

The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $\text{N}_2\text{O}_4=2\text{NO}_2=2\text{NO}+\text{O}_2$

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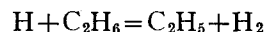
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exchanged. It follows that in Steacie and Phillips' work the apparent D content of ethane due to the presence of deuteromethane was 5.7 percent. Allowing for this we obtain the corrections to Steacie and Phillips' data shown in Table V.

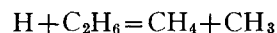
It follows that the formation of methane found here introduces only a negligible correction into Steacie and Phillips' value of the activation energy of the exchange reaction.

The formation of methane is not, therefore, a sufficient explanation of the discrepancy between the results of Steacie and Phillips and of Trenner, Morikawa, and Taylor for the exchange reaction. In order to explain this discrepancy on the basis of methane formation in Steacie and Phillips' investigation, it would be necessary to assume that 60 percent of their ethane decomposed, as compared with a mean value of 8.2 percent found here. It does not appear to be possible at the moment to offer any explanation of the lack of agreement between the two investigations.

It was pointed out in the previous paper that the activation energy of the reaction



is of considerable importance in connection with the Rice-Herzfeld free radical chain theory.⁶ It was shown that an activation energy of 6.3 Kcal. for this reaction introduces insurmountable difficulties into the application of the scheme to the ethane decomposition. It is worth pointing out that even the much higher value of Trenner, Morikawa, and Taylor would introduce serious difficulties into the application of the scheme. Also, the presence of the reaction



with an activation energy of about 8 Kcal. would fundamentally alter the nature of the chain carrying steps in the Rice-Herzfeld scheme, and would destroy its agreement with experiment.

⁶ Rice and Herzfeld, *J. Am. Chem. Soc.* **56**, 284 (1934).

The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $\text{N}_2\text{O}_4 = 2\text{NO}_2 = 2\text{NO} + \text{O}_2$

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The heat capacity of nitrogen tetroxide has been measured from 15°K to the boiling point, 294.25°K. The melting point is 261.90°K. The heats of fusion and vaporization were found to be 3502 and 9110 cal./mole, respectively. The vapor pressures of solid and liquid nitrogen tetroxide were measured with a mercury manometer by means of an arrangement in which carbon dioxide protected the mercury surface from reaction with the nitrogen tetroxide. The data have been represented by the equations: Liquid nitrogen tetroxide 261.90 to 294.9°K $\log_{10} P(\text{int. cm Hg}) = -1753.000/T + 8.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6}T^2$. Solid nitrogen tetroxide 240.3 to 261.90°K, $\log_{10} P(\text{int. cm Hg}) = -2460.000/T + 9.58149 + 7.6170 \times 10^{-3}T - 1.51335 \times 10^{-6}T^2$. By applying the third law of thermodynamics to the calorimetric measurements, the entropy of the gas, which is dissociated to the extent of 16.1 percent into nitrogen dioxide at the boiling point, was found to be 80.62 cal./deg. per mole of gas as N_2O_4 . From a consideration of the available data on the equilibria

$\text{N}_2\text{O}_4 = 2\text{NO}_2 = 2\text{NO} + \text{O}_2$ in combination with spectroscopic data for the several substances, and the experimental entropy value given above, a number of quantities of thermodynamic interest have been evaluated. For $\text{N}_2\text{O}_4(g)$, $S_{298.1}^0 = 72.73$ and for $\text{NO}_2(g)$, $S_{298.1}^0 = 57.47$ cal./deg. per mole. These values, which are the ones which should be used in ordinary thermodynamic calculations, do not include the nuclear spin entropy, $R \ln 3 = 2.183$, for each nitrogen atom. The absolute entropies are $\text{N}_2\text{O}_4(g)$, $S_{298.1}^0 = 77.10$; $\text{NO}_2(g)$, $S_{298.1}^0 = 59.65$ cal./deg. per mole. For the reactions: $2\text{NO}_2 = \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = -1,110$ cal., $\Delta H_{298.1}^0 = -13,693$ cal.; $\text{N}_2 + 2\text{O}_2 = \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = 23,440$ cal., $\Delta H_{298.1}^0 = 2,239$ cal.; $\text{NO} + \frac{1}{2}\text{O}_2 = \text{NO}_2$, $\Delta F_{298.1}^0 = -8,375$ cal., $\Delta H_{298.1}^0 = -13,562$ cal.; $\frac{1}{2}\text{N}_2 + \text{O}_2 = \text{NO}_2$, $\Delta F_{298.1}^0 = 12,275$ cal., $\Delta H_{298.1}^0 = 7,964$ cal. The experimental entropy value obtained in this investigation, together with band spectrum data, has made possible a much better correlation of the various measurements on the above equilibria than has hitherto been possible. The good agree-

ment demonstrates that the entropy value obtained from the experimental measurements and the third law of thermodynamics is the correct one. In the course of the calculations several points concerning the molecular structures of nitrogen dioxide and nitrogen tetroxide were investigated. Accepting the band spectrum evidence, that NO₂ is a symmetrical nonlinear molecule, it was possible to show from the equilibrium measurements that the statistical weight of the normal electronic state is 2. One would also infer this from existing magnetic data which are consistent with the value to be expected from a ²Σ state.

It is difficult to draw accurate conclusions with respect to the structure of the N₂O₄ molecule; however, the experimental entropy value seems to be more consistent with the symmetrical form O₂N—NO₂ which would have considerably less entropy than would be expected in the case of an unsymmetrical N₂O₄ molecule. The measurements exclude the possibility of free rotation of NO₂ groups in symmetrical O₂N—NO₂. The calculations do not permit an estimate of the potential barrier concerned in the rotational oscillations of these groups. An extensive summary of the N₂O₄ = 2NO₂ = 2NO + O₂ equilibria data is given.

THE determination of the entropies of nitrogen tetroxide and nitrogen dioxide gases from the third law of thermodynamics is complicated by the fact that these two substances are present at appreciable mole fractions under all conditions of equilibrium between the liquid and gaseous states. Although the dissociation equilibrium has been repeatedly studied during the past fifty years it has not been found possible to obtain the entropy change of the reaction N₂O₄ = 2NO₂ from the equilibrium measurements alone without an uncertainty of several entropy units per mole. It is desirable to obtain the entropies of gases to about a tenth of an entropy unit.

In order to obtain accuracy the following procedure was adopted: The entropy of the gas in equilibrium with liquid at the boiling point was evaluated in the usual way from the third law of thermodynamics. Then

$$S^0_{\text{mixture}} = (1 - \alpha)S^0_{\text{N}_2\text{O}_4} + 2\alpha S^0_{\text{NO}_2} - (1 - \alpha)R \ln \frac{1 - \alpha}{1 + \alpha} - 2\alpha R \ln \frac{2\alpha}{1 + \alpha} \quad (1)$$

where α is the degree of dissociation of N₂O₄. The equilibrium concentrations of the two gases are known with sufficient accuracy and the entropy of nitrogen tetroxide can be found if an independent value of the entropy of nitrogen dioxide is obtained. Unfortunately the spectroscopic interpretation of the nitrogen dioxide molecule is not sufficiently complete to permit the full use of this method. The molecule is known to be triangular in shape and electron diffraction measurements have indicated the approximate values of its moments of inertia.

The three fundamental vibration frequencies are known from its band spectrum. Nitrogen dioxide contains an odd number of electrons so there must be a multiplicity due to the unbalanced electron moment. Fortunately the equilibrium 2NO₂ = 2NO + O₂ has been carefully investigated and the spectroscopic interpretations of nitric oxide and of oxygen are exceptionally well known. Thus it is possible, by methods which will be discussed later, to make an evaluation of the entropy of nitrogen dioxide from these data. The *a priori* weight of the normal electronic state was taken as $p_e = 2$, in agreement with experiments by Havens,¹ who found that the magnetic susceptibility of nitrogen dioxide corresponded to the spin of one electron. Having obtained a reliable value for the entropy of nitrogen tetroxide by the above procedure, it has been possible to give a very satisfactory treatment of the equilibrium data for the reaction N₂O₄ = 2NO₂.

The calorimetric apparatus and procedure have been described previously.²

TABLE I. Melting point of nitrogen tetroxide.

TIME	% MELTED	T, °K RESISTANCE THERMOMETER	T, °K THERMO- COUPLE
8:55 A.M.	20	Heated into melting point	
12:07 P.M.		261.86	261.84
12:53 P.M.		Supplied heat	
2:23 P.M.	40	261.88	261.87
3:48 P.M.	40	261.88	261.87
4:30 P.M.	60	Supplied heat	
6:55 P.M.		261.89	261.89
7:41 P.M.		Supplied heat	
9:52 P.M.	80	261.89	261.90
10:16 P.M.	80	261.89	261.90
		Accepted value	261.90

¹ Havens, Phys. Rev. **41**, 337 (1932).

² Kemp and Giauque, J. Am. Chem. Soc. **59**, 79 (1937).

TABLE II. Vapor pressure of nitrogen tetroxide. Boiling point 294.25°K (0°C = 273.10°K).

T, °K		P	$P_{\text{obs.}} - P_{\text{calc.}}$		$T_{\text{obs.}} - T_{\text{calc.}}$	
THERMOCOUPLE	RESISTANCE THERMOMETER	INTERNATIONAL CM (Hg)	THERMOCOUPLE	RESISTANCE THERMOMETER	THERMOCOUPLE	RESISTANCE THERMOMETER
240.298	240.296	1.997	-0.001	-0.001	+0.007	+0.005
240.315	240.322	2.011	+ .009	+ .008	- .046	- .040
248.476	248.476	4.358	- .002	- .002	+ .004	+ .004
255.622	255.620	8.246	+ .002	+ .004	- .003	- .006
258.782	258.782	10.821	+ .026	+ .029	- .029	- .032
261.875	261.884	13.975				
261.890	261.904	13.973				
(261.90)	(261.90)	(13.978)				
264.042	264.050	15.825	- .008	- .015	+ .009	+ .016
268.043	268.041	19.872	- .007	- .005	+ .007	+ .005
271.943	271.940	24.666	+ .005	+ .009	- .003	- .006
275.939	275.929	30.563	- .002	+ .014	+ .001	- .009
279.326	279.324	36.493	+ .001	+ .005	- .000	- .003
284.217	284.212	46.785	- .010	+ .002	+ .004	- .001
288.202	288.210	56.945	- .014	- .037	+ .007	+ .013
292.137	292.138	68.807	+ .002	- .002	- .000	+ .000
294.898	294.893	78.329	- .004	+ .014	+ .001	- .004

NITROGEN TETROXIDE

Preparation

C.P. lead nitrate was dried in an oven for twelve hours at 120°C. The lead nitrate was then placed in a reaction flask attached to the preparation line and a vacuum of 10^{-5} mm Hg was obtained throughout the preparation system. The reaction flask was heated to 200°C by means of an electric oven and pumped until there was no sign of water condensing in the cold part of the line. The oven temperature was then raised to about 450°C. The nitrogen tetroxide which was generated was passed through phosphorus pentoxide and finally condensed in a bulb cooled by a bath of solid carbon dioxide and ether. The oxygen which was produced with the nitrogen tetroxide was allowed to escape through a mercury bubbler trap. The first 10 cc of liquid condensed was discarded. Any oxygen entrapped in the solid nitrogen tetroxide was removed by subliming the nitrogen tetroxide and pumping on it with a high vacuum pump. By means of observations on the change of melting point with the percentage melted, and later, on the pre-melting heat capacities, the impurity was estimated to be about one part in ten thousand.

Melting point

The melting point was observed for various percentages of nitrogen tetroxide melted. Table I gives a summary of these observations.

The vapor pressure of nitrogen tetroxide

To permit the use of a mercury manometer for measuring vapor pressures of nitrogen tetroxide the gas pressure was balanced by an equal pressure of carbon dioxide. The liquid or solid nitrogen tetroxide was kept in the calorimeter during the measurements and the inlet line of the calorimeter was connected by means of capillary tubing to a manometer system filled with carbon dioxide. A stopcock was located in the middle of the capillary line and bulbs of about 25 cc capacity were located on each side of the stopcock. Also in order to determine, approximately, the carbon dioxide pressure needed, an auxiliary manometer could be connected to the calorimeter. In this manometer the nitrogen tetroxide was allowed to come in contact with the mercury. The resulting reaction corroded the mercury but the position of balance could be determined within about 0.5 mm Hg. The procedure for measuring vapor pressures was as follows: The calorimeter line was thoroughly swept out before each measurement by evaporating some of the material in the calorimeter. All other lines were completely evacuated at the same time. The calorimeter was then heated to the desired temperature. The approximate pressure was measured and the auxiliary line disconnected. The manometer system was then filled with carbon dioxide to approximately the correct pressure and the stop-

cock between the carbon dioxide and nitrogen tetroxide was opened. The two gases intermixed slightly in one of the mixing bulbs as the pressures equalized, but the capillary lines contained practically pure gases and eliminated any appreciable diffusion.

A Société Gènevoise cathetometer with a precision of 0.002 cm was used to compare the mercury levels with a standard meter. A diagram of the manometer has been given previously.³ The meniscus height corrections were taken from the work of Cawood and Patterson.⁴ The standard acceleration of gravity was taken as 980.665 cm/sec.² and the acceleration of gravity for this location was taken as 979.973 g/cm².⁵ Other data needed to correct the pressures to international cm Hg were taken from the "I.C.T." A small correction, amounting to 0.25 mm Hg when the pressure was 1 atmosphere, was applied to the measurements to take account of the difference in density of the carbon dioxide and nitrogen tetroxide gases in the manometer system.

The data have been represented by the equations: Liquid nitrogen tetroxide 261.90 to 294.9°K,

$$\log_{10} P(\text{int. cm Hg}) = -1753.000/T + 8.00436 - 11.8078 \quad (2)$$

$$\times 10^{-4}T + 2.0954 \times 10^{-6}T^2.$$

Solid nitrogen tetroxide 240.3 to 261.90°K,

$$\log_{10} P(\text{int. cm Hg}) = -2460.000/T + 9.58149 + 7.61700 \quad (3)$$

$$\times 10^{-3}T - 1.51335 \times 10^{-5}T^2.$$

The observations have been compared with the equations in Table II. The temperatures were measured with both a thermocouple and a gold resistance thermometer. The vapor pressure measurements were made in a separate investigation about one year after the melting point observations, given in Table I, and the heat capacity measurements, which are to be presented below. The impurity, as estimated from

³ Giauque and Egan, J. Chem. Phys. 5, 45 (1937).

⁴ Cawood and Patterson, Trans. Faraday Soc. 29, 1522 (1933).

⁵ Sternwarte, Landolt, Börnstein and Roth, *Physikalische-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923).

the change of melting point with the fraction melted, was about 5 parts in 10,000 whereas the previous material contained only 1 part in 10,000 on a molal (N₂O₄) basis.

The vapor pressure of nitrogen tetroxide has been measured by Ramsay and Young,⁶ Guye and Drouguine,⁷ Scheffer and Treub,⁸ Russ,⁹ Baume and Robert,¹⁰ and by Mittasch, Kuss and Schlueter.¹¹ The melting and boiling point observations of previous investigators are compared with the present results in Table III.

Measurement of the amount of nitrogen tetroxide

As nitrogen tetroxide boils at room temperature, it was possible to condense it in a weighed evacuated bulb and determine the amount in the calorimeter directly.

TABLE III. *Melting and boiling point temperatures of nitrogen tetroxide.*

MELTING POINT °K	BOILING POINT °K	OBSERVER
....	299	Gay Lussac ¹² (1816)
....	301	Dulong ¹³ (1816)
259.6	Fritzsche ¹⁴ (1841)
....	295	Pelilot ¹⁵ (1841)
261.6	Muller ¹⁶ (1862)
263	Deville and Troost ¹⁷ (1867)
....	294.74	Tharp ¹⁸ (1880)
....	295.6 at 750 mm	Nadejdine ¹⁹ (1885)
....	295.0	Bousfield ²⁰ (1888)
262.96	Ramsay ²¹ (1890)
....	295.07	Tharp and Rodger ²² (1894)
262.15	299	Geuther, Bruni and Berti ²³ (1900)
....	293 at 720 mm	Lunge and Berl ²⁴ (1906)
263.5	295	Guye and Drouguine ⁷ (1910)
262.3	294.3	Scheffer and Treub ⁸ (1912)
262.7	Edgerton ²⁵ (1914)
264.06	295-296	Oddo ²⁶ (1915)
....	294.0	Mittasch, Kuss and Schlueter ¹¹ (1926)
261.90	294.25	This research

⁶ Ramsay and Young, Phil. Trans. London A177, 71 (1887).

⁷ Guye and Drouguine, J. Chim. Phys. 8, 473 (1910).

⁸ Scheffer and Treub, Zeits. f. physik Chemie 81, 308 (1912).

⁹ Russ, Zeits. f. physik Chemie 82, 217 (1913).

¹⁰ Baume and Robert, Comptes rendus 168, 1201 (1919).

¹¹ Mittasch, Kuss and Schlueter, Zeits. f. anorg. allgem. Chemie 159, 1 (1926).

¹² Gay Lussac, Ann. Chim. Phys. 1, 394 (1816).

¹³ Dulong, Ann. Chim. Phys. 2, 317 (1816).

¹⁴ Fritzsche, J. prakt. Chem. 22, 21 (1841).

¹⁵ Pelilot, Ann. Chim. Phys. 2, 58 (1841).

¹⁶ Muller, Liebig's Ann. 122, 1 (1862).

¹⁷ Deville and Troost, Compt. rendus 64, 237 (1867).

¹⁸ Tharp, J. Chem. Soc. 37, 244 (1880).

¹⁹ Nadejdine, Bull. Acad. St. Petersburg 30, 327 (1885).

²⁰ Bousfield, J. Chem. Soc. 53, 621 (1888).

²¹ Ramsay, Zeits. f. physik. Chemie 5, 221 (1890).

²² Tharp and Rodger, Phil. Trans. 185A, 397 (1900).

²³ Geuther, Bruni and Berti, Gazz. Chim. Ital. 30, ii, 151 (1900).

²⁴ Lunge and Berl, Zeits. f. angew. Chemie 19, 807 (1906).

²⁵ Edgerton, J. Chem. Soc. 105, 647 (1914).

²⁶ Oddo, Gazz. Chem. Ital. 45, i. 433 (1915).

TABLE IV. Heat capacity of nitrogen tetroxide, 0°C $\approx 273.10^{\circ}\text{K}$ (molecular weight, 92.016; 1.9259 moles in calorimeter).

$T, ^{\circ}\text{K}$	ΔT	C_p cal./deg./mole	$T, ^{\circ}\text{K}$	ΔT	C_p cal./deg./mole
16.80	2.765	1.315	148.89	4.859	18.26
19.10	1.979	1.833	153.87	5.098	18.65
21.46	2.829	2.370	158.93	4.908	19.01
24.11	2.626	3.000	163.83	4.739	19.35
26.95	3.041	3.718	168.69	4.789	19.66
30.18	3.389	4.539	173.79	5.037	20.03
33.70	3.680	5.442	178.90	4.861	20.39
38.51	5.672	6.544	184.06	5.089	20.72
44.08	5.351	7.652	189.40	5.105	21.12
49.10	4.585	8.546	194.62	4.929	21.53
54.09	4.388	9.345	199.98	5.335	21.93
58.84	5.036	10.02	205.60	5.138	22.32
62.23	5.309	10.52	210.97	4.961	22.73
63.66	4.528	10.76	216.37	4.792	23.10
67.31	4.814	11.16	221.53	4.635	23.50
72.44	5.416	11.68	226.30	5.087	23.83
77.66	5.015	12.32	232.37	5.360	24.31
82.52	4.707	12.77	238.12	5.172	24.78
87.50	5.231	13.35	243.65	5.011	25.19
93.03	5.844	13.88	249.27	5.259	25.60
98.69	5.460	14.41	254.65	4.320	25.94
103.99	5.147	14.87	258.26	1.921	26.23
109.02	4.885	15.26	261.90	Melting point	
113.77	4.549	15.66	265.44	3.146	32.79
118.69	5.217	15.99	269.91	4.492	32.92
123.82	4.967	16.40	275.38	5.212	33.10
128.86	5.041	16.82	281.19	5.083	33.34
133.97	5.192	17.19	286.86	4.955	33.60
140.15	4.998	17.58	291.28	2.739	33.74
144.09	4.797	17.95	294.25	Boiling point	

TABLE V. Heat capacity of nitrogen tetroxide (molecular weight, 92.016). Values taken from smooth curve through observations.

$T, ^{\circ}\text{K}$	C_p cal./deg./mole	$T, ^{\circ}\text{K}$	C_p cal./deg./mole
20	2.03	160	19.07
30	4.50	170	19.76
40	6.86	180	20.46
50	8.70	190	21.18
60	10.20	200	21.92
70	11.46	210	22.66
80	12.56	220	23.41
90	13.58	230	24.15
100	14.51	240	24.89
110	15.34	250	25.63
120	16.15	260	26.36
130	16.90	270	32.93
140	17.63	280	33.28
150	18.36	290	33.71

The heat capacity of nitrogen tetroxide

Table IV gives the observed heat capacities of nitrogen tetroxide. Table V contains the heat capacity values taken from the smooth curve. The data are shown in Fig. 1.

Heat of fusion

The heat of fusion was measured in the usual manner. Table VI summarizes the data.

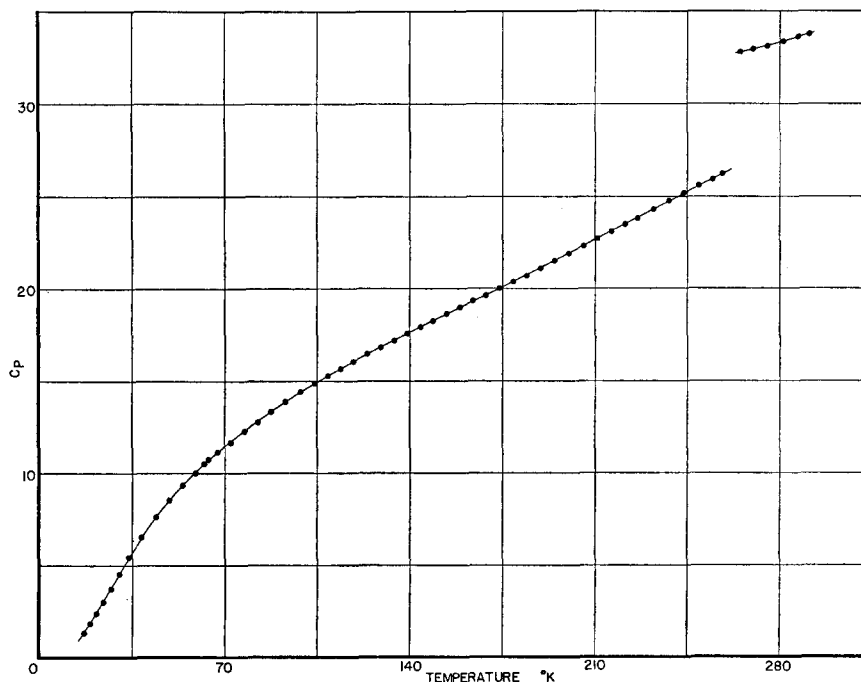


FIG. 1. Heat capacities in calories per degree per mole of nitrogen tetroxide.

Heat of vaporization

The nitrogen tetroxide vaporized during the heat of vaporization measurements was absorbed in alkali and the amount determined by the increase in weight of the absorption bulb. The gas was bubbled through a small mercury trap in the bottom of the absorption bulb. Each absorption bulb was filled with 150 cc of solution containing 63 grams of KOH and 25 grams of KI. Previous experiments had shown that the absorption bulb would become clogged with mercury salts in the absence of the KI. The results are summarized in Table VII.

A calculation of the heat of vaporization was made from the vapor pressure data, as represented by Eq. (2), by means of the equation

$$\Delta H = T\Delta V(d\rho/dT).$$

The calculation is complicated by uncertainties in the degree of dissociation and the correction for gas imperfection in the N₂O₄, NO₂ mixture. From the latter part of this paper α , the degree of dissociation was taken as 0.161, $(PV)_{\text{N}_2\text{O}_4} = RT(1 - 0.01P)$ and $(PV)_{\text{NO}_2} = RT(1 - 0.005P)$. The resulting value obtained for the heat of vaporization is 9233 cal./mole (92.016 g), as compared to the reliable calorimetric value 9110 cal./mole. The difference is within the limit of error of the gas imperfection correction.

The entropy from calorimetric data

Table VIII gives an itemized account of the entropy calculation for the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide at the boiling point.

The free energy of nitrogen dioxide

Before interpreting the experimental result on the entropy of the gaseous mixture of nitrogen tetroxide and nitrogen dioxide it is necessary to obtain an independent value for the entropy of

TABLE VI. *Heat of fusion of nitrogen tetroxide. Melting point 261.90°K, 0°C=273.10°K (molecular weight, 92.016).*

TEMPERATURE INTERVAL	CORRECTED HEAT IN- PUT/MOLE	$\int C_p dT$ +PREMELTING	ΔH CAL./MOLE
260.737-265.643	3676	176	3500
261.074-263.905	3584	85	3499
257.039-263.665	3748	242	3506
		Mean value	3502 ± 3 cal.

TABLE VII. *Heat of vaporization of nitrogen tetroxide. Boiling point, 294.25°K; 0°C=273.10°K. Molecular weight, 92.016.*

MOLES VAPORIZED	TIME OF ENERGY INPUT, MINUTES	ΔH AT 760 MM CAL./MOLE
0.23860	70	9102
0.22359	65	9106
0.20846	65	9118
0.20949	65	9115
		Mean value 9110 ± 9 cal.

TABLE VIII. *Calculation of the entropy of the equilibrium mixture.*

Debye function, 0-15°K	0.34
Graphical, 15-261.90°K	31.98
Fusion, 3502/261.90	13.37
Graphical, 261.90-294.25°K	3.87
Vaporization, 9110/294.25	30.96
	80.52 ± 0.15
Correction for gas imperfection	0.10
Entropy of 92.016 g of equilibrium mixture of N ₂ O ₄ and NO ₂ gases at the boiling point.	80.62 E.U.

one of these gases. This is possible in the case of nitrogen dioxide. Spectroscopic observations on the vibrational frequencies of this molecule have been made by several experimenters. The data have been summarized by Sutherland and Penney²⁷ who give the values $\nu_1 = 641$, $\nu_2 = 1373$ and $\nu_3 = 1615$ cm⁻¹.

The moments of inertia have not been obtained spectroscopically but their product can be obtained by combining the molecular constants, which are known, with existing equilibrium data on the reaction, $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$. The above data are used with the equations

$$\Delta F^0/T = -R \ln K = \Delta(F^0 - H_0^0)/T + \Delta H_0^0/T \quad (4)$$

and for an asymmetrical top molecule

$$\begin{aligned} (F^0 - H_0^0)/T = & -3/2R \ln M - 4R \ln T \\ & - R/2 \ln I_1 I_2 I_3 - R \ln p_e + R \ln \sigma \\ & - 257.401 + \sum_{\nu_1 \nu_2 \nu_3} F_{\text{vib}}/T \quad (5) \end{aligned}$$

where I_1 , I_2 , I_3 are the principal moments of inertia, p_e is the *a priori* weight of the electronic state, σ is the symmetry number, which is equal to 2 in this case, and the other symbols have their usual meanings. $p_e = 2$ from the magnetic susceptibility determinations of Havens¹

²⁷ Sutherland and Penney, *Nature* **136**, 146 (1935).

TABLE IX. Calculation of ΔH_0^0 for the reaction $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$ from the data of Bodenstein and Lindner.

T, °K	$-\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
499.0	2.108	- 1
503.5	2.039	-36
519.4	1.876	* *
519.6	1.867	- 8
521.9	1.850	12
564.1	1.422	24
570.5	1.353	1
577.6	1.288	11
593.2	1.134	-45
617.0	0.961	35
617.9	.943	-11
626.5	.878	- 5
627.6	.876	14
662.1	.620	- 6
668.4	.581	5
671.5	.559	7
685.1	.464	-17
699.9	.371	-11
727.8	.209	- 4
731.2	.190	- 2
733.3	.179	16
752.8	.068	-12
786.9	-.107	-11
792.4	-.125	19
796.4	-.149	8
798.6	-.158	3
799.9	-.164	8
825.4	-.285	- 9

Average value of ΔH_0^0 12795 \pm 13.

* Value not included in average.

mentioned above. The values of $(F^0 - H_0^0)/T$ for

$$\Delta\left(\frac{F^0 - H_0^0}{T}\right) = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{NO}} + \frac{1}{2}\left(\frac{F^0 - H_0^0}{T}\right)_{\text{O}_2} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{NO}_2} \quad (6)$$

nitric oxide have been tabulated by Johnston and Chapman²⁸ and those for oxygen have been calculated by Johnston and Walker.²⁹ For both oxygen and nitric oxide the values are based on very accurate spectroscopic data and are thus subject to practically no error.

The dissociation of nitrogen dioxide has been measured by Richardson,³⁰ by Bodenstein and Katayama,³¹ and by Bodenstein and Lindner.³²

²⁸ Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).

²⁹ Johnston and Walker, J. Am. Chem. Soc. **55**, 172, 5075 (1933).

³⁰ Richardson, J. Chem. Soc. London **51**, 397 (1887).

³¹ Bodenstein and Katayama, Zeits. f. physik. Chemie **69**, 26 (1909).

³² Bodenstein and Lindner, Zeits. f. physik. Chemie **100**, 82 (1922).

Only the data of Bodenstein and Lindner were considered in our final calculations; however summaries of the other data have been presented for the sake of completeness.

The value of the product $I_1 I_2 I_3$ was found by trial so that the value of ΔH_0^0 remained constant. The results are given below for the case $I_1 I_2 I_3 = 1.44 \times 10^{-116} \text{ g}^3 \text{ cm}^6$. In terms of entropy an error of 0.05 cal./deg. per mole would produce a linear trend of 16 calories in ΔH_0^0 over the range of temperature covered by the experiments. The values at the lower temperatures are somewhat more inaccurate because the degree of dissociation in this region was too small for the most accurate evaluation of the equilibrium constant.

The data of Bodenstein and Lindner³² are presented in Table IX, those of Bodenstein and Katayama³¹ in Table X. No corrections were made for the effect of gas imperfection of nitric

TABLE X. Value of ΔH_0^0 for the reaction $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$ from the data of Bodenstein and Katayama.

SERIES	TEMPERATURE RANGE, °K	NUMBER OF DETERMINATIONS	ΔH_0^0
I	521-890	8	12,534 \pm 383
II	517-849	8	12,330 \pm 195
III	506-976	16	12,717 \pm 217
IV	492-974	17	12,428 \pm 379
V	513-772	10	12,933 \pm 36
Total		59	12,593 \pm 253

TABLE XI. Free energy of nitrogen dioxide and ΔF for $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$.

T, °K	$-\left(\frac{F - H_0^0}{T}\right)_{\text{NO}_2}$	$-\Delta\left(\frac{F^0 - H_0^0}{T}\right)$	$\Delta F^\circ_{\text{cal.}}$	$K = \frac{(\text{NO})(\text{O}_2)^{\frac{1}{2}}}{(\text{NO}_2)}$
275	48.536	14.617	8775	1.060×10^{-7}
298.1	49.202	14.826	8375	7.229×10^{-7}
300	49.252	14.849	8340	8.385×10^{-7}
325	49.918	15.028	7911	4.781×10^{-6}
350	50.538	15.222	7467	2.172×10^{-5}
375	51.122	15.379	7028	8.008×10^{-5}
400	51.670	15.535	6581	2.534×10^{-4}
425	52.195	15.667	6137	6.978×10^{-4}
450	52.676	15.799	5886	1.384×10^{-3}
500	53.617	15.998	4796	8.006×10^{-3}
550	54.471	16.176	3898	2.824×10^{-2}
600	55.266	16.326	2999	8.082×10^{-2}
650	56.010	16.455	2099	1.968×10^{-1}
700	56.709	16.564	1200	4.220×10^{-1}
750	57.373	16.661	299	8.181×10^{-1}
800	57.992	16.753	- 607	1.469
850	58.583	16.833	-1513	2.455
900	59.152	16.901	-2416	3.870

oxide, oxygen or nitrogen dioxide in treating the dissociation of nitrogen dioxide as it may be shown from order of magnitude calculations, based on typical equations of state, that the effect is unimportant at the temperatures concerned.

The data of Richardson,³⁰ consisting of 14 determinations over the temperature range 495–767°K, lead to a value of $\Delta H_0^0 = 13,275 \pm 411$.

The molecular constants of nitrogen dioxide

It will be of interest at this point to draw certain conclusions about the molecular structure of the nitrogen dioxide molecule. The product

$$I_1 = 2M_O(d \sin \theta)^2,$$

$$I_2 = \frac{2M_O M_N}{2M_O + M_N} (d \cos \theta)^2,$$

$$I_3 = I_1 + I_2, \text{ where } \theta \text{ is the half-angle.}$$

$$d = \left(\frac{I_1 I_2 I_3 (2M_O + M_N)^2}{8M_O^3 M_N \sin^2 \theta \cdot \cos^2 \theta [(2M_O + M_N) \sin^2 \theta + M_N \cos^2 \theta]} \right)^{1/6}. \quad (7)$$

$I_1 I_2 I_3 = 1.44 \times 10^{-116} \text{ g}^3 \text{ cm}^6$ is probably known to about 5 percent and this value may be used to obtain a reliable equation relating angle and distance in the nitrogen dioxide molecule. The results of this calculation are presented in Table XII. Sutherland and Penney,²⁷ and Badger and Herzberg²⁷ have expressed the opinion that the band spectrum characteristics of nitrogen dioxide indicate an angle of 110–120°. The electron diffraction experiments of Maxwell, Mosley and Deming³³ showed that it was difficult to give an unambiguous interpretation of the electron diffraction results. Several alternative combinations of angle and distance were in agreement with their measurements. They considered the most reasonable possibilities to be N–O = 1.15Å, $2\theta = 120^\circ$; N–O = 1.15Å, $2\theta = 90^\circ$; and N–O = 1.30Å, $2\theta = 90^\circ$. If the angle lies between 90 and 120° an accurate value for the N–O distance can be given; however, in a personal communication, Professor Linus Pauling has expressed the opinion that the NO₂ angle may be greater than 120° by as much as 10 or 15°.

Another point of interest is that the agreement in Table IX is sufficient to determine the *a priori* weight of the normal electronic state as 2, independently of the magnetic susceptibility results of Havens,¹ mentioned above. The electron diffraction interpretation of Maxwell, Mosley and Deming³³ is sufficiently explicit to eliminate such possibilities as $p_e = 4$ and as a matter of fact our first calculations were made in this manner to establish the value of p_e .

Since the above calculations were made, a paper by Zeise,³⁴ treating the $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$ equilibrium in a somewhat similar manner, has appeared. He finds the *a priori* weight of the normal electronic state to be $p_e = 4$. We are not able to understand this result since essentially the same data are used. The present calculations have been carefully checked and it may be stated that the *a priori* weight of the normal state is unambiguously determined as 2 rather than 4, even without considering the magnetic data.

The entropy of nitrogen dioxide

With the above data it is possible to obtain a reliable value for the entropy of nitrogen dioxide.

$$S^0 = 3/2R \ln M + 4R \ln T + R/2 \ln I_1 I_2 I_3 - R \ln \sigma + R \ln p_e + 265.349 + \sum_{\nu_1 \nu_2 \nu_3} S_{\text{vib.}} \quad (8)$$

Substituting, in Eq. (8), the various values given above, the entropy of NO₂ at 25°C is found to

TABLE XII. N–O distance in nitrogen dioxide as a function of the angle assumed $I_1 I_2 I_3 = 1.44 \times 10^{-116} \text{ g cm}^2$.

2θ	$d \times 10^8 \text{ cm}$
80	1.144 ± 0.01
90	1.120 ± 0.01
100	1.108 ± 0.01
110	1.111 ± 0.01
120	1.130 ± 0.01
130	1.165 ± 0.01
140	1.225 ± 0.01
150	1.324 ± 0.01

³³ Maxwell, Mosley and Deming, J. Chem. Phys. 2, 331 (1934).

³⁴ Zeise, Zeits. f. Elektrochemie 42, 785 (1936).

be 57.47 cal./deg. per mole. The above value, which is the one which should be used in ordinary thermodynamic calculations, does not include the nuclear spin entropy. For completeness the nuclear spin contribution, $R \ln 3 = 2.18$, is added to give the absolute entropy 59.65 cal./deg. per mole. The entropy of nitrogen dioxide at the boiling point of nitrogen tetroxide, 294.25°K is found to be 57.35 cal./deg. per mole.

The entropy of nitrogen tetroxide

Before applying Eq. (1), given above, the relative amounts of nitrogen dioxide and nitrogen tetroxide in the equilibrium mixture at the boiling point must be known.

The degree of dissociation of nitrogen tetroxide has been measured by Natanson and Natanson,³⁵ Bodenstein and Katayama,³¹ Wourtsel,³⁶ Bodenstein and Boës,³⁷ and by Verhoek and Daniels.³⁸ Wourtsel, and Bodenstein and Boës carried out experiments both below and considerably above the boiling point. Verhoek and Daniels made isothermal measurements at many different pressures, at the three temperatures 25, 35 and 45°. Wourtsel's measurements were made at pressures of between 0.1 and 0.2 atmosphere, so that very little correction for gas imperfection is necessary. Bodenstein and Boës made six series of measurements with pressures which varied from 0.29 to 0.76 atmos. In order to obtain values at the boiling point the separate series were interpolated graphically. Values of $K_{294.25^\circ}$ were then calculated for each series, using the formula $P_1V = P_0V_0(1 + \lambda P)$ to correct for gas imperfection. P was taken as the total gas pressure. For NO_2 , λ was assumed to be -0.005 . This value corresponds to the λ calculated from Berthelot's equation for carbon dioxide. For N_2O_4 , $\lambda = -0.01$. This approximate value was selected because it gave a reasonably constant series of dissociation constants from the data at various pressures, otherwise one might expect the value of λ to be somewhat larger numerically. Verhoek and Daniels corrected their data on

the assumption that the gas mixture behaved like sulfur dioxide.

A preliminary calculation of ΔS for the reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$ showed the ΔS given by Verhoek and Daniels to be too high by about 2.8 cal./deg. per mole. This is principally due to the fact that the 20 degree range covered by their measurements is not sufficient to accurately determine the temperature coefficient. Accordingly the value for $K(V. \text{ and } D.)$ was obtained by extrapolating the value given at 298.1 to 294.25°K by means of the ΔS determined by this research. In a similar manner the value of K was calculated from the K given at 298.3° by Wourtsel. The resulting values for 294.25 are $K(W.) = 0.106$, $K(V. \text{ and } D.) = 0.105$, and $K(B. \text{ and } B.) = 0.106$ atmos. The value $K_{294.25} = 0.106$ was selected. The exactness of this choice, which corresponds to a degree of dissociation, $\alpha = 0.161$, does not greatly affect the final value for the entropy of nitrogen tetroxide; however this choice was found to be identical with the best value which could be selected after the final detailed calculations on all available data.

From Eq. (1)

$$S^0_{\text{N}_2\text{O}_4} = \frac{1}{1-\alpha} S_{\text{mixture (1 atm.)}} - \frac{2\alpha S^0_{\text{NO}_2}}{1-\alpha} + R \ln \frac{1-\alpha}{1+\alpha} + \frac{2\alpha R}{1-\alpha} \ln \frac{2\alpha}{1+\alpha}. \quad (9)$$

The values of the various quantities at the boiling point, 294.25°K, as given above, are $\alpha = 0.161$, $S^0_{\text{mixture}} = 80.62$ cal./deg. per mole, as N_2O_4 , and $S^0_{\text{NO}_2} = 57.35$ cal./deg. per mole. The entropy of nitrogen tetroxide, N_2O_4 , $S^0_{294.25}$ is 72.5 cal./deg. per mole. Then $\text{N}_2\text{O}_4 = 2\text{NO}_2$, $\Delta S^0_{294.25} = 42.2$ cal./deg.

This value of ΔS permits a more reliable correlation of the data at various temperatures than has previously been possible. The data could be treated by the more conventional thermodynamic methods; however, although the spectroscopic and other molecular data of nitrogen tetroxide are by no means complete, it appears advantageous to make use of such data as exist.

Sutherland³⁹ has offered an interpretation of

³⁹ Sutherland, Proc. Roy. Soc. London **A141**, 342 (1933).

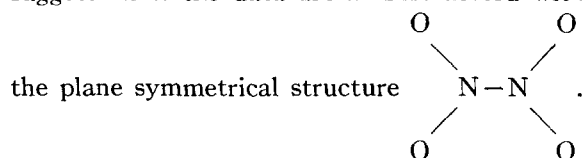
³⁵ Natanson and Natanson, Ann. d. Physik [3] **24**, 454 (1885); **27**, 606 (1886).

³⁶ Wourtsel, Comptes rendus **169**, 1397 (1919).

³⁷ Bodenstein and Boës, Zeits. f. physik. Chemie **100**, 75 (1922).

³⁸ Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

the vibrational data obtained from the infrared absorption bands and Raman spectra. Sutherland suggests that the data are in best accord with



Hendricks⁴⁰ believes that x-ray data, obtained by Vegard,⁴¹ indicate the symmetrical form given above, except that the NO₂ planes may be oriented at any angle between 0 and 25°. Pauling and Brockway⁴² have suggested an unsymmetrical form, with a nitrogen oxygen linkage between the NO₂ groups, on the basis of the adjacent charge rule. The moments of inertia of nitrogen tetroxide have not been determined but order of magnitude calculations made in connection with present work, while perhaps not decisive, indicate that the symmetrical form is probably correct. The symmetrical forms would have a considerably smaller entropy and this seems more consistent with the experimental value determined from the third law of thermodynamics and dissociation equilibrium measurements.

The possibility of any considerable error in the third law value due to false equilibrium in the solid at low temperatures seems to be precluded by the agreement with equilibrium data over the range 282 to 404°K. The present entropy value definitely excludes free rotation of the NO₂ groups. The vibrational analysis is not sufficiently definite to permit an estimate of the potential barrier hindering the relative rotation of the NO₂ groups. The calculations to be given below assume that the barrier is high enough so that this motion can be treated as a harmonic oscillation.

The vibrational data relating to the twelve vibrational degrees of freedom of nitrogen tetroxide have been summarized by Sutherland.³⁹

$\nu_1=1265$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=1749$, $\nu_6=1724$, $\nu_7(\text{torsion})=?$, $\nu_8=283$, $\nu_9=380$, $\nu_{10}=500$, $\nu_{11}=(680)$, $\nu_{12}=(1480)$ cm⁻¹.

⁴⁰ Hendricks, Zeits. f. Physik **70**, 699 (1931).

⁴¹ Vegard, Zeits. f. Physik **68**, 184 (1931).

⁴² Pauling and Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

The absorption spectrum of nitrogen tetroxide has been investigated and discussed by Harris and King,⁴³ who give the following frequency assignments: $\nu_1=1260$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=\nu_6=1744$, $\nu_7(\text{torsion})=?$, $\nu_8=283$, $\nu_9=\nu_{11}=500\sim 382$, $\nu_{10}=\nu_{12}=\sim 682$ cm⁻¹. As pointed out by Harris and King,⁴³ three of the frequencies have a double weight when the NO₂ planes are perpendicular to each other.

For the purpose of the calculations given below the symmetrical perpendicular model was assumed. The following experimental values were used for the various frequencies: $\nu_1=1265$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=\nu_6=1744$, $\nu_7(\text{torsion})=?$, $\nu_8=283$, $\nu_9=\nu_{11}=380$, $\nu_{10}=\nu_{12}=500$ cm⁻¹.

ν_7 was assumed to be low enough so that the equipartition value, R , of the heat capacity had been reached at room temperature. Except for the double frequencies no structural significance is attached to the various values and it may be shown that it is of little importance in the present calculations which two of the three values, 283, 380 and 500 cm⁻¹, are selected to have a double weight.

$$S^0_{\text{N}_2\text{O}_4} = 3/2R \ln M + 4R \ln T + R/2 \ln I_1 I_2 I_3 - R \ln \sigma + 265.349 + \sum_{\nu_1 \text{ to } \nu_{12}} S_{\text{vib.}} \quad (10)$$

From which

$$S^0_{\text{N}_2\text{O}_4} = 5R \ln T + \sum_{\nu_1-\nu_6, \nu_8-\nu_{12}} S_{\text{vib}} + k_1. \quad (11)$$

$S^0_{\text{N}_2\text{O}_4}=72.5$ at 294.25°K and the constant, k_1 , of Eq. (11) is 10.675 cal./deg. per mole.

TABLE XIII. Free energy function of nitrogen tetroxide.

$T, ^\circ\text{K}$	$-\left(\frac{F^0-H_0^0}{T}\right)_{\text{N}_2\text{O}_4}$	$-\Delta\left(\frac{F^0-H_0^0}{T}\right)_{\text{N}_2\text{O}_4=2\text{NO}_2}$
275	58.021	39.051
298.1	59.106	39.298
300	59.192	39.312
325	60.302	39.534
350	61.365	39.711
375	62.377	39.867
400	63.363	39.977
425	64.301	40.093

⁴³ Harris and King, J. Chem. Phys. **2**, 51 (1934).

TABLE XIV. Calculation of ΔH_0^0 for the reaction $N_2O_4 = 2NO_2$ from the data of Bodenstein and Boës.

$T, ^\circ K$	$\log_{10} K'$	α'	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0	$T, ^\circ K$	$\log_{10} K'$	α'	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
281.82	-1.449	0.1593	-1.427	+ 3	338.69	0.351	0.6390	0.363	+ 2
282.58	-1.394	0.1934	-1.380	-21	339.53	0.379	0.5811	0.396	-15
284.56	-1.372	0.1473	-1.340	+10	341.02	0.407	0.6338	0.421	+ 6
285.04	-1.316	0.1823	-1.297	-10	342.57	0.459	0.7326	0.469	- 7
285.83	-1.273	0.2179	-1.261	-20	342.82	0.445	0.7734	0.452	+30
286.07	-1.323	0.1443	-1.285	+23	343.41	0.474	0.6473	0.489	- 5
287.89	-1.193	0.2354	-1.182	-24	344.19	0.493	0.6910	0.506	0
288.42	-1.185	0.2072	-1.168	-20	351.50	0.681	0.8025	0.693	-10
288.85	-1.197	0.1591	-1.161	- 7	352.56	0.696	0.8443	0.706	+10
289.56	-1.137	0.2483	-1.126	-19	353.21	0.709	0.7412	0.725	+ 5
291.17	-1.138	0.1757	-1.107	+31	353.91	0.732	0.7714	0.747	- 3
291.82	-1.091	0.1953	-1.067	+ 9	356.03	0.784	0.7559	0.802	-12
293.05	-1.022	0.2761	-1.012	- 6	356.60	0.798	0.7333	0.818	-16
294.20	-1.007	0.1773	-0.969	-10	361.96	0.903	0.8899	0.916	+26
295.09	-0.951	0.2599	-0.937	-12	362.41	0.949	0.8708	0.964	-36
297.44	-0.881	0.2174	-0.854	-16	363.26	0.932	0.8005	0.951	+17
302.07	-0.729	0.2763	-0.711	0	364.36	0.962	0.8183	0.981	+ 9
302.64	-0.749	0.3096	-0.737	+62	366.84	1.024	0.8524	1.044	- 4
306.24	-0.589	0.2655	-0.563	-16	369.12	1.079	0.8196	1.103	-19
305.84	-0.612	0.2887	-0.596	+12	372.12	1.139	0.8780	1.160	- 5
305.97	-0.587	0.4045	-0.580	- 5	372.98	1.146	0.9293	1.165	+17
313.48	-0.351	0.4873	-0.344	- 7	373.29	1.145	0.8566	1.169	+22
313.54	-0.347	0.4392	-0.338	-13	374.62	1.214	0.9189	1.234	-43
317.00	-0.291	0.3477	-0.270	+40	374.68	1.184	0.8727	1.209	+ 2
315.95	-0.284	0.4081	-0.271	- 4	383.19	1.352	0.8992	1.382	+ 8
316.47	-0.274	0.3883	-0.258	0	384.94	1.378	0.9092	1.410	+22
320.29	-0.159	0.4192	-0.143	- 3	385.34	1.444	0.9016	1.482	-91
323.96	-0.043	0.6019	-0.036	- 4	386.96	1.425	0.9270	1.459	+ 7
324.15	-0.036	0.5519	-0.027	- 9	387.49	1.412	0.9575	1.439	+59
326.00	0.014	0.4476	0.032	-19	390.84	1.543	0.9571	1.581	-77
326.24	0.015	0.5136	0.027	- 1	394.85	1.572	0.9367	1.612	+ 5
326.76	0.024	0.4912	0.038	+ 4	395.33	1.562	0.9312	1.600	+46
334.88	0.255	0.5655	0.270	- 9	398.22	1.660	0.9536	1.684	-10
334.87	0.254	0.7105	0.261	+ 4	403.93	1.744	0.9526	1.774	+17
335.51	0.276	0.6681	0.286	- 8					

Average value of ΔH_0^0 , $12,873 \pm 16$ cal.

The expression for the free energy of nitrogen tetroxide is

$$(F^0 - H_0^0)/T = -\frac{3}{2}R \ln M - 4R \ln T \\ - R/2 \ln I_1 I_2 I_3 + R \ln \sigma + 4R \\ - 265.349 + \sum_{\nu_1 \text{ to } \nu_{12}} (F^0 - H_0^0)_{\text{vib}}/T. \quad (12)$$

From which

$$(F^0 - H_0^0)_{N_2O_4}/T = -5R \ln T \\ + \sum_{\nu_1 - \nu_6, \nu_8 - \nu_{12}} (F^0 - H_0^0)_{\text{vib}}/T + 5R - k_1. \quad (13)$$

The constants, k_1 , of Eqs. (11) and (13) are identical.

The $(F^0 - H_0^0)/T$ values for nitrogen tetroxide, as calculated from Eq. (13), are given in Table XIII. The values are given to 0.001 unit only for relative consistency.

In Table XIV the final calculations on the data of Bodenstein and Boës are given. In correcting for gas imperfection as a function of temperature the following considerations were used. As has been stated above the data over a considerable range of pressure at the boiling point, where gas imperfection is rather considerable, were found to be in agreement with the expression $P_1 V = RT(1 + \lambda P)$ where $\lambda_{N_2O_4} = -0.01$ and $\lambda_{NO_2} = -0.005$ atmos.⁻¹. It may be shown from Berthelot's equation of state that λ is approximately proportional to T^{-3} . Thus it was assumed that $\lambda_{N_2O_4} = -0.01(294/T)^3$ and $\lambda_{NO_2} = -0.005(294/T)^3$. The calculation of the equilibrium constant, K , in terms of fugacities is considerably simplified by the choice of $\lambda_{N_2O_4} = 2\lambda_{NO_2} = \beta = -0.01(294/T)^3$.

$$K = \frac{4P(\alpha' + \beta P)^2}{1 - (\alpha' + \beta P)^2}, \quad (14)$$

TABLE XV. Calculation of ΔH_0^0 for the reaction $N_2O_4 = 2NO_2$ from the data of Wourtsel.
Average value of ΔH_0^0 , 12,876 \pm 14 cal.

T, °K	log ₁₀ K'	log ₁₀ K	DEVIATION FROM AV. ΔH_0^0
273.1	-1.756	-1.752	-16
273.1	-1.758	-1.754	-19
298.3	-0.835	-0.832	-9
298.3	-0.841	-0.839	+1
298.3	-0.834	-0.832	-8
323.4	-0.068	-0.064	+11
323.4	-0.073	-0.067	+16
323.4	-0.072	-0.062	+14
359.6	0.878	0.893	-27
359.6	0.855	0.870	+11
359.6	0.847	0.862	+24

where α' has been evaluated by neglecting gas imperfection.

$$\alpha' = \frac{(PV)_{\text{obs}}}{RT} - 1, \quad K' = \frac{4P\alpha'^2}{1 - \alpha'^2}.$$

In Table XIV the second and third columns give α' and log₁₀ K', the uncorrected values of Bodenstein and Boës. In column four the corrected log₁₀ K is given. Column five gives the deviation from the average of values of ΔH_0^0 calculated from the relation

$$\Delta H_0^0/T = R \ln K + \Delta(F^0 - H_0^0)/T. \quad (15)$$

The average value, $\Delta H_0^0 = 12,873$ cal. per mole of N₂O₄, is in good agreement with the results over the entire range of temperature, 282 to 404°K. The deviations are somewhat larger at the extremes of the temperature region

TABLE XVI. Calculation of ΔH_0^0 for the reaction $N_2O_4 = 2NO_2$ from the data of Verhoek and Daniels.

P _{atmos.}	-log ₁₀ K'	log ₁₀ K	DEVIATION FROM AV. ΔH_0^0	P _{atmos.}	-log ₁₀ K'	-log ₁₀ K	DEVIATION FROM AV. ΔH_0^0
Temperature = 298.1°K				Temperature = 308.1°K			
0.1566	0.860	0.855	-18	0.2382	0.498	0.493	-38
0.2118	.848	.841	-37	.3533	.530	.522	+4
.2172	.878	.871	+4	.3649	.510	.502	-23
.5129	.859	.840	-38	.4086	.532	.523	+5
.2889	.861	.851	-24	.4287	.530	.520	0
.6543	.878	.851	-24	.4391	.530	.520	0
.5699	.867	.845	-31	.4400	.522	.512	-11
.3150	.893	.882	+19	.4871	.541	.529	+13
.3271	.833	.822	-63	.5378	.544	.530	+14
.3357	.870	.858	-14	.5659	.521	.507	-17
.3660	.880	.867	-2	.5823	.544	.529	+13
.3793	.883	.870	+2	.6623	.518	.500	-37
.3841	.880	.866	-3	.7065	.578	.559	+65
.3941	.873	.859	-12	.8902	.552	.525	+8
.3942	.873	.859	-12	.9470	.554	.525	+8
.4021	.880	.866	-3	Average value of ΔH_0^0 , 12,878 \pm 17			
.4213	.885	.870	+2	Temperature 318.1°K			
.4369	.898	.883	+21	0.2662	0.169	0.164	-57
.4588	.888	.871	+4	.4064	.188	.182	-29
.4598	.893	.876	+11	.4554	.215	.209	+11
.4743	.860	.843	-34	.4889	.214	.207	+8
.4843	.890	.872	+6	.4903	.203	.196	-8
.5107	.856	.837	+57	.5446	.206	.198	-5
.5254	.888	.868	0	.5985	.222	.213	+18
.5435	.899	.878	+13	.6295	.201	.191	-15
.5443	.895	.874	+8	.6484	.217	.207	+8
.5554	.890	.869	+1	.7349	.200	.188	-19
.5719	.889	.867	-2	.7834	.254	.240	+56
.5996	.850	.826	-56	.9814	.243	.221	+28
.6007	.896	.872	+5	1.0474	.227	.204	+4
.6214	.914	.889	+29	Average value of ΔH_0^0 , 12,862 \pm 20			
.6349	.919	.893	+34	Average of the values for 25, 35 and 45°C = 12,882 \pm 19 cal.			
.6373	.950	.924	+77				
.8081	.908	.871	+4				
.8623	.893	.853	-21				
Average value of ΔH_0^0 , 12,907 \pm 20							

Average of the values for 25, 35 and 45°C = 12,882 \pm 19 cal.

covered by the experiments since either small or large values of the degree of dissociation make it difficult to accurately evaluate $K = 4P\alpha^2/1 - \alpha^2$. The greatest accuracy should be obtained in the region near $\alpha = 0.7$.

The constancy of the ΔH_0^0 values in Table XIV shows that the value of the entropy of nitrogen tetroxide obtained from the third law of thermodynamics is correct. For example, if false equilibrium had existed in the solid at low temperatures during the heat capacity measurements, to an extent which produced an entropy error of $R \ln 2$, then the ΔH_0^0 values would have shown a trend of over 200 calories in Table XIV. Actually no significant drift is found.

The earlier data of Bodenstein and Katayama,³¹ consisting of 20 determinations over the temperature range 291–367°K, lead to a value of $\Delta H_0^0 = 12,856 \pm 125$ cal. The deviations are considerably larger than those in the later work of Bodenstein and Boës so the above value was given no weight.

The data of Wourtsel have been considered in Table XV. The nitrogen tetroxide used in these measurements was obtained by mixing nitric oxide with excess oxygen. The total pressures, due to N_2O_4 , NO_2 and O_2 , were used in making the gas imperfection corrections. The corrections were quite small in this case since all of the experiments were carried out at rather low pressures. The average value of $\Delta H_0^0 = 12,876$ cal. per mole of N_2O_4 is in almost perfect agreement with that obtained from the measurements of Bodenstein and Boës.

The results obtained from the data of Verhoek and Daniels are shown in Table XVI.

While there is a small trend with temperature in the values of ΔH_0^0 shown in Table XVI, the average result, $\Delta H_0^0 = 12,882 \pm 19$ cal. per mole of nitrogen tetroxide, is in excellent agreement with the values, $12,873 \pm 16$, and $12,876 \pm 14$, calculated from the experiments of Bodenstein and Boës, and of Wourtsel, respectively.

The final value of ΔH_0^0 was taken as 12,875 cal. for the dissociation of 1 mole of N_2O_4 . The first extensive experiments on the nitrogen tetroxide dissociation were carried out by Natanson and

TABLE XVII. Data relating to the formation of nitrogen dioxide and nitrogen tetroxide.

REACTION	ΔH_0^0 CAL.	$\Delta F_{298.1}^0$ CAL.	$\Delta H_{298.1}^0$ CAL.	$\Delta S_{298.1}^0$ CAL./DEG.
$2NO_2 = N_2O_4$	-12875	-1110	-13693	-42.21
$N_2 + 2O_2 = N_2O_4$	4333	23440	2239	-71.12
$NO + \frac{1}{2}O_2 = NO_2$	-12771	-8375	-13562	-17.40
$\frac{1}{2}N_2 + O_2 = NO_2$	8602	12275	7964	-14.46

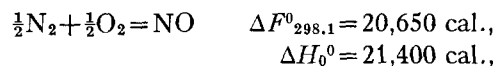
Natanson.³⁵ Their measurements were nearly all made under conditions where the degree of dissociation was near unity. These data have been calculated in detail leading to the result $\Delta H_0^0 = 13,500 \pm 600$ cal. As has been pointed out above, it is experimentally difficult to determine the dissociation constant accurately when α is near 1. Only 5 of their 49 measurements fall in the most favorable experimental region $\alpha^2 = 0.4$ to 0.6. The average, $\Delta H_0^0 = 12,901 \pm 33$ cal. for these five measurements, compares well with the more recent experiments.

The various data make it possible to evaluate some quantities of especial interest for several reactions. Using the equations

$$\Delta F^0 = T\Delta\left(\frac{F^0 - H_0^0}{T}\right) + \Delta H_0^0 \quad (16)$$

$$\text{and} \quad \Delta H^0 = \Delta F^0 + T\Delta S^0 \quad (17)$$

together with the calculations of Giauque and Clayton⁴⁴ on the reaction



the free energy and heat of reaction data tabulated in Table XVII are found. The entropies of NO ,^{28, 45} N_2 ,⁴⁴ and O_2 ⁴⁶ at 298.1°K were taken as 50.35, 45.79 and 49.03 cal./deg. per mole, respectively. The entropies of NO_2 and N_2O_4 calculated above are 57.47 and 72.73 cal./deg. per mole at 298.1°K, respectively.

⁴⁴ Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

⁴⁵ Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).

⁴⁶ Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).