 0 and 250°K. The entropy has also been calculated.

TABLE IV
HEAT CAPACITY AND ENTROPY FOR NITROGEN PENTOXIDE (CAL./MOLE) FROM 0 TO 250°K.

T, °K.	C_p	$S_T - S_0$	T, °K.	C_p	$S_T - S_0$
10	(0.50)	0.33	140	20.55	18.40
20	(1.80)	1.06	150	21.65	19.85
30	(3.50)	2.11	160	22.75	21.28
40	(5.35)	3.37	170	23.75	22.69
50	(7.25)	4.77	180	24.75	24.08
60	(9.00)	6.25	190	25.65	25.45
70	(10.70)	7.77	200	26.45	26.78
80	(12.30)	9.31	210	27.25	28.09
90	13.85	10.85	220	28.05	29.37
100	15.35	12.39	230	28.75	30.64
110	16.70	15.91	240	29.40	31.88
120	18.05	15.43	250	30.10	33.09
130	19.30	16.92			

The dash circular points in Fig. 6 represent theoretical values for the heat capacity of the pentoxide as calculated from the Raman frequencies of pentane, which has nearly the same kind of internal vibration as the pentoxide. Details of this calculation will be given in a later paper.

Summary

A method for measuring specific heats, based on the heat of vaporization of oxygen has been developed. The method consists of heating the sample to a definite temperature, dropping it in the liquid and measuring the gas evaporated.

Experiments were made on Pyrex glass, nitrogen pentoxide and sodium chloride.

The values obtained for sodium chloride were compared with values found by Nernst, and the values for the nitrogen pentoxide were corrected on the basis of this deviation.

The entropy was calculated.

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