The Entropies of Nitric Acid and its Mono- and Tri-hydrates. Their Heat Capacities from 15 to 300°K. The Heats of Dilution at 298.1°K. The Internal Rotation and Free Energy of Nitric Acid Gas. The Partial Pressures over its Aqueous Solutions

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The thermodynamic properties of nitric acid and its water solutions are not known nearly as accurately as will be necessary in deciding several points of importance and interest. The purpose of the experiments presented here is to increase the information relating to the free energy and other properties of this important substance.

At the start of the present investigation nothing was known about nitric acid at low temperatures except the melting point–composition diagram of its water solution which has been determined by Kuster and Kremann.[1] This shows that stable mono- and tri-hydrates exist.

A knowledge of the entropies of solutions and their constituents combined with heats of reaction enable the calculation of the free energies of dilution and formation.

When the third law of thermodynamics is used to determine directly the entropies of solutions, compositions corresponding to compounds, and also eutectic mixtures when no solid solutions are formed, lend themselves well to calorimetric technique. Other compositions could be investigated if pure phases crystallized out, although it would be somewhat inconvenient to have the fusion occurring over a long temperature range, and the changing composition of the liquid phase would at least in most cases make equilibrium difficult.

In starting this problem we were also interested in drawing any conclusions possible about zero point entropy due to hydrogen bond randomness in nitric acid or its hydrates. This is at once a difficulty and a most interesting subject for investigation. Little is known concerning the extent to which false equilibrium in systems containing hydrogen bonds leads to zero point randomness but Pauling[2] has suggested several situations where the effect is to be expected.

Giauque and Stout[3] have shown experimentally that H₂O, and Long and Kemp[4] have shown that D₂O has zero point entropy corresponding to complete hydrogen bond randomness as suggested by Pauling.

The heat capacities of nitric acid and its mono- and tri-hydrates were measured in an apparatus that has been given the laboratory designation Gold Calorimeter IV. A description of this calorimeter with references to calorimetric procedures has been given by Kemp and Giauque.[5] The only addition to the procedures previously described was that the two solutions were poured down the glass tube leading to the gold calorimeter by means of a long thin gold tube made for the purpose. The calorimeter is of the type used in this Laboratory for investigating condensed gases which can be distilled in and out without dismantling the calorimeter. The nitric acid and the trihydrate were removed by distillation. However, the monohydrate was withdrawn by introducing the long gold tube so that the same sample could be used in heat of dilution experiments.

Preparation and Purity of the Samples.—Pure nitric acid was prepared by vacuum distillation from a mixture of sodium nitrate and concentrated sulfuric acid. The sample was collected directly in the calorimeter which was kept a few degrees above the melting point of the acid. The nitric acid was frozen as soon as the calorimeter was filled. These precautions were observed because of the instability of liquid nitric acid, especially near room temperature, with respect to the reaction: $2HNO_3 = 2NO_2 + H_2O + \frac{1}{2}O_2$. From the rise in the heat capacity just below the melting point, caused by pre-melting, the impurity in the sample was calculated to be of the order of magnitude of 0.01 mole per cent. This approximate calculation assumes the absence of solid solutions and a perfect solution of the impurity in the liquid.

Nitric acid mono-hydrate was prepared by generating some pure nitric acid by the method described above, except that it was collected in a glass flask surrounded by liquid air and later diluted to the proper composition. A small amount of color was noted in this preparation which appeared to be due to heating the generating flask more than in the previous case. The material was recrystallized, broken up to the consistency of wet snow, and then filtered on a sintered glass filter. Sixty per cent. of the material was melted and discarded. The material which remained was colorless. The sample was melted and immediately poured into the calorimeter by means of the gold tube mentioned above. This procedure was carried out at a temperature near the melting point of the acid, which was frozen as soon as the sample had been placed in the calorimeter. From the premelting heat capacity effect the substance was estimated to be within 0.03 mole % of the correct composition for $HNO_3 \cdot H_2O$.

Nitric acid tri-hydrate was prepared from reagent qual-

(1) Kuster and Kremann, Z. anorg. Chem., **41**, 1 (1904).
(2) Pauling, THIS JOURNAL, **57**, 2680 (1935).
(3) Giauque and Stout, ibid., **58**, 1144 (1936).
(4) Long and Kemp, ibid., **58**, 1829 (1936).
(5) Kemp and Giauque, ibid., **59**, 79 (1937).

ity 70% nitric acid. The first step in the preparation was to bubble pure dry air through the solution for six hours to remove oxides of nitrogen and bring it to the constant boiling composition. A sample was quickly weighed and frozen to prevent decomposition, and after analysis the calculated amount of water was added. The sample was then brought to a temperature just above its melting point and poured into the assembled calorimeter, which had been precooled. Calculation of the impurity from the premelting effect indicated either lack of adjustment or impurity of 0.02 mole per cent.

After all measurements were completed on the nitric acid and the tri-hydrate, they were vacuum distilled at room temperature from the calorimeter into a glass bulb surrounded by liquid air. The sample and bulb were weighed after coming to equilibrium with the balance case. The weight of the empty bulb was determined under similar conditions. The weights were corrected to vacuum. In the case of the mono-hydrate, most of the sample was withdrawn through a tube, as mentioned above, and then weighed. The small residue was washed out and titrated.

Heat Capacity Data.—Tables I, II and III contain the observed values of the heat capacities of nitric acid, the mono-hydrate and tri-hydrate. The measurements constitute an investigation over the entire temperature range considered, as may be noted from the temperature intervals

TABLE I

HEAT CAPACITY OF NITRIC ACID

Mol. wt., 63.016; 80.571 g. = 1.2786 moles in calorimeter; 0°C. = 273.10°K.

T, °K.	ΔT	C_p Cal. deg.$^{-1}$ mole^{-1}	T, °K.	ΔT	C_p Cal. deg.$^{-1}$ mole^{-1}
13.51	1.927	0.547	137.76	6.103	11.813
16.17	3.226	.798	143.71	5.830	12.084
19.11	2.684	1.168	149.75	6.281	12.369
22.94	3.395	1.618	156.46	7.412	12.665
25.50	3.175	2.056	163.58	7.058	12.990
28.39	2.557	2.457	170.41	6.728	13.257
31.17	2.993	2.945	177.00	6.482	13.584
34.57	3.808	3.579	183.41	6.200	13.878
38.68	4.455	4.262	189.94	6.644	14.180
42.68	3.784	4.845	196.84	6.994	14.537
46.89	4.456	5.464	203.64	6.730	14.895
51.61	5.028	6.061	210.19	6.478	15.235
56.34	4.458	6.618	216.70	6.848	15.651
61.06	5.041	7.125	220.83	5.802	15.916
66.10	5.617	7.629	225.42	3.611	16.436
71.43	5.092	8.099	231.51		Melting point
76.73	5.603	8.541	238.57	5.872	26.73
82.12	5.166	8.983	244.55	5.755	26.64
87.54	5.723	9.359	250.49	5.667	26.64
93.04	5.327	9.672	256.93	6.464	26.61
98.61	5.825	9.987	263.81	6.219	26.57
104.17	5.447	10.293	270.51	6.194	26.47
109.54	5.202	10.544	277.26	6.080	26.33
114.98	5.740	10.795	283.90	5.921	26.45
120.49	5.438	11.029	290.55	5.779	26.26
126.15	5.895	11.312	302.89	4.856	26.32
131.91	5.630	11.554			

TABLE II

HEAT CAPACITY OF NITRIC ACID MONO-HYDRATE

Mol. wt., 81.032; 172.971 g. = 2.1346 moles in calorimeter; 0°C. = 273.10°K.

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
14.91	2.932	0.610	131.66	5.755	14.69
17.39	1.972	.870	137.61	6.049	15.07
19.98	3.106	1.230	143.52	5.780	15.45
23.59	3.790	1.761	144.78	6.860	15.84
27.58	4.219	2.391	156.81	7.163	16.28
31.91	4.469	3.165	163.79	6.766	16.69
36.46	4.671	4.067	169.60	7.068	17.08
41.22	4.901	4.894	177.40	6.380	17.46
46.79	6.212	5.780	184.34	7.368	17.85
52.46	5.185	6.716	191.90	7.560	18.27
57.84	5.381	7.553	199.51	7.708	18.70
63.21	5.603	8.306	207.00	7.320	19.21
68.91	5.810	9.029	214.42	7.570	19.55
68.99	2.903	9.037	221.79	7.260	19.86
72.85	4.806	9.479	227.53	5.890	21.55^a
78.21	5.907	10.16	235.48		Melting point
84.62	6.935	10.91	239.89	5.990	42.94
90.87	5.583	11.51	250.57	7.269	43.25
96.59	5.939	11.90	258.49	8.538	43.06
102.28	5.490	12.51	266.72	8.182	43.44
107.92	5.825	13.00	274.70	7.816	43.47
113.88	6.130	13.42	282.48	7.810	43.55
119.83	5.777	13.85	290.14	7.647	43.46
125.78	6.081	14.29	298.63	7.340	43.78

^{a} Premelting.

TABLE III

HEAT CAPACITY OF NITRIC ACID TRI-HYDRATE

Mol. wt., 117.065; 162.598 g. = 1.3890 moles in calorimeter; 0°C. = 273.10°K.

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
14.84	2.373	0.924	141.97	6.123	26.12
18.58	5.171	1.678	147.93	5.807	26.85
22.76	3.166	2.710	153.60	5.578	27.49
25.97	3.151	3.552	165.20	5.723	29.04
29.27	3.403	4.456	170.95	5.900	29.74
33.07	4.199	5.747	176.74	5.643	23.43
37.00	3.717	6.978	182.28	5.440	31.00
40.73	3.769	8.063	187.84	5.603	31.78
44.51	3.816	9.043	193.51	5.764	32.44
48.27	3.730	9.996	199.26	5.762	33.15
52.52	4.561	11.148	205.22	6.110	33.79
57.13	4.601	12.325	211.22	5.897	34.44
61.87	4.805	13.333	217.31	6.238	35.14
66.92	5.310	14.384	223.47	5.979	36.03
71.97	4.815	15.378	229.47	5.881	39.37
76.82	4.810	16.443	235.73	6.493	38.11
81.85	5.108	17.394	242.20	6.245	39.06
86.96	4.731	18.294	248.69	6.395	41.11
91.87	4.705	19.136	254.63		Melting point
96.68	4.922	19.842	254.85	6.376	74.43
101.59	4.863	20.611	261.06	6.182	75.15
106.94	5.824	21.397	267.12	6.022	75.86
112.61	5.342	22.22	273.05	5.892	76.11
118.28	5.859	22.96	278.81	5.740	76.84
124.26	6.064	23.71	284.50	5.648	76.88
130.17	5.738	24.56	290.10	5.532	77.21
135.98	5.924	25.34	295.58	5.401	77.71
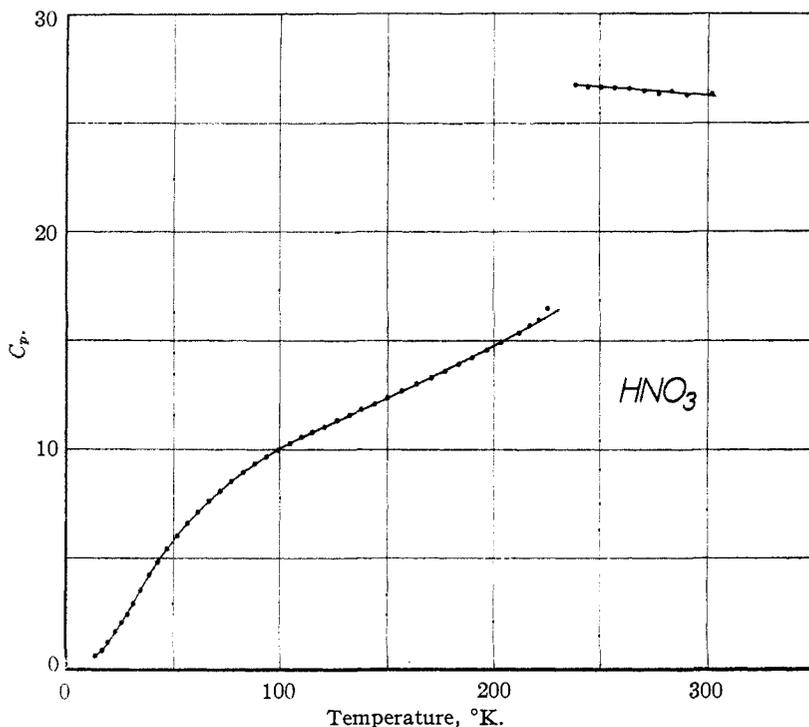
Fig. 1.—Heat capacity in calories per degree per mole of nitric acid.

which are also given. In calculating energy, 4.1833 international joules was taken as one calorie. A small amount of helium was added to the calorimeter to facilitate heat conduction. The heat capacities of liquid nitric acid were corrected for the small amount vaporized into the few cubic centimeters of gas space above the liquid in the calorimeter. This correction is completely negligible in all other measurements.

Table IV contains values of the heat capacities taken from smooth curves through the data. The curves are believed to represent the data to about 0.1% above 35°K. Below this temperature, the results become less accurate due to decreasing sensitivity of the resistance thermometer and the small values of the heat capacity. At 20°K. the results may be in error by 1%, and at 15°K. by as much as 3%.

Kuster and Kremann[1] give the eutectic temperature for the phases $HNO_3\cdot3H_2O-H_2O$ as 230°K., and that for the phases $HNO_3\cdot3H_2O-HNO_3\cdot H_2O$ as 231°K. The heat capacity curve of the trihydrate goes over a small peak as shown in Fig. 3 with a maxi-

mum at 230.2°K. This is in agreement with either of the eutectic temperatures given above, within the limit of accuracy. In either case the explanation of the small heat absorption near 230°K. is to be found in the very small deviation from perfect adjustment to the exact composition corresponding to $HNO_3\cdot3H_2O$.

The size and shape of the peak were investigated under various conditions by several series of heat capacity measurements using very short temperature intervals. It was found that the area on a graph between the peak and a smooth curve through the normal points depended on the history of the sample. For example, after the sample had been cooled to liquid hydrogen temperatures the area under the peak corresponded to 15 cal. mole^{-1}. After the sample had been cooled
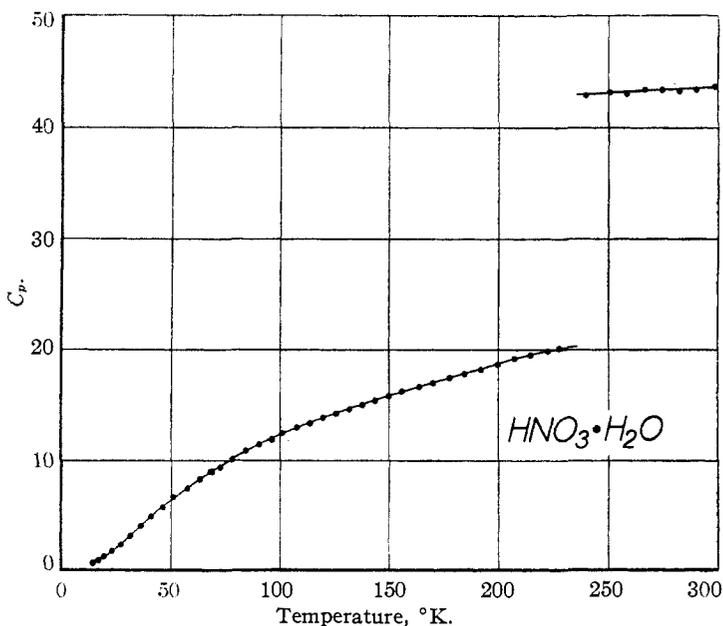
Fig. 2.—Heat capacity in calories per degree per mole of nitric acid mono-hydrate.

to and held at 150°K. for six days the area corresponded to 12 cal. mole^{-1}. When measurements were made immediately after cooling the sample

TABLE IV

HEAT CAPACITY OF NITRIC ACID, THE MONO-HYDRATE AND TRI-HYDRATE

Mol. wts.: HNO_3, 63.016; $HNO_3 \cdot H_2O$, 81.032; $HNO_3 \cdot 3H_2O$, 117.065; 0°C. = 273.10°K.; C_p in cal. deg.$^{-1}$ mole^{-1}.

T, °K.	C_p, HNO_3	C_p, $HNO_3 \cdot H_2O$	C_p, $HNO_3 \cdot 3H_2O$
15	0.677	0.615	0.965
20	1.238	1.228	2.009
25	1.934	1.977	3.283
30	2.740	2.820	4.708
35	3.609	3.772	6.321
40	4.468	4.708	7.826
45	5.193	5.539	9.190
50	5.855	6.348	10.49
55	6.463	7.134	11.76
60	7.012	7.862	12.95
65	7.522	8.540	14.00
70	7.988	9.164	15.04
75	8.419	9.784	16.07
80	8.825	10.37	17.06
85	9.187	10.91	17.96
90	9.510	11.42	18.82
95	9.794	11.90	19.60
100	10.06	12.35	20.37
110	10.56	13.15	21.85
120	11.09	13.88	23.23
130	11.47	14.57	24.55
140	11.92	15.22	25.85
150	12.37	15.87	27.12
160	12.81	16.46	28.38
170	13.27	17.05	29.62
180	13.72	17.61	30.83
190	14.20	18.18	32.04
200	14.70	18.77	33.22
210	15.25	19.35	34.29
220	15.82	19.81	35.51
230	16.46	20.16	37.01
240	26.70	43.02	38.67
250	26.65	43.19	40.61
260	26.59	43.32	74.99
270	26.51	43.41	75.94
280	26.42	43.48	76.72
290	26.33	43.54	77.31
300	26.24	43.62	77.80

just below the temperature region of the peak the area was equivalent to only 3 cal. mole^{-1}.

The heat absorbed near the eutectic is considerably larger than the amount which might be estimated from the premelting data. However, such estimates, based on ideal solution laws, can hardly be expected to correspond to more than the order of magnitude in the present case. The experimentally determined energy absorption at the eutectic as well as that connected with other premelting should be included in the heat of fusion. The error made by treating the heat of fusion of that fraction of the eutectic mixture which is impurity as though it were $HNO_3 \cdot 3H_2O$ is very small.

Melting Points.—The melting points of the three substances were determined as a function of the per cent. melted. The values with a small percentage melted are of course low because of the relatively high proportion of impurity in the liquid. The determinations were not carried out above 75% melted because it is difficult to get good equilibrium when a small amount of solid rests on the bottom of the calorimeter.

The nitric acid was observed for two days, the mono-hydrate for three days, and the tri-hydrate for six days. During the period of melting point observations the heavy metal block surrounding the calorimeter was never more than a few degrees away from the melting point temperature and it was adjusted to and held within a few hundredths of a degree of the melting point for at least an hour before each reading.

The observations are given in Table V.

TABLE V

MELTING POINT OF NITRIC ACID, THE MONO-HYDRATE AND TRI-HYDRATE, 0°C. = 273.10°K.

Time, hr.	% melted	T, °K., resistance thermometer	T, °K., thermocouple
	Nitric acid		
0	Supplied heat		
5.0	10	231.42	231.42
5.42	Supplied heat		
8.92	30	231.50	231.49
9.33	Supplied heat		
17.17	50	231.51	231.51
17.50	Supplied heat		
24.92	70	231.52	231.51
		Accepted value	231.51
	Nitric acid monohydrate		
0	Supplied heat		
12.50	10	235.47	235.48
13.25	Supplied heat		
15.50	30	235.47	235.48
15.75	Supplied heat		
35.50	50	235.48	235.55
37.00	Supplied heat		
49.25	70	235.48	235.47
		Accepted value	235.48
	Nitric acid trihydrate		
0	Supplied heat		
62.75	8	254.59	254.63
63.00	Supplied heat		
93.50	25	254.61	254.62
93.67	Supplied heat		
117.50	50	254.62	254.62
117.67	Supplied heat		
141.50	75	254.64	254.63
		Accepted value	254.63

Table VI contains a comparison of the melting
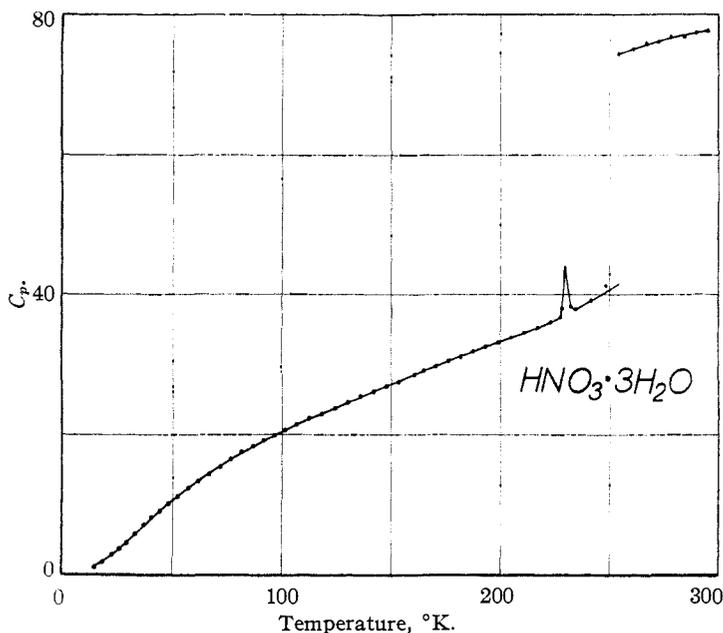
Fig. 3.—Heat capacity in calories per degree per mole of nitric acid tri-hydrate.

points obtained in this research with those obtained by other observers.

TABLE VI

MELTING POINTS OF NITRIC ACID, NITRIC ACID MONO-
HYDRATE AND NITRIC ACID TRI-HYDRATE, 0 °C. =
273.10 °K.

Substance	Melting point, °C.	Observer
HNO₃	228.1	Veley and Manley[6] (1898)
HNO₃	231.9	Kuster and Kremann[1] (1904)
HNO₃	232.0	Kuster and Munch[7] (1905)
HNO₃	232.0	Mischtschenko[8] (1929)
HNO₃	231.51	This research
HNO₃·H₂O	236.3	Pickering[9] (1893)
HNO₃·H₂O	235.1	Kuster and Kremann (1904)
HNO₃·H₂O	235.48	This research
HNO₃·3H₂O	255.1	Pickering (1893)
HNO₃·3H₂O	254.9	Veley and Manley (1898)
HNO₃·3H₂O	254.6	Kuster and Kremann (1904)
HNO₃·3H₂O	254.63	This research

Heats of Fusion.—The heats of fusion were determined by starting energy input a few degrees below the melting point and ending a few degrees above. A correction was made for the ∫ $C_p dt$ of the liquid and solid. Heat absorbed due to premelting including that absorbed in the small eutectic maximum in the case of the trihydrate was included in the heat of fusion. The details are given in Tables VII, VIII and IX.

(6) Veley and Manley, Proc. Roy. Soc. (London), 62, 233 (1898).
(7) Kuster and Munch. Z. anorg. Chem., 43, 350 (1905).
(8) Mischtschenko, Zhur. Prikladnoi Khim?, 2, 521 (1929).
(9) Pickering, J. Chem. Soc., 63, 436 (1893).

The Heat of Dilution of Nitric Acid.—The samples were dissolved in sufficient water to produce a final solution of about 0.135 *M*. The heat effect was measured in a calorimeter which has been described previously.[10] All weights were corrected to vacuum. The resistance thermometer in the calorimeter was calibrated at 25°C., by comparing it with a Bureau of Standards 24–26° mercury-in-glass thermometer, in order that the heats of dilution could be given at 25°C. exactly. The thermostat was kept at 26°C. in order to avoid the possibility of distillation heat effects. The heat equivalent of the calorimeter and its contents was determined before and after mixing the acid and water, except for the monohydrate.

The samples were prepared in the same manner as described above in connection with the heat capacities and all samples were kept at the temperature of liquid air until used. Handled in this way there was no evidence of decomposition of nitric acid over a period of a month during which the measurements were made.

TABLE VII

HEATS OF FUSION OF NITRIC ACID AND ITS HYDRATES

Melting points. °K.		Molecular weights
HNO₃	231.51	63.016
HNO₃·H₂O	235.48	81.032
HNO₃·3H₂O	254.63	117.065

Temperature interval, °K.	Total heat input	∫ $C_p dt$ premelting at start	ΔH, Cal. mole⁻¹
		HNO₃	
228.723–237.474	2808.8	304.4	2504
228.355–233.868	2680.8	177.3	2504
228.539–233.992	2676.1	175.3	2501
		Mean	2503 ± 2
		HNO₃·H₂O	
231.378–239.499	4488.0	301.7	4186
231.107–241.549	4595.7	411.8	4184
231.292–240.486	4536.2	353.2	4183
		Mean	4184 ± 1
		HNO₃·3H₂O	
251.904–258.872	7440	486	6954
251.503–259.376	7513	553	6960
251.717–259.156	7470	522	6948
		Mean	6954 ± 4

In the case of the monohydrate a portion of the

(10) Giauque and Archibald, THIS JOURNAL, 59, 561 (1937).

TABLE VIII

HEATS OF DILUTION OF NITRIC ACID AND ITS HYDRATES AT 298.1 °K.

Mol. wt., HNO₃, 63.016; HNO₃·H₂O, 81.032; HNO₃·3H₂O, 117.065.

Substance	Acid, g.	Water, g.	Final concn. moles/1000 g. H_2O	ΔH/cal.	ΔH, cal. mole⁻¹	ΔH, cal. mole⁻¹ infinite dilution
HNO_3	7.624	899	0.1346	−951..0	−7861	−7974
HNO_3	7.547	899	.1332	−941.1	−7858	−7971
HNO_3	7.630	899	.1347	−951.1	−7855	−7968
HNO_3	7.519	899	.1327	−937.7	−7856	−7969
					Mean	−7971 ± 10
$HNO_3 \cdot H_2O$	9.478	897	.1299	−540.5	−4620	−4732
$HNO_3 \cdot H_2O$	9.352	897	.1287	−533.0	−4619	−4731
					Mean	−4732 ± 8
$HNO_3 \cdot 3H_2O$	14.425	892	.1371	−247.82	−2011	−2125
$HNO_3 \cdot 3H_2O$	14.442	892	.1372	−247.93	−2010	−2124
$HNO_3 \cdot 3H_2O$	14.447	892	.1373	−247.40	−2005	−2119
					Mean	−2123 ± 5

material used in the low temperature calorimeter was withdrawn and used.

Separate analyses on the nitric acid tri-hydrate checked to 0.02% and the absolute accuracy of the analysis was within 0.1%.

Table VIII gives the results of the heats of dilution together with the calculations of the heats of dilution to infinite dilution made with the assistance of data summarized by Rossini.[11]

TABLE IX

CALCULATION OF THE ENTROPY OF NITRIC ACID

0–15°K., Debye extrapolation	0.243
15–231.51°K., graphical	19.443
Fusion, 2503.0/231.51	10.812
231.51–298.1°K., graphical	6.688
Entropy of liquid at 298.1°K., cal. deg.⁻¹ mole⁻¹	37.19

TABLE X

CALCULATION OF THE ENTROPY OF NITRIC ACID MONO-HYDRATE

0–15°K., Debye extrapolation	0.219
15–235.48°K., graphical	23.640
Fusion, 4184/235.48	17.768
235.48–298.1°K., graphical	10.211
Entropy of liquid at 298.1°K., cal. deg.⁻¹ mole⁻¹	51.84

TABLE XI

CALCULATION OF THE ENTROPY OF NITRIC ACID TRI-HYDRATE

0–15°K., Debye extrapolation	0.372
15–254.63°K., graphical	43.225
Fusion 6954/254.63	27.310
254.63–298.1°K., graphical	12.020
Entropy of liquid at 298.1°K., cal. deg.⁻¹ mole⁻¹	82.93

(11) Rossini, *Bur. Standards J. Research*, (a) **6**, 791 (1931); (b) **7**, 47 (1931).

The Entropy from Calorimetric Data.—Tables IX, X, and XI summarize the calculation of the entropies of nitric acid and its hydrates at 298.1°K.

In making third law comparisons the entropy of water will be necessary. We have used the values, $H_2O(g)$, $S_{298.1} = 45.13$ cal. deg.⁻¹ mole⁻¹ and $H_2O(l)$, $S_{298.1} = 16.73$ cal. deg.⁻¹ mole⁻¹. These values are obtained from the calculation of the entropy of the gas from spectroscopic data by Gordon[12] with the rotational stretching correction as calculated by Wilson[13] and the heat of vaporization of water, $\Delta H_{298.1} = 10,520$ cal. mole⁻¹ given by Keenan and Keyes.[14]

Comparison of the Third Law Data with the Entropy of Isothermal Hydration. The Partial Pressures over Aqueous Nitric Acid Solution.—The free energy of hydration for the reactions

$$HNO_3(l) + 3H_2O(l) = HNO_3 \cdot 3H_2O \qquad (1)$$

and

$$HNO_3(l) + H_2O(l) = HNO_3 \cdot H_2O \qquad (2)$$
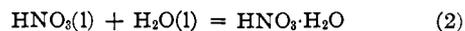
can be evaluated by means of the equations

$$\Delta F_1 = RT \ln \frac{P_{1_{HNO_3}}}{P^0_{HNO_3}} + 3RT \ln \frac{P_{1_{H_2O}}}{P^0_{H_2O}} \qquad (3)$$

and

$$\Delta F_2 = RT \ln \frac{P_{2_{HNO_3}}}{P^0_{HNO_3}} + RT \ln \frac{P_{2_{H_2O}}}{P^0_{H_2O}} \qquad (4)$$

where $P^0_{HNO_3}$ and $P^0_{H_2O}$ refer to the vapor pressures of the pure liquid nitric acid and water, respectively. The other pressure symbols refer to the partial pressures of the components over the solutions.

(12) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(13) Wilson, *ibid.*, **4**, 526 (1936).

(14) Keenan and Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, New York, N. Y., 1936.

From the heat of solution measurements given in Table VIII, the heats of reaction corresponding to Eqs. 1 and 2 can be calculated. These are found to be

$$\Delta H_1 = -5848 \text{ cal. at } 25°C.$$
$$\Delta H_2 = -3239 \text{ cal. at } 25°C.$$
$$\Delta S_1 = \frac{\Delta H_1}{T} - \frac{\Delta F_1}{T} \text{ and } \Delta S_2 = \frac{\Delta H_2}{T} - \frac{\Delta F_2}{T}.$$

These ΔS values may be compared with values obtained from the third law of thermodynamics

$$\Delta S_1 = S_{HNO_3 \cdot 3H_2O} - 3S_{H_2O(l)} - S_{HNO_3(l)}$$
$$\Delta S_2 = S_{HNO_3 \cdot H_2O} - S_{H_2O(l)} - S_{HNO_3(l)}$$

The partial pressures of water and nitric acid over their solutions have been investigated by numerous experimenters and we had believed that the partial pressures were fairly well known. However, in investigating the available work we have found that much of it contains larger errors than were previously suspected.

Most of the work has been summarized by Taylor[15] for the "International Critical Tables." More recently papers have appeared by Klemenc and Nagel[16] and Wilson and Miles.[17] Nearly all of the experimenters have employed the method of passing a known volume of gas through nitric acid solution and analyzing the absorbed material for nitric acid and water. Various analytical and other precautions have been taken in an attempt to eliminate errors due to possible decomposition products of nitric acid. Except for the case of the pure acid all of the methods have involved the assumption that the vapor in equilibrium with nitric acid solutions involves no association in the gas state. We may state at once that we have been able to prove the correctness of this assumption.

Although practically all observers have recorded both the partial pressures of water and of nitric acid, we have found no indication that anyone has applied the well-known Duhem equation to calculate the variation of the nitric acid pressures from those of the water or *vice versa*. When we tested some of the data by means of the Duhem equation

$$d \log P_{HNO_3} = -\frac{N_{H_2O}}{N_{HNO_3}} d \log P_{H_2O} \quad (5)$$

it was immediately apparent that either the nitric acid or water vapor pressures or both were in error by factors ranging to 2 or 3. Errors of this

magnitude could lead to entropy errors of several cal. deg.$^{-1}$ mole^{-1} in the present calculations and make it impossible to compare the entropies obtained from the third law.

In this situation we decided to test several of the more promising experiments in the desired concentration ranges in the hope of finding some portions of the various researches that would stand the test of the Duhem equation. The first suitable data were found in the work of Burdick and Freed[18] at 50°C. The agreement of the data with the Duhem equation is shown in Table XII.

TABLE XII

PARTIAL PRESSURES OVER AQUEOUS NITRIC ACID SOLUTION COMPARED BY MEANS OF THE DUHEM EQUATION

Data of Burdick and Freed, 50°C.; P in mm. Hg.

%HNO$_3$	P_{H_2O} Obsd.	P_{HNO_3} Obsd.	P_{HNO_3} Calcd.
24.1	78.0	0.103	0.056
33.8	63.6	.330	.33
40.2	55.4	.752	.75
45.1	50.0	1.17	1.22
49.4	44.2	1.97	(1.97)
69.9	17.7	16.6	(16.6)

For $HNO_3 \cdot 3H_2O = 53.83\%$; $P_{H_2O} = 38.2$ mm.; $P_{HNO_3} = 3.19$ mm.

The values at 49.4 and 69.9% HNO$_3$ have each been indicated as reference values because the concentrations are too far apart for unambiguous application of the Duhem equation. The other values show excellent agreement except in the most dilute solution where the experiment was most difficult. The agreement of Burdick and Freed's observed values at 50°C. also shows that the assumption of non-association in the gas is substantially correct. Burdick and Freed also investigated solutions at 25 and 75°C. but the data can be shown to be more inaccurate at these temperatures.

TABLE XIII

PARTIAL PRESSURES OVER AQUEOUS NITRIC ACID SOLUTIONS COMPARED BY MEANS OF THE DUHEM EQUATION

Data of Taylor and Sproesser, 70°C. P in mm. Hg.

%HNO$_3$	P_{H_2O} Obsd.	P_{HNO_3} Obsd.	P_{HNO_3} Calcd.
80	37	77	(77)
70	58	41.5	45.9
60	85	19.0	21.9
50	117	7.0	8.69
40	149	2.0	3.11
30	176	..	1.07
20	199	..	.29
10	219	..	.040

For $HNO_3 \cdot H_2O = 77.77\%$; $P_{H_2O} = 41$ mm.; $P_{HNO_3} = 68$ mm.

(15) *Ind. Eng. Chem.*, **17**, 633 (1925); "International Critical Tables," Vol. III, 1928, p. 305.

(16) Klemenc and Nagel, *Z. anorg. allgem. Chem.*, **155**, 257 (1926).

(17) Wilson and Miles, *Trans. Faraday Soc.*, **36**, 356 (1940).

(18) Burdick and Freed, THIS JOURNAL, **43**, 526 (1921).

TABLE XIV

COMPARISON OF THE FREE ENERGY CHANGES OBTAINED FROM THE THIRD LAW DATA WITH THOSE CALCULATED FROM VAPOR PRESSURES

$HNO_3(l) + H_2O(l) = HNO_3 \cdot H_2O$; P in mm. Hg

T	ΔS third law	ΔH calorimetric	$P^0_{HNO_3}$ pure	$P^0_{H_2O}$ pure	$P_{HNO_3}{}^a$ solution	$P_{H_2O}{}^a$ solution	ΔF third law	ΔF Equation 3 or 4
					HNO_3·H_2O			
293.1	−2.08	−3236	48.0	17.54	8.43	1.10	−2626	(−2626)
298.1	−2.09	−3239					−2616	
343.1	−2.13	−3254	460	234	68	41	−2523	−2495
			$HNO_3(l) + 3H_2O(l) = HNO_3 \cdot 3H_2O$					
					HNO_3·3H_2O			
293.1	−4.42	−5834	48.0	17.54	0.345	6.77	−4538	(−4538)
298.1	−4.46	−5848					−4518	
323.1	−4.65	−5906	215	92.5	3.19	38.2	−4404	−4406

[a] The values for P_{HNO_3} and P_{H_2O} for 293.1 °K. are obtained from the data described in Table XVII.

In the range of the monohydrate, 77.77% HNO₃, the data of Sproesser and Taylor[19] near 70°C. were found in agreement with the Duhem equation. As their experiments were not made at exact temperatures, we have used the interpolated values given by the authors for 70°C. The results of the calculation are given in Table XIII.

The agreement of the values between 80 and 60% acid is reasonably good. As the measured quantities are of the same magnitude it is difficult to decide whether the partial pressures of nitric acid or of water are the more accurate. In order to obtain values corresponding to the composition of the monohydrate, smooth curves were drawn through each series of partial pressures. The values obtained were $P_{H_2O} = 41$ mm., $P_{HNO_3} = 68$ mm. The data of Taylor and Sproesser at 30°C. were also tested and inconsistency to the extent of about a factor of 2 was found to exist over the range 60 to 80% acid.

Klemenc and Nagel[16] have made measurements on solutions with normal concentrations of 1.52, 8.02, 10.81 and 16.35 nitric acid at 12.5°C. and at concentrations of 2.06, 2.41 and 8.02 at 30°C. On the basis of these data they present rather elaborate tables of smoothed data. The smoothed values at 12.5°C. which are given to a small fraction of a per cent. were tested by means of the Duhem equation and it was found that the values over the range 1.5 to 19 normal were inconsistent by a factor of about 2.5.

We had not anticipated that it would be necessary to consider the hydration of nitric acid above ordinary temperatures so the heat capacity measurements extend only to 300°K. However, there is little error involved in making the heat capacity

(19) Sproesser and Taylor, THIS JOURNAL, **43**, 1784 (1921).

extrapolation to 323.1 and 343.1°K. Due to the fact that an error in ΔC_p affects ΔH and $-T\Delta S$ in such a way as to largely cancel in ΔF, the extrapolation leads to a negligible uncertainty. For example, if ΔC_p for the formation of monohydrate were to gradually attain an erroneous value by 1 cal. deg.⁻¹ at 70°C., it would cause an error of only about 2 or 3 cal. in ΔF at that temperature.

A summary of the data used in testing the third law values of the entropy is given in Table XIV. The values for the vapor pressure of pure nitric acid at 323.1° and 343.1°K. are taken from the summary by Taylor.[15]

The excellent agreement of the values of ΔF at 323.1 and 343.1°K. in the last two columns indicates that nitric acid and its mono- and trihydrate approach zero entropy as they approach the absolute zero of temperature. Thus we conclude that if hydrogen bonds are present in these solids, as seems probable, no random orientation exists at low temperatures.

In terms of entropy the agreement may be given as follows: for the formation of the monohydrate

$$\Delta S_{343.1} = -2.13 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ (Third Law)}$$
$$= -2.21 \qquad \text{(Isothermal)}$$

for the formation of the trihydrate

$$\Delta S_{323.1} = 4.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ (Third Law)}$$
$$= 4.64 \qquad \text{(Isothermal)}$$

The differences of the ΔS values are somewhat less than the possible inaccuracies of the absolute entropies measured, but the absolute values are all likely to be a little high or all a little low since the measurements were all made in the same calorimeter; thus cancellation of error is to be expected.

As an example of how the present data may be of assistance in determining the partial pressures over aqueous nitric acid solutions, we shall consider the recent data of Wilson and Miles.[17] These data, which cover the range from 50–100% HNO_3 at 20°C., do not agree well with the Duhem equation. There would, however, seem to be a reasonable basis for assuming that the errors arise principally in the very small partial pressures of water over the more concentrated acid and in the small partial pressure of acid over the more dilute solution, especially since Wilson and Miles measured total pressures.

By a method which required the use of successive approximations in the region between 50 and 60% acid, a curve was drawn which gave agreement with the third law values for concentrations corresponding to the mono- and trihydrates. Values of P_{HNO_3} obtained from the curve and values of P_{H_2O} evaluated by integration are, by the method of calculation, in agreement with the Duhem equation. The values obtained are given in Table XV beside the observed values of Wilson and Miles. In arriving at the value 7.9 mm. for the partial pressure of water at 49.95% acid the total pressure of 8.1 mm. was taken into consideration.

TABLE XV

EXAMINATION OF PARTIAL PRESSURE DATA FOR AQUEOUS NITRIC ACID SOLUTIONS BY MEANS OF DUHEM EQUATION

Data of Wilson and Miles at 20°C.; P in mm. Hg.

% HNO_3	P_{HNO_3} Obsd.	P_{HNO_3} from curve	P_{H_2O} Obsd.	P_{H_2O} from curve
49.94	0.355	0.183	7.75	7.9
53.83	$HNO_3 \cdot 3H_2O$	(.345)	..	(6.77)
60.12	0.95	.93	4.85	4.80
69.62	2.90	2.86	2.90	2.65
69.70	2.88	2.90	2.92	2.62
76.5	6.87	6.89	1.95	1.33
77.77	$HNO_3 \cdot H_2O$	(8.43)	..	(1.10)
78.65	9.58	9.49	1.92	0.97
79.5	9.79[a]	10.32	1.02[a]	.89
81.6	12.49	11.90	1.11	.75
81.92	13.13[a]	12.73	0.77[a]	.66
86.0	18.34	18.95	.71	.385
89.72	25.70	25.84	.50	.201
91.2	29.11	29.07	.35	.146
91.45	29.94	29.17	.37	.144
94.3	36.08	35.97	.24	.065
96.48	41.59	41.59	.11	.028

[a] Wilson and Miles consider these observations to be somewhat doubtful.

It should be realized that the third law data do not give either P_{HNO_3} or P_{H_2O} but their product,

so the values given in Table XV are all dependent on those results of Wilson and Miles which have been accepted as the more reliable. For this reason we shall apply a rather sensitive test of the accuracy of the partial pressure of water over the solution with the composition $HNO_3 \cdot 3H_2O$. The data in this region were most difficult to treat in obtaining the values given in Table XV.

From Eq. 19 to be given later we have

$$3NO_2 + H_2O(g) = NO + 2HNO_3(g) \qquad (19)$$
$$\Delta H_{298.1} = 9184 \text{ cal.;} \quad \Delta S_{298.1} = -39.77 \text{ cal. deg.}^{-1}$$
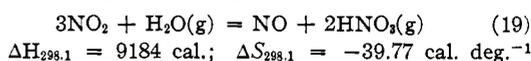
and from Eq. 1 and Eqs. 15 and 16 given later

$$2HNO_3(g) + 6H_2O(g) = 2HNO_3 \cdot 3H_2O(l) \qquad (6)$$
$$\Delta H_{298.1} = -93,526 \text{ cal.} \quad \Delta S_{298.1} = 232.18 \text{ cal. deg.}^{-1}$$
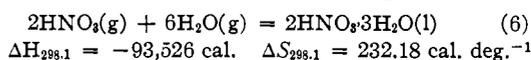
Adding Eqs. 19 and 6 we obtain

$$3NO_2 + 7H_2O(g) = NO + 2HNO_3 \cdot 3H_2O \qquad (7)$$
$$\Delta H_{298.1} = -102,710 \text{ cal.;} \quad \Delta S_{298.1} = 271.95 \text{ cal. deg.}^{-1}$$
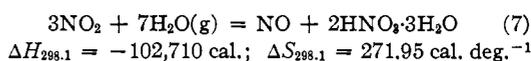
From the known heat capacities of reactants and products of Eq. 7

$$\Delta H_{298.1} = -102,684 \text{ cal.;} \quad \Delta S_{298.1} = 271.91 \text{ cal. deg.}^{-1}$$
$$\frac{\Delta F_{298.1}}{T} = \frac{-102,684}{293.1} + 271.91 = -78.43 \text{ cal. deg.}^{-1} =$$
$$-4.5750 \log K$$

$$K = \frac{P_{NO}}{P_{NO_2}^3 \, P_{H_2O}^7} = 1.39 \times 10^{17} \text{ atm.}^{-9}$$

From the data of Chambers and Sherwood[20] to be discussed later

$$\log \frac{P_{NO}}{P_{NO_2}^3} = 2.75 \qquad \frac{P_{NO}}{P_{NO_2}^3} = 5.62 \times 10^2 \text{ atm.}^{-2}$$

from which

$$P_{H_2O} = \sqrt[7]{\frac{5.62 \times 10^2}{1.39 \times 10^{17}}} = 8.79 \times 10^{-3} \text{ atm.} = 6.68 \text{ mm.}$$

which is in good agreement with the value 6.77 mm. in Table XV. Due to the fact that the partial pressure of water occurs to the seventh power in Eq. 7, an error of about 600 cal. in ΔH or an error of about a factor of 3 in $P_{NO}/P_{NO_2}^3$ would be required to cause an error of 1 mm. in P_{H_2O}. The large numerical values for ΔH and ΔS of Eq. 7 may at first sight cause some doubt as to their absolute accuracies but a large portion of these quantities consists of seven times the heat or entropy of vaporization of water. Since the standard entropy of vaporization depends primarily on the heat of vaporization, errors in this quantity will practically all cancel.

It is beyond the scope of the present paper to consider all of the vapor pressure data of nitric acid solutions with the idea of eliminating the observations which may be shown to be the more in-

(20) Chambers and Sherwood, This Journal, 59, 316 (1937).

accurate. However, our investigations have proceeded far enough to indicate that the whole problem of the partial pressures over nitric acid solutions is badly in need of new experimental work. It is to be hoped that when such work is undertaken the experimenters will make use of the Duhem equation to assist in the detection of the sources of error which seem to make accurate measurements difficult. The fact that the more reliable data were found at the higher concentrations and at the higher temperatures is certainly not what one would have expected from the comments of the several experimenters. The explanation is probably that the measured quantities are larger and perhaps also that although decomposition is greater the products of decomposition of the acid are more readily swept out at the higher temperatures. Support for the latter suggestion may be found in the careful experiment of Klemenc and Nagel,[16] who found an apparent ten-fold decrease in P_{HNO_3} over 2.06 N_{HNO_3} at 30°C., when nitrogen was passed through the solution for eight days.

The Entropy of Nitric Acid Gas.—The heat of vaporization of nitric acid has been determined calorimetrically by Wilson and Miles.[17] They give experimental values of 9415 and 9436 (average 9426) cal. mole^{-1} at 20°C. They also give a value of 9450 cal. mole^{-1}, calculated from their two vapor pressure points at 0 and 25°C., by means of the equation

$$\ln P = -\Delta H/RT + C \qquad (8)$$

These investigations give no details of their calorimetric determinations. However, the large temperature coefficient of the heat of vaporization, to be mentioned later, would require a correction of about −100 cal. mole^{-1} to the value obtained from Eq. 8, leading to a corrected vapor pressure value of 9350 cal. mole^{-1} at 20°C. We are not inclined to take the value from vapor pressures very seriously and the agreement is quite good considering the method.

By combining the entropy of liquid nitric acid with the calorimetric value of the entropy of vaporization the entropy of nitric acid gas is obtained.

From spectroscopic data to be mentioned later the heat capacity of the gas between 20 and 25°C. is estimated at about 12.1 cal. deg.$^{-1}$ mole^{-1} which with the heat capacity of the liquid leads to a value of 9355 cal. mole^{-1} for the heat of vaporization at 298.1°K.

From the vapor pressure and calorimetric data of Wilson and Miles the vapor pressure of nitric acid at 25°C. may be calculated to be 62.9 mm. Hg. For the reaction HNO$_3$(l) = HNO$_3$ (gas at 62.9) at 25°C., ΔS = 9355/298.1 = 31.38 cal. deg.$^{-1}$ mole^{-1}. The change in entropy in compressing the gas from 62.9 mm. to 1 atm. is R ln (62.9/760) = −4.95 cal. deg.$^{-1}$ mole^{-1}. These values combined with the entropy of the liquid given in Table IX give the result HNO$_3$ (gas, 1 atm.) $S_{298.1}$ = 63.62 cal. deg.$^{-1}$ mole^{-1}.

Badger and Bauer[21] have compared the spectrum of nitric acid gas with that of nitrate ion in solution and have assigned values to six of the nine characteristic frequencies. These are 607, 667, 916, 1292, 1665 and 1687 cm.$^{-1}$. Since the frequencies given are all identified with similar ones connected with motions of oxygen and nitrogen in the nitrate ion, unknown frequencies are evidently associated primarily with motions of the hydrogen atom. The only low frequency which would be expected is connected with the restricted rotation of the hydrogen atom about the (OH)–N axis of the nitric acid molecule.

Maxwell and Mosley[22] have shown that their electron diffraction measurements on nitric acid are in good agreement with a planar model. This was not unexpected since Elliott[23] has shown that nitrate ion is planar in a crystal lattice.

In calculating moments of inertia we have taken the O–N–O angles and distances given by Maxwell and Mosley. These are given in Fig. 4. The O–H distance has been assumed to be 0.96 Å., the value in the gaseous water molecule. The H–O–N angle was taken as 90° although one would expect it to be less than this due to hydrogen bonding as we have indicated in Fig. 4. The hydrogen would be 1.92 Å. from the loosely bonded oxygen if the H–O–N angle is taken as 90°. In ice, for example, the distance between a hydrogen and its loosely bonded oxygen is 1.80 Å. and the distance may be even less in the present case. Moreover, the (OH)–N bond direction would not be expected to bisect the O–N–O angle exactly. Fortunately, an exact knowledge of the H–O–N angle is a matter of little importance in the present calculations. The product of the principal moments of inertia was found to be 5.93 × 10^{-115} g.^{3}

(21) Badger and Bauer, *J. Chem. Phys.*, **4**, 711 (1936).

(22) Maxwell and Mosley, *ibid.*, **8**, 738 (1940).

(23) (a) Elliott, THIS JOURNAL, **59**, 1380 (1937); (b) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 194.
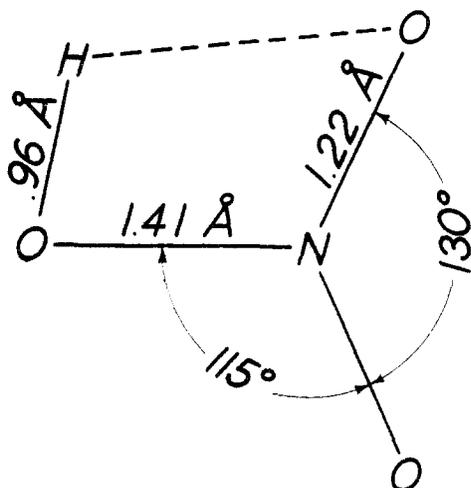
Fig. 4.—Nitric acid molecule.

cm.[6]. The reduced moment of inertia for the internal rotation was calculated to be 1.48×10^{-40} g. cm.[2].

The translational and rotational contributions to the entropy were calculated from the equations

$$S_{\text{Trans.}} = \frac{R}{2} \ln (M^3 T^5 / P) - 2.300$$

$$S_{\text{Rot.}} = \frac{R}{2} \ln I_1 I_2 I_3 T^3 + 267.650$$

The small amount of vibrational entropy was calculated by means of the Einstein function. The entropy due to restricted rotation of the hydrogen was obtained by difference and the potential barrier and other related data were obtained from the tables of Pitzer.[24] A summary of the entropy calculation is given in Table XVI.

TABLE XVI

Itemized Contributions to the Entropy of Nitric Acid Gas at 298.1°K.

Translation	38.35
Molecular rotation	23.34
Vibration; $\nu = 607$ cm.[-1]	0.44
Einstein $\nu = 667$	.35
Function $\nu = 916$	.13
$\nu = 1292$	.03
$\nu = 1665$	.00
$\nu = 1687$	.00
Entropy less internal rotation contribution	62.64
From third law of thermodynamics	63.62
Entropy due to restricted rotation, by difference, cal. deg.[-1] mole[-1]	0.98

There are two potential maxima for the restricted rotation of the hydrogen and it is found that an entropy of 0.98 cal. deg.[-1] mole[-1] corre-

(24) Pitzer, J. Chem. Phys., 5, 469 (1937).

sponds to a barrier of 7000 cal. mole[-1]. With this value and the other data given above the thermodynamic properties for nitric acid gas have been calculated. The natural constants used are those given in the "I. C. T."

Although the assumed simple form of the potential curve so far used in calculations of restricted rotation is open to question, the potential barrier is so high in the present case that it could have been treated as a case of simple harmonic oscillation. Thus the results would not be appreciably altered even if the form of the potential barrier were considerably different from the one assumed.

The potential barrier of 7000 cal. mole[-1] corresponds to a value of about 430 cm.[-1] for the energy of the first vibration of the restricted rotator. It should be pointed out that the potential barrier is rather sensitive to differences in entropy, and since all error in the entropy determination is included in the 0.98 cal. deg.[-1] mole[-1], obtained by difference and used to calculate the barrier, the value obtained may be in error by about a thousand calories. This estimate is based on the assumption that Wilson and Miles'[17] heat of vaporization is accurate to within 0.2% and that the entropy of the gas is known to 0.1 cal. deg.[-1] mole[-1]. Such an error in the potential barrier would make little difference in the thermodynamic properties considered in this paper, which are substantially fixed by the experimental entropy values.

The thermodynamic properties for nitric acid gas are given in Table XVII.

TABLE XVII

Thermodynamic Properties of HNO₃ Gas

T	S	$(H^0 - H_0^0)/T$	$(F - H_0^0)/T$
275	63.24	9.16	54.08
298.1	63.62	9.37	54.25
300	63.70	9.39	54.31
325	64.67	9.62	55.05
350	65.62	9.84	55.78
375	66.52	10.07	56.45
400	67.44	10.31	57.13
425	68.29	10.54	57.75
450	69.14	10.79	58.35
475	70.00	11.02	58.98
500	70.78	11.25	59.53

Although we have not made the calculation, perhaps it should be pointed out that the $(F^0 - H_0^0)/T$ values in Table XVII, combined with the calorimetric data on liquid nitric acid, would permit the calculation of its fugacity as a function of temperature.

The Reaction of $2HNO_3 + NO = H_2O + 3NO_2$.—We are now in a position to consider several important reactions. The reaction

$$2HNO_3(g) + NO = H_2O(g) + 3NO_2 \qquad (9)$$

has been investigated by Burdick and Freed,[18] Abel, Schmid and Stein[25] and Chambers and Sherwood.[20] All of these investigators measured partial pressures over aqueous nitric acid solutions but unfortunately only Burdick and Freed measured the partial pressures of nitric acid and water. The later workers have assumed that these quantities were known although, as we have mentioned above, the data at 25°C. are not in satisfactory agreement with the Duhem equation.

Abel, Schmid and Stein, and Chambers and Sherwood agree fairly well on the ratios of $P_{NO}/P_{NO_2}^3$ although their values are considerably different from those of Burdick and Freed.

Since the thermodynamic properties of all the gases taking part in the reaction indicated in Eq. 9 are well known we can determine the constants of this reaction as a function of temperature. In order to obtain the heat of reaction we shall consider the following reactions

$$2NO + O_2 = N_2O_4(g) \qquad (10)$$
$$\Delta H_{298.1} = -40,817 \text{ cal.}[26]$$
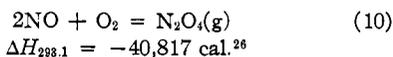
Making a small correction for temperature change $\Delta H_{291.1} = -40,782$ cal.

$$N_2O_4(g) + aq. = N_2O_4(aq) \qquad (11)$$
$$\Delta H_{291.1} = -14,140 \text{ cal.}$$

$$N_2O_4(aq) + \tfrac{1}{2}O_2 + H_2O(l) = 2HNO_3\text{``(aq)''} \qquad (12)$$
$$\Delta H_{291.1} = -18,309 \text{ cal.}$$
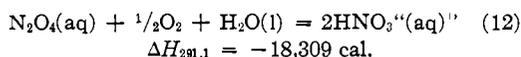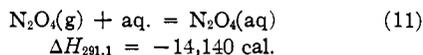
The ΔH values for Eqs. 11 and 12 were obtained from the work of Thomsen.[27] The values for the ΔH's of Eqs. 11 and 12 are perhaps the most uncertain portions of the heat of reaction data but the accuracy gains some support from the fact that the result given in the case of Eq. 12 is an average of values obtained for two different methods which agree fairly well. Thomsen obtained $-18,264$ cal. when he used chlorine as an oxidizing agent and $-18,354$ cal. when potassium permanganate was used. His values have all been corrected to the 15° calorie by the relation 1 cal. $(18 - 20°) = 0.9993$ cal. $(15°)$.

From the several references to nitric acid solutions in Thomsen's work we arrived at the conclusion that $HNO_3\text{``(aq)''}$ means $HNO_3 + 300 H_2O$.

(25) Abel, Schmid and Stein, Z. Elektrochem., **36**, 692 (1930).
(26) Giauque and Kemp, J. Chem. Phys., **6**, 40 (1938).
(27) Thomsen, "Thermochemistry," translated by K. A. Burke, Longmans, Green and Co., London, 1908.

From the summary of dilution data by Rossini[11] one finds

$$HNO_3 + 300H_2O = HNO_3(aq) \qquad (13)$$
$$\Delta H_{291.1} = -88.5 \text{ cal.}$$
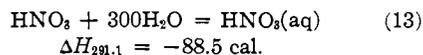
Combining Eqs. 10, 11, 12 and 13 we obtain

$$2NO + \tfrac{3}{2}O_2 + H_2O(l) = 2HNO_3(aq) \qquad (14)$$
$$\Delta H_{291.1} = -73,408 \text{ cal.}$$
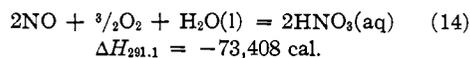
From the well-known heat capacity data for gaseous nitric oxide, oxygen and water, and the partial molal heat capacity of nitric acid in aqueous solution from the summary by Rossini,[11b] we estimate $\Delta C_p = -91.5$ cal. deg.$^{-1}$ for Eq. 14. With this the value for Eq. 14 becomes

$$\Delta H_{298.1} = -74,048 \text{ cal.}$$

From the discussion given previously in this paper we obtain Eqs. 15, 16 and 17.

$$H_2O(g) = H_2O(l) \qquad (15)$$
$$\Delta H_{298.1} = -10,520 \text{ cal.}$$

$$2HNO_3(aq) = 2HNO_3(l) \qquad (16)$$
$$\Delta H_{298.1} = 15,988 \text{ cal.}$$

$$2HNO_3(l) = 2HNO_3(g) \qquad (17)$$
$$\Delta H_{298.1} = 18,710 \text{ cal.}$$

From the calculations of Giauque and Kemp[26]

$$3NO_2 = 3NO + \tfrac{3}{2}O_2 \qquad (18)$$
$$\Delta H_{298.1} = 40,686 \text{ cal.}$$
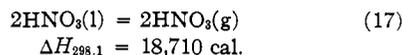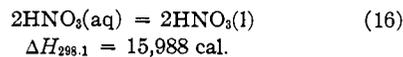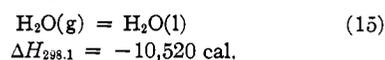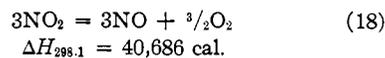
Adding Eqs. 14, 15, 16, 17 and 18 one obtains

$$3NO_2(g) + H_2O(g) = NO(g) + 2HNO_3(g) \qquad (19)$$
$$\Delta H_{298.1} = -9184 \text{ cal.}$$
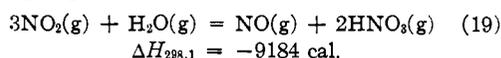
From the entropy values for the four gases

$$NO_2,^{26} \; S_{298.1} = 57.47 \text{ cal. deg.}^{-1}$$
$$H_2O,^{12,13} \; S_{298.1} = 45.13 \text{ cal. deg.}^{-1}$$
$$NO,^{28} \; S_{298.1} = 50.53 \text{ cal. deg.}^{-1}$$
$$HNO_3, \; S_{298.1} = 63.62 \text{ cal. deg.}^{-1}$$

For Eq. 19

$$\Delta S_{298.1} = -39.77 \text{ cal. deg.}^{-1}$$
$$\Delta F_{298.1} = 2671 \text{ cal.}$$

From the $(F^0 - H_0^0)/T$ values in Table XVII combined with $(F - H_0^0)/T$ values for the several gases from the same sources as those quoted for the entropy values immediately above we obtain the values given in Table XVIII.

The value of ΔH_0^0 was obtained from the relation

$$\frac{\Delta F^0}{T} = \frac{(\Delta F^0 - H_0^0)}{T} + \frac{\Delta H^0}{T} \qquad (20)$$

which was used at 298.1°K. ΔH_0^0 was found to be -7259 cal.

ΔH_0^0 may be evaluated in another way. By interpolating the equilibrium data of Chambers and Sherwood[20] we find $\log P_{NO}/P_{NO_2}^3 = 2.75$ at

(28) Johnston and Chapman, This Journal, **55**, 153 (1933).

293.1°K. and for 53.83% nitric acid corresponding to $HNO_3 \cdot 3H_2O$. From Table XV we find

$$\frac{P^2_{HNO_3}}{P_{H_2O}} = 2.31 \times 10^{-5} \text{ atm.}$$

$$\log \frac{P^2_{HNO_3}}{P_{H_2O}}, \frac{P_{NO}}{P^3_{NO_2}} = -1.886$$

$$\Delta F_{293.1} = -RT \ln K = 4.575 \times 293.1 \times 1.886 = 2529 \text{ cal.}$$

Again making use of Eq. 20 and Table XVIII we find

$$\Delta H_0^0 = -7199 \text{ cal.}$$

compared to the value −7259 cal. given above. These values agree within the limit of error and we can do no better than select an average $\Delta H_0^0 = -7230$ cal. This value has been used to obtain the values of the equilibrium constant given in Table XVIII.

TABLE XVIII

THE FREE ENERGY CHANGE IN THE REACTION $3NO_2 + H_2O(g) = NO + 2HNO_3(g)$
$\Delta H_0^0 = -7230$ cal.

T, °K.	$\dfrac{\Delta F^0 - H_0^0}{T}$	$\dfrac{\Delta F^0}{T}$	ΔF^0	K atm.
275	32.80	6.51	1790	3.78×10^{-2}
293.1	33.19	8.52	2497	1.37×10^{-2}
298.1	33.31	9.06	2701	1.05×10^{-2}
300	33.35	9.25	2775	9.51×10^{-3}
325	33.87	11.62	3777	2.83×10^{-3}
350	34.36	13.70	4795	1.01×10^{-3}
375	34.77	15.49	5809	4.11×10^{-4}
400	35.14	17.06	6824	1.87×10^{-4}
425	35.48	18.47	7850	9.18×10^{-5}
450	35.80	19.73	8879	4.86×10^{-5}
475	36.07	20.85	9904	2.77×10^{-5}
500	36.34	21.88	10940	1.65×10^{-5}

Making use of the results of Giauque and Kemp[26] on the free energy of formation of nitric oxide from nitrous oxide and oxygen we have tabulated two more reactions of interest in Tables XIX and XX.

TABLE XIX

THE FREE ENERGY CHANGE IN THE REACTION $H_2O(g) + 2NO_2 + \frac{1}{2}O_2 = 2HNO_3(g)$. $\Delta H_0^0 = -20,025$ CAL.

T, °K.	$\Delta(F^0 - H_0^0)/T$	$\Delta F^0/T$	ΔF^0	K atm.$^{-3/2}$
275	47.42	−25.40	−6985	3.56×10^5
298.1	48.14	−19.04	−5676	1.45×10^4
300	48.20	−18.55	−5565	1.13×10^4
325	48.90	−12.72	−4134	6.03×10^2
350	49.58	− 7.63	−2671	4.65×10
375	50.15	− 3.25	−1219	5.13
400	51.68	+ 1.62	+ 648	4.43×10^{-1}
425	51.15	4.03	1713	1.32×10^{-1}
450	51.60	7.10	3195	2.81×10^{-2}
475	51.96	9.80	4655	7.21×10^{-3}
500	52.34	12.29	6145	2.06×10^{-3}

TABLE XX

THE FREE ENERGY CHANGE IN THE REACTION $H_2O(g) + \frac{3}{2}O_2 + 2NO = 2HNO_3(g)$. $\Delta H_0^0 = -45,543$ CAL.

T, °K.	$\Delta(F^0 - H_0^0)/T$	$-\Delta F^0/T$	$-\Delta F^0$	K atm.$^{-5/2}$
275	76.75	89.12	24508	3.02×10^{19}
298.1	77.79	75.23	22426	2.78×10^{16}
300	77.90	74.15	22245	1.61×10^{16}
325	78.95	61.40	19955	2.64×10^{13}
350	80.03	50.30	17605	9.87×10^{10}
375	80.91	40.73	15274	7.99×10^8
400	81.75	32.29	12916	1.14×10^7
425	82.48	24.85	10561	2.70×10^5
450	83.20	18.17	8177	9.37×10^3
475	83.80	12.23	5809	4.71×10^2
500	84.33	6.90	3450	3.22×10

Becker and Roth[29] have measured the heat of formation of nitric acid from its elements by an indirect method. They give

$$Aq + \frac{1}{2}N_2 + \frac{5}{4}O_2 + \frac{1}{2}H_2O(1) = HNO_3(0.05 \ M) \quad (21)$$
$$\Delta H_{298.1} = -14,855 \text{ cal.}$$
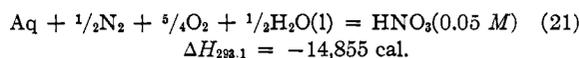
From ΔC_p we find

$$\Delta H_{298.1} = -15,075 \text{ cal.}$$

From the summary by Rossini[11a,b]

$$HNO_3(0.05 \ M) + aq = HNO_3(aq) \quad (22)$$
$$\Delta H_{298.1} = -86 \text{ cal.}$$
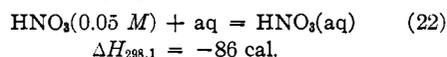
Combining Eqs. 21 and 22, which refer to total heats of solution, with the data in Table VIII and the heat of formation of water given by Rossini

$$H_2 + \frac{1}{2}O_2 = H_2O(1) \quad (23)$$
$$\Delta H_{298.1} = -68,318 \text{ cal.}$$

we find

$$\frac{1}{2}N_2 + \frac{3}{2}O_2 + \frac{1}{2}H_2 = HNO_3(1) \quad (24)$$
$$\Delta H_{298.1} = -41,349 \text{ cal.}$$
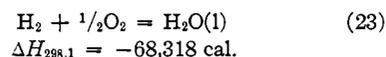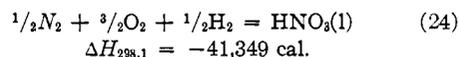
The entropies of the reactants are as follows: N_2,[30] $S_{298.1} = 45.79$ cal. deg.$^{-1}$ mole^{-1}.

$$O_2,[31] \ S_{298.1} = 49.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$H_2,[32] \ S_{298.1} = 31.23 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$\Delta S_{298.1} = -74.87 \text{ cal. deg.}^{-1}$$

and

$$\Delta F^0_{298.1} = -11,539 \text{ cal.}$$

From the vapor pressure data

$$HNO_3(1) = HNO_3(g) \quad (25)$$
$$\Delta F^0_{298.1} = RT \ln (760/62.9) = 1082 \text{ cal.}$$

Combining Eqs. 24 and 25

$$\frac{1}{2}N_2 + \frac{3}{2}O_2 + \frac{1}{2}H_2 = HNO_3(g) \quad (26)$$
$$\Delta F^0_{298.1} = -10,457 \text{ cal.}$$
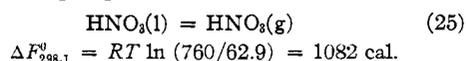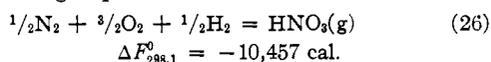
Latimer, Pitzer and Smith[33] have summarized the data on ionic entropies and for the partial

(29) Becker and Roth, Z. Elektrochem., **40**, 836 (1934).
(30) Giauque and Clayton, This Journal, **55**, 4875 (1933).
(31) Giauque and Johnston, ibid., **51**, 2300 (1929).
(32) Giauque, ibid., **52**, 4816 (1930).
(33) Latimer, Pitzer and Smith, ibid., **60**, 1829 (1938).

molal entropy of nitric acid at unit activity they give

$$\bar{S}_{298.1} = 35.0 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

The total heat of solution of liquid nitric acid in an infinite amount of water is the same as the $H - \bar{H}$ for the reaction

$$HNO_3(l) = HNO_3 \ (a = 1) \qquad (27)$$
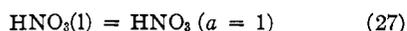
From Table VIII and the entropy values we find

$\Delta H_{298.1} = -7971 \text{ cal.}$ $\Delta S_{298.1} = -2.2 \text{ cal. deg.}^{-1}$
$\Delta F^0_{298.1} = -7315 \text{ cal.}$

and from Eqs. 24 and 27

$$^1/_2N_2 + {}^3/_2O_2 + {}^1/_2H_2 = HNO_3 \ (a = 1) \quad (28)$$
$$\Delta F^0_{298.1} = -18,854 \text{ cal.}$$
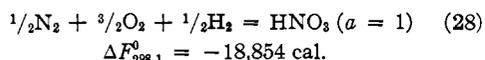
We thank Dr. T. R. Rubin for assistance with the experimental measurements.

Summary

The heat capacities of nitric acid and its monohydrate and trihydrate have been measured from 15 to 300°K.

The melting points, heats of fusion, heats of dilution, and entropies are as given below. The entropy values do not include the nuclear spin effect since this cancels in chemical reactions.

THERMODYNAMIC PROPERTIES OF NITRIC ACID AND ITS HYDRATES

	HNO₃	HNO₃·H₂O	HNO₃·3H₂O
Melting point, °K.	231.51	235.48	254.63
Heat of fusion, cal. mole⁻¹	2503	4184	6954
ΔH of infinite dilution, cal. mole⁻¹	−7971	−4732	−2123
Entropy, cal. deg.⁻¹ mole⁻¹	37.19	51.84	82.93

The available partial pressure data over aqueous nitric acid solutions have been investigated by means of the Duhem equation and rather large errors in many of the experimental observations have been made evident. It has been possible to conclude that no appreciable association exists in the vapor over nitric acid solutions.

As an example the present observations have, with the aid of the Duhem equation, been used to

supplement the experimental partial pressure observation of Wilson and Miles and to calculate the partial pressures over the range from 50 to 100% nitric acid at 20°C.

The above entropies were used with the known entropy of water and the measured heats of hydration to calculate the free energies of hydration. These were compared with the free energies for isothermal hydration.
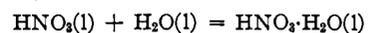
$$HNO_3(l) + H_2O(l) = HNO_3 \cdot H_2O(l)$$
$\Delta F_{243.1°K.} = -2523 \text{ cal. (Third Law)}$
$= -2495 \text{ cal. (Isothermal)}$
$$HNO_3(l) + 3H_2O(l) = HNO_3 \cdot 3H_2O$$
$\Delta F_{223.1°K.} = -4404 \text{ cal. (Third Law)}$
$= -4406 \text{ cal. (Isothermal)}$
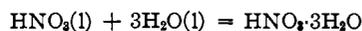
The excellent agreement above indicates that the $\int_0^T C_p \ d \ln T$ gives the correct entropies for nitric acid and its hydrates, and incidentally that if hydrogen bonding occurs in the lattice structure of these solids, as seems probable, no randomness exists at low temperatures.

The entropy of nitric acid gas was found to be 63.62 cal. deg.⁻¹ mole⁻¹ at 298.1°K. and 1 atm.

The entropy of nitric acid gas has been combined with available molecular data to investigate the internal rotation of the nitric acid molecule. It is found that the rotation is restricted by a double potential barrier of 7000 cal. mole⁻¹.

The free energy, heat content and entropy functions of nitric acid gas have been tabulated.

The heats of reaction at the absolute zero and equilibrium constants to 500°K. have been given for the reactions

$$2HNO_3(g) + NO = H_2O(g) + 3NO_2$$
$$2HNO_3(g) = H_2O(g) + 2NO_2 + {}^1/_2O_2$$
$$2HNO_3(g) = H_2O(g) + 2NO + {}^3/_2O_2$$
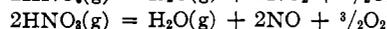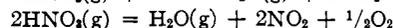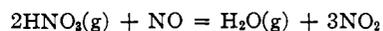
The free energies and heats of formation from the elements were calculated.

$$^1/_2N_2 + {}^3/_2O_2 + {}^1/_2H_2 = HNO_3(l)$$
$\Delta H_{298.1} = -41,349 \text{ cal.,} \quad \Delta F^0_{298.1} = -11,539 \text{ cal.}$
$$^1/_2N_2 + {}^3/_2O_2 + {}^1/_2H_2 = HNO_3(g)$$
$\Delta H_{298.1} = -3199 \text{ cal.,} \quad \Delta F^0_{298.1} = -10,457 \text{ cal.}$
$$^1/_2N_2 + {}^3/_2O_2 + {}^1/_2H_2 = HNO_3(aq. \ a = 1)$$
$\Delta H_{298.1} = -49,320 \text{ cal.,} \quad \Delta F^0_{298.1} = -18,854 \text{ cal.}$