Summary

A copper catalyst has been prepared which has a limited number of very active centers.

It has been shown that such a catalyst suffers sufficiently great loss of active centers in catalyzing the $H_2 + C_2H_4 = C_2H_6$ reaction, as to render it inactive after the first or second run, and that this deactivation is not due to the temperature of oxidation of the copper, to the temperature of evacuation of the catalyst bulb, to the temperature of reduction in preparation of the catalyst nor to fixation of surface crystals on the catalyst.

A catalyst unrestricted to a very few very active centers, prepared from the same original oxide, has been found to behave normally, giving permanent activity.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE SPECIFIC HEAT OF GASEOUS NITROGEN TETROXIDE[1]

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Investigation of the heat capacity of gaseous nitrogen tetroxide makes an interesting study, because it involves a large absorption of heat caused by dissociation. Density measurements have shown that there are two gases in equilibrium, as given by the equation $N_2O_4 \rightleftarrows 2NO_2$. When the temperature is raised, heat is absorbed not only in increasing the kinetic energy of the molecules, but also in breaking down nitrogen tetroxide molecules into nitrogen dioxide. This heat of dissociation has been calculated from equilibrium measurements at different temperatures, and it was the purpose of this investigation to determine the specific heat over small temperature ranges.

The research was undertaken with the idea that the thermal measurements of a simple system of this type, in which the equilibrium conditions are known, might help in the interpretation of more complex systems. In a previous communication from this Laboratory[2] it has been shown that certain organic liquids exhibit irregularities in their specific heat-temperature curves due, in all probability, to a transformation of one molecular species into another as the temperature is raised. In some cases a negative temperature coefficient of specific heat was observed and an actual maximum in the specific heat-temperature curve for one liquid was located. The specific-heat measurements on nitrogen tetroxide

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[1] This communication is based on a thesis presented in 1925 at the University of Wisconsin for the degree of Doctor of Philosophy. The investigation was carried out under the direction of Professor Farrington Daniels.

[2] Williams and Daniels, THIS JOURNAL, 46, 1569 (1924).

presented here exhibit a very pronounced maximum, followed by a negative temperature coefficient of specific heat.

The only previously reported measurements on the specific heat of gaseous nitrogen tetroxide were made by Berthelot and Ogier,[3] but in this case an average value was obtained over 40° or more and no account was taken of barometer fluctuations. It is plainly evident from their determinations over three different ranges that the heat of dissociation constitutes a large part of the apparent specific heat.

It was necessary to devise a new calorimeter capable of measuring the specific heats of a corrosive gas when the temperature difference was only 1–3°.[4]

Since the heat capacity of a gas is small it is necessary to use a constant-flow method. It seems to be the universal practice to pass a heated gas into a calorimeter and measure the rise in temperature. It is a very much better method, however, to pass *cooled* gas through the calorimeter and offset the cooling effect with a measured input of electrical energy. In this way it is unnecessary to measure either the temperature change or the water equivalent of the calorimeter and the electrical measurements can be made with precision. It is strange that this principle is not in more general use in measuring specific heats. The calorimeter described in the following section is based on this principle.

Description of Apparatus

The apparatus is shown in Fig. 1.

A thermostat was mounted directly over a second thermostat which contained a calorimeter. The upper thermostat was 1–3° colder than the lower one; and the gas, on passing from the glass coil A to the small glass coil B, tended to lower the temperature of the inner can of the calorimeter. This cooling effect was exactly counterbalanced by regulating the current through the heating coil I to maintain a zero reading on the copper-constantan thermel.

The upper coil A was made of glass tubing 5 mm. in diameter and 1400 cm. long. The rates of flow were such that each molecule of the gas was in the coil for about 45 minutes—certainly a sufficient time to bring the gas to the temperature of the thermostat. The small, lower coil B was made of special glass tubing 0.25 mm. in wall thickness. It was 2 mm. in diameter and 270 cm. long. For the rates of flow ordinarily used, each molecule was in the small coil about four minutes. The two glass coils were fused together and the lower one was surrounded by the oil of the calorimeter can.[5]

The thick-walled brass tube L, 2.5 cm. long, was soldered to the bottom of the upper thermostat. The thin-walled glass tube, surrounded by a cork, passed through this brass tube. Copper foil was wrapped around the thin-walled glass tube below the

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[3] Berthelot and Ogier, *Ann. chim. phys.*, **5**, 382 (1883).

[4] For the construction of various gas calorimeters, see Partington's "Specific Heats of Gases," D. Van Nostrand Co., New York, **1924**, p. 44.

[5] In the first experiments aluminum tubes, containing spirals of aluminum wire, were used, but an unexpected evolution of heat from the nitrogen tetroxide and aluminum forced the use of the glass tubing.

point L, so that any heat lost would be conducted along the copper foil into the oil. These arrangements made possible a steep temperature gradient in the tube and made sure that the cold gas absorbed heat only from the oil in the calorimeter can, where the amount of heat required could be measured.

The outer junctions of the thermel were placed in the small Dewar flask D to smooth out any fluctuations in the temperature of the oil-bath R. The maximum temperature variation of the oil-bath was 0.004°, and experiments showed that a change ten times as great as this did not cause a variation of 0.001° in the thermel readings over a period of four hours. When the temperature of the calorimeter bath R was changed, no measurements were made for a day, in order to make sure that the oil in the Dewar flask had attained the temperature of the bath. The heating coil I was of manganin wire 23 cm. long with a resistance of 2.72 ohms. The ends of the manganin wire were soldered to copper wire, the joint being below the surface of the oil so that all of the heat was generated in the oil-bath. The fall of potential across this heating coil was determined by means of a potentiometer. The current sent through the heating coil was measured by determining the fall of potential across a known resistance of 2.1965 ohms immersed in oil.

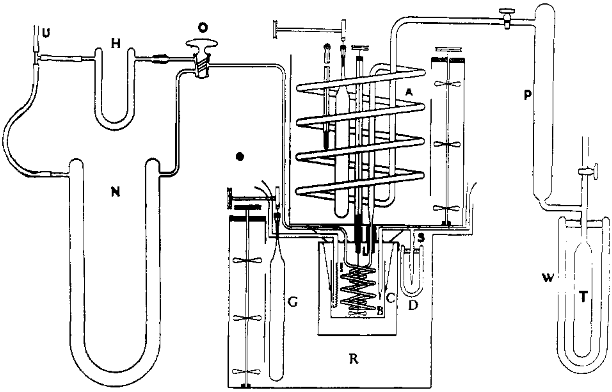

Fig. 1.—Constant-flow calorimeter and accessories for the determination of the specific heat of gaseous nitrogen tetroxide.

The calorimeter can C was of very thin copper and had a capacity of 200 cc. It was suspended from the cover of the outer can by means of three threads and tied to the coil B to keep it from swinging. The water equivalent of this inner can and contents, including the oil, was about 90 g. but since the temperature was kept constant, the water equivalent did not enter into the calculations.

The oil in the can C was stirred by means of the paddle which was driven by the copper rod running down through the copper tube in the upper thermostat. The metallic connection was broken by a piece of ebonite to minimize heat conduction.

The air gap between the inner and outer can of the calorimeter was 2.5 cm. The openings in the cover of the outer can through which the glass tubing and the wires passed were made oil-tight by means of water glass (sodium silicate solution) in which finely divided asbestos had been suspended. After hardening, the water glass was coated with shellac.

The cover of the calorimeter was fastened to the upper thermostat by strips of copper soldered to the bottom of the thermostat and to the cover, the metallic connection being broken by means of pieces of wood about 3 mm. thick. In this way everything was assembled as a unit, the outer calorimeter can was screwed to the cover and the entire apparatus placed in position. The height of the oil in the bath R was such that the cover of the calorimeter was covered by a layer of oil one cm. thick. The thermostats were insulated by means of felt and sawdust.

The thermo regulators were of Pyrex glass, as shown in Fig. 2. Each regulator contained 275 cc. of mercury. A smooth, round constriction was made in the glass tube, and contact made between the mercury and the platinum wire. This constriction gave the sensitivity of a small capillary while maintaining a freedom from "sticking" which is characteristic of the larger capillaries. The regulator was set for any temperature by means of a machine-cut screw passing through a cork. A platinum wire, immersed in a layer of mercury above the cork, completed the electrical circuit.

Each regulator was equipped with an oscillating contact which pierced the surface of the mercury about every three seconds. These regulators were very reliable over long periods of time. They were capable of holding the temperature to within 0.003° for 20 hours at a time.

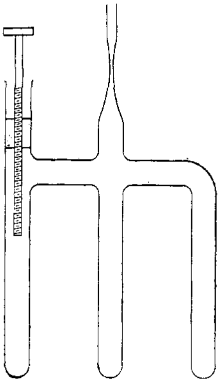

Fig. 2.—Thermoregulator of mercury in Pyrex glass.

Each thermostat was equipped with two heating coils, one of which was operated continuously and the other controlled by the thermo regulator. Each heating coil was connected in series with a slide-wire rheostat. These rheostats had to be set carefully in order to get close temperature regulation.

The nitrogen tetroxide was made by passing air through an electric arc and absorbing the gas on silica gel.[6] Some nitrogen tetroxide was also made by heating lead nitrate. After the liquid nitrogen tetroxide had been allowed to stand for several days with phosphorus pentoxide, it was distilled into the container T which was placed in a Dewar beaker.

The rate of flow of nitrogen tetroxide was regulated by changing the temperature of the water in the Dewar flask. After passing through the large tube of phosphorus pentoxide P and the calorimeter, the gas passed through the two-way stopcock O. The stopcock was connected to the U tubes H and N filled with dry silica gel to adsorb the nitrogen tetroxide. The exit tube U led to a large barostat which maintained the pressure at 760 mm. Most of the circuit was made of fused glass tubing and the three necessary stopcocks and ground-glass joint were lubricated with sirupy phosphoric acid. To keep the lubricant from absorbing moisture from the air, the stopcocks were sealed with beeswax which was melted and allowed to solidify after each turning.

Procedure

It was necessary, first of all, to find the correction to be made for the heat which was lost by conduction along the glass tube and stirrer from the inner can to the upper thermostat. This was done by setting the upper and lower thermostats at the desired temperatures and then passing current through the heating coil I. The rate of flow of gas through the calorimeter was so very slow that the temperature gradient was not changed by the gas flow.

The amount of current was regulated by means of a rheostat, the fine adjustments being made by means of a resistance wire dipping into a

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[6] McCollum and Daniels, *Ind. Eng. Chem.*, **15**, 1173 (1923).

bath of mercury. It required, as a rule, about five hours to determine just how much current should be passed through the heating coil in order to compensate for the heat losses. One milliampere too much or too little caused the galvanometer in the thermel circuit to move 3 mm. from the normal position, but the time lag was 45 minutes. After a change was made in the current of the heating circuit, it was necessary to wait for nearly an hour to determine whether the adjustment was correct. After the final adjustments were made the calorimeter was allowed to run for an additional hour to make sure the balance was correct. The fall of potential across the heating coil I and across the known resistance was then determined by means of a potentiometer.

After the correction for the heat losses had been determined, the current passing through the heating coil was increased, usually about five or six milliamperes. The nitrogen tetroxide was then admitted and the rate of flow was adjusted so that the heat taken up by the cooler gas just compensated for this additional electrical energy. While the adjustments were being made, the nitrogen tetroxide was collected in the larger U-tube of silica gel N.

When the adjustment was made the two-way stopcock O was turned and the nitrogen tetroxide was collected for a measured length of time in the previously weighed U-tube of silica gel H. The flow, in the meantime, was kept constant by keeping the temperature of the nitrogen tetroxide constant in a large thermostated Dewar beaker. Usually the nitrogen tetroxide was collected for about an hour and a half, or long enough to give about 1 g. of the nitrogen tetroxide. The fall of potential across the heating coil and across the known resistance was then determined. The U-tube was weighed accurately. The nitrogen tetroxide was driven off from the silica gel by means of heat and used over again after being dried with phosphorus pentoxide, practically all of it being recovered.

After each experiment, the gas was shut off and the correction for the heat losses determined again, in order to see whether it was the same. If the two values were not the same, the whole experiment was discarded.

The temperature of each experiment was determined by means of a calibrated 0.1° thermometer immersed in the lower bath. The difference in temperature of the two thermostats was determined to 0.002° by means of Beckmann thermometers.

In order to check the calorimeter the specific heats of air and carbon dioxide were determined. At 42.5° air was found to have a specific heat of 0.211 and at 72.6° carbon dioxide was found to have a specific heat of 0.199. These values check with the values of other investigators, although the calorimeter was not designed for gases of such low specific heats and with these gases it would have been better to use metallic tubing and a calorimeter of smaller heat capacity.

Probably the largest error in the determinations of the specific heat of nitrogen tetroxide is caused by variations in the rate of flow of the gas. Attempts were made to use a flowmeter but no suitable inert material could be found for the flowmeter liquid. It was found possible, however, to keep the rate of flow fairly constant by keeping the vapor pressure of the liquid nitrogen tetroxide constant to 0.1° or less at a definite temperature. Another difficulty lies in the rather large correction for the natural transfer of heat from the calorimeter to the upper thermostat. This cooling effect was usually two or three times as great as the cooling effect of the gas itself, but it could be determined so accurately and the results checked so nicely that it cannot be considered a serious source of error.

Experimental Results

A typical experiment is given to show the method of calculation.

Temperature upper thermostat	44.30°
Temperature lower thermostat	45.70°
Average temperature	45.20°
Temperature difference by Beckmann thermometer	1.398°

Correction for Natural Heat Loss (No Gas Flowing)

Potential drop across heating coil	0.1168 v.
Potential drop across standard resistance of 2.1965 ohms	0.0946 v.

Energy input = (0.1168 × 0.0946)/(4.183 × 2.1965) = 0.001202 cal. per second.

Heat Loss with Nitrogen Tetroxide Flowing

Potential drop across heating coil	0.1330 v.
Potential drop across standard resistance of 2.1965 ohms	0.1070 v.

Energy input = (0.1330 × 0.1070)/(4.183 × 2.1965) = 0.001550 cal. per second.

Heat absorbed in raising temperature of nitrogen tetroxide = 0.001550 − 0.001202 = 0.000348 cal. per second.

Total weight of N_2O_4 by increase in weight of silica gel tube = 0.7560 g.

Time of collection of N_2O_4 = 5040 seconds.

Wt. of N_2O_4 flowing per second = 0.7560/5040 = 0.0001500 g.

Heat capacity (apparent) per g. of nitrogen tetroxide at 45.20 = 0.000348/(0.0001500 × 1.398) = 1.66.

Molar heat capacity of nitrogen tetroxide (apparent) = 92 × 1.66 = 153 cal. per degree.

The results of all the experiments are summarized in Table I. Col. A gives the chronological number of the experiment, while Col. B gives the temperature difference between the thermostats, and Col. C gives the average temperature. The heat absorbed in raising the nitrogen tetroxide, given in Col. F, is obtained by subtracting the normal cooling effect recorded in Col. D from the cooling effect observed while nitrogen tetroxide is passing through the calorimeter as shown in Col. E. The apparent specific heats, given in Col. H, are obtained by dividing the figures of Col. F, by the corresponding weights of nitrogen tetroxide given in Col. G and by the temperature intervals of Col. B. The average apparent specific heats thus obtained are plotted against the temperature in the upper curve of Fig. 3.

TABLE I

RESULTS

A	B	C	D	E	F	G	H
Expt.	Temp. int.	$\frac{T_1 + T_2}{2}$	Corr., cal. per sec. × 10^3	Total cal. per sec. × 10^3	Cal. N_2O_4 per sec. × 10^3	Flow, g. per sec. × 10^3	Sp. heat
32	2.590	54.99	1.215	2.0645	0.8495	0.1606	2.04
33	2.660	54.94	1.300	2.216	0.9155	.1964	1.75
49	2.634	55.10	2.414	3.507	1.0908	.2166	1.91
50	2.624	55.10	2.414	3.532	1.1185	.2202	1.94
70	1.403	55.01	1.245	1.742	0.49712	.1866	1.90
	Av.	55.03					1.91
36	2.580	60.90	1.249	2.100	0.8523	.1681	1.97
37	2.616	60.89	1.264	2.163	0.8990	.1829	1.89
	Av.	60.90					1.94
34	2.657	63.32	1.423	2.390	0.9670	.1887	1.92
35	2.595	63.32	1.249	2.277	1.0290	.1970	2.02
72	1.961	63.35	1.195	1.470	0.2749	.0737	1.90
	Av.	63.33					1.95
39	2.625	70.80	1.783	3.523	1.740	.2930	1.69
40	2.647	70.79	1.742	3.028	1.286	.2683	1.81
48	2.560	70.68	2.151	3.291	1.140	.2547	1.76
47	2.530	70.78	2.151	3.442	1.291	.2852	1.78
72	2.172	70.69	0.1548	0.2151	0.6030	.1477	1.88
73	2.172	70.69	.1548	.2115	.5666	.1367	1.91
74	2.174	70.67	.1548	.1816	.2684	.0674	1.83
	Av.	70.70					1.83
41	2.660	80.89	2.192	3.113	.921	.2246	1.54
42	2.666	80.89	2.192	2.839	.647	.1782	1.36
43	2.665	80.89	1.653	2.629	.976	.2411	1.52
44	2.665	80.89	1.653	2.839	1.186	.250	1.78
	Av.	80.89					1.53
45	4.390	97.53	2.237	3.231	0.994	.2131	1.06
46	4.200	97.49	2.237	3.490	1.253	.3086	0.97
	Av.	97.51					1.01
55	2.810	33.75	2.653	3.112	.9590	.2536	1.34
56	2.810	33.75	2.653	3.418	.7650	.1989	1.37
64	1.82	33.71	1.936	2.533	.5975	.2406	1.36
65	1.82	33.71	1.936	2.462	.5258	.2099	1.38
	Av.	33.73					1.37

Table I (*Concluded*)

Expt.	Temp. int.	$\frac{T_1 + T_2}{2}$	Corr. cal. per sec. $\times 10^3$	Total cal. per sec. $\times 10^3$	Cal. N_2O_4 per sec. $\times 10^3$	Flow, g. per sec. $\times 10^3$	Sp. heat
57	2.810	40.99	2.304	3.442	1.138	.227	1.78
58	2.810	40.99	2.304	3.107	0.803	.187	1.53
59	2.800	41.00	2.391	3.546	1.155	.269	1.53
60	2.800	41.00	2.391	3.674	1.283	.305	1.50
61	2.800	41.00	2.391	2.902	0.598	.137	1.56
62	2.796	41.00	2.391	2.892	.501	.113	1.58
63	2.796	41.00	2.391	2.892	.501	.113	1.59
71	1.184	40.90	0.956	0.125	.289	.148	1.65
	Av.	41.00					1.59
66	1.398	44.00	1.199	1.470	.270	.110	1.75
67	1.398	44.00	1.199	2.747	1.548	.668	1.66
68	1.401	44.00	1.200	1.729	0.528	.226	1.66
69	1.400	44.00	1.200	1.470	.270	.120	1.60
	Av.	44.00					1.67

The Apparent and the True Heat Capacities

The total heat absorbed in raising the temperature of one gram molecule of the gas (92 g.) at constant pressure will be called the apparent molal heat capacity, $C_{p(\mathrm{a})}$. It comprises three different quantities, as shown in the following equation

$$C_{p(\mathrm{a})} = (1 - \alpha)\, C_{p,\ N_2O_4} + 2\alpha C_{p,\ NO_2} + (\mathrm{d}\alpha/\mathrm{d}t)_p \Delta H \qquad (1)$$

The first term, $(1 - \alpha)C_{p,\ N_2O_4}$, represents the heat absorbed in raising the temperature of the undissociated nitrogen tetroxide at constant pressure; α is the percentage dissociation of one molecule of the nitrogen tetroxide into two of nitrogen dioxide.

The second term, $2\alpha C_{p,\ NO_2}$, is the heat required to raise the temperature of the dissociated part of the gas, the nitrogen dioxide, at constant pressure.

The third term, $(\mathrm{d}\alpha/\mathrm{d}t)_p$, ΔH, is a measure of the heat absorbed in the dissociation of the tetroxide into two molecules of dioxide as the temperature is raised. ΔH is the heat of dissociation of a gram molecule of the tetroxide and $(\mathrm{d}\alpha/\mathrm{d}t)_p$ is the temperature coefficient of dissociation at constant pressure.

In this equation $C_{p(\mathrm{a})}$ is measured experimentally and α may be calculated from the following equation of Schreber[7] which gives the equilibrium constant K_p (expressed in mm. of mercury) as a function of temperature.[8]

$$\log K_p = \log P^2_{NO_2}/P_{N_2O_4} = \log T - 2866.2/T + 9.13242 \qquad (2)$$

The relation between K_p and the degree of dissociation, α, is given by the equation

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[7] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

[8] All the calculations were made also using Bodenstein's equation [*ibid.*, **100**, 78 (1922)]. Although this equation is more accurate it could not be used for the present work at full atmospheric pressure.

$$K_p = 4(760)\alpha^2/(1 - \alpha^2) \tag{3}$$

The heat absorbed in dissociation, ΔH, is calculated from the familiar Van't Hoff equation

$$\mathrm{d}\log K_p/\mathrm{d}t = \Delta H/2.303\ RT^2 \tag{4}$$

Differentiating Equation 2 with respect to temperature

$$\mathrm{d}\log K_p/\mathrm{d}t = 0.4343/T + 2866.2/T^2 \tag{5}$$

Substituting the right-hand member of Equation 5 for the left-hand member of Equation 4,

$$\Delta H/2.303RT^2 = 0.4343/T + 2866.2/T^2, \text{ and } \Delta H = 1.99\ T + 13{,}166 \tag{6}$$

The value of $(\mathrm{d}\alpha/\mathrm{d}t)_p$ can be determined from Equations 3 and 5 as follows.

Writing Equation 3 as

$$\log K_p = \log 4 + \log 760 + \log \alpha^2/(1 - \alpha^2)$$

and differentiating with respect to α,

$$\mathrm{d}\log K_p/\mathrm{d}\,\alpha = 2 \times 0.4343/(1 - \alpha^2)\alpha \tag{7}$$

Dividing Equation 5 by Equation 7

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_p = \left(\frac{0.4343}{T} + \frac{2866.2}{T^2}\right)\frac{\alpha(1 - \alpha^2)}{2 \times 0.4343} = \alpha - \alpha^3\left(\frac{1}{2T} + \frac{3300}{T^2}\right) \tag{8}$$

In the first four columns of Table II are given the numerical values of the quantities necessary for calculating the term $(\mathrm{d}\alpha/\mathrm{d}t)_p\Delta H$. This term expresses the heat absorbed in dissociating the tetroxide as the temperature is raised, and its numerical values are given in the fifth column. The apparent heat capacities, $C_{p(\mathrm{a})}$, determined experimentally (Table I) are recorded in the sixth column. The true heat capacities $C_{p,\ \mathrm{true}}$ of

TABLE II

CALCULATION OF THE TRUE HEAT CAPACITY OF NITROGEN TETROXIDE

1	2	3	4	5	6	7
T, °C.	α	ΔH	$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_p \times 10^3$	$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_p \Delta H$	$C_{p(\mathrm{a})}$	$C_{p,\ \mathrm{true}}$
33.73	0.2415	13,729	8.35	114.6	126	11.4
41.00	.3076	13,744	9.76	134.2	146	12.0
44.00	.3377	13,750	10.30	141.6	154	12.0
55.03	.4509	13,772	11.68	160.8	176	15.2
60.90	.5291	13,784	11.85	163.3	178	14.7
63.33	.5578	13,789	11.78	162.4	179	16.6
70.70	.6425	13,803	11.09	153.1	168	14.9
80.89	.7465	13,824	9.13	126.9	143	16.1
97.51	.8675	13,857	5.45	75.5	93	17.5
100.00	.8800	13,858	4.96	68.7	87.5[a]	18.8[a]
110.00	.9213	13,878	3.33	46.2	65.1[a]	18.9[a]
120.00	.9482	13,898	2.17	30.2	49.2[a]	19.0[a]
130.00	.9710	13,918	1.20	16.7	35.8[a]	19.1[a]
140.00	.9806	13,938	0.77	10.8	30.0[a]	19.2[a]
150.00	.9868	13,958	.49	6.9	26.3[a]	19.4[a]
160.00	.9909	13,978	.34	4.7	24.2[a]	19.5[a]

[a] Calcd.

the seventh column are obtained by subtracting the heat of dissociation from the observed heat capacity, that is, by subtracting the values of the fifth column from those of the sixth.

The data of the last three columns are shown graphically in Fig. 3, where the upper curve gives the apparent molar heat capacities, the middle curve gives the heat absorbed in the dissociation of the nitrogen tetroxide, and the lower curve gives the true heat capacity.

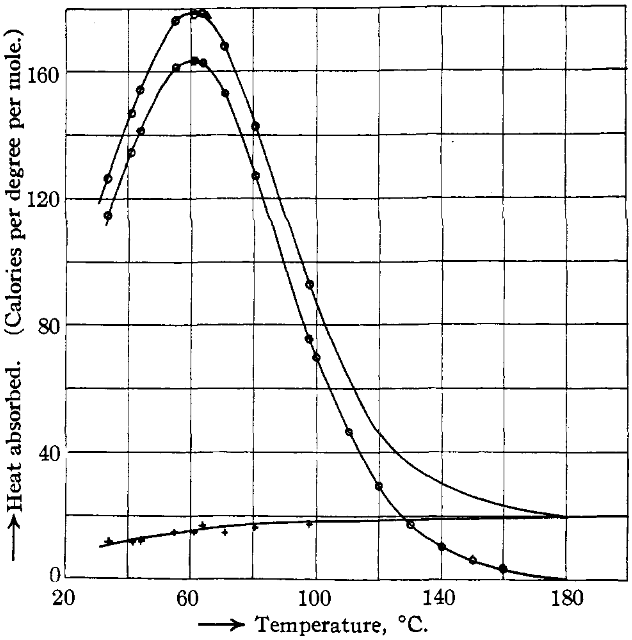

Fig. 3.—Molar heat capacity of gaseous N_2O_4 and NO_2. Upper curve, apparent heat capacity ($C_{p,a.}$), experimentally determined. Middle curve, heat absorbed in dissociation, calculated. Lower curve, true heat capacity ($C_{p,\text{ true}}$), calculated.

The experimental determinations could not be carried out accurately above 100° but at temperatures above 150° the tetroxide is so completely dissociated into the dioxide that the heat of dissociation becomes negligibly small. The apparent heat capacity then becomes the true heat capacity of nitrogen dioxide, and it may be estimated, with the help of the empirical equation of Lewis and Randall,[9] for the heat capacity of carbon dioxide and sulfur dioxide. Nitrogen dioxide is a triatomic gas, so similar to these gases that the use of the equation is justified; $C_p = 7.00 + 0.0071T - 0.00000186T^2$. Between 100° and 160° the heat capacity may be estimated by calculating the heat of dissociation and add-

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[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 80.

ing to it the calculated heat capacity of $2NO_2$. Less than 3% of the gas still remains as tetroxide and no appreciable error is introduced by calculating it as dioxide.

Conclusions

The two curves of Fig. 3 are very similar and it is plainly evident that the abnormally large heat capacity of nitrogen tetroxide and the negative temperature coefficient are due to the heat absorbed in dissociation. It seems reasonable to assume that similar cases of negative temperature coefficients and maxima discovered in the specific heats of liquids,[2] are likewise due to dissociation.

The relative heat capacities of N_2O_4 and $2NO_2$ are of theoretical interest in the study of specific heats and it was hoped that the data of the present research would permit an experimental determination of these separate quantities. However, the true heat capacity is so small in comparison with the heat of dissociation that the experimental errors in the apparent heat capacity introduce large errors in the true heat capacity. Furthermore the equation of Schreber (Equation 2) is sufficiently uncertain to introduce large errors. It is evident, however, that the true heat capacity increases as the temperature rises, that is, as the proportion of dioxide increases. The heat capacity of N_2O_4, then, is less than that of $2NO_2$. It is sufficient to state that several calculations, in which the calculated heat capacity of the dioxide is subtracted from the true heat capacity of the mixed gases, indicate that $C_{p,\, N_2O_4}$ is slightly greater than $C_{p,\, NO_2}$.

It is hoped that future experimental determinations of the equilibrium between the tetroxide and the dioxide at full atmospheric pressure will permit a more accurate calculation of the true heat capacities of these substances, and of their ratios at constant pressure and constant volume.

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Summary

1. A flow calorimeter has been developed for measuring the specific heats of gas over small temperature intervals. The gas is cooled before entering the calorimeter and the cooling effect is counterbalanced with electrical heating.
2. The apparent heat capacity of gaseous nitrogen tetroxide has been measured over small temperature intervals from 33° to 98°.
3. The apparent heat capacity is very large on account of the dissociation. It reaches a maximum value at 62° and then decreases.
4. The true heat capacity of gaseous nitrogen tetroxide has been determined by subtracting the heat absorbed by dissociation, from the apparent heat capacity.

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