THE PHYSICOCHEMICAL PROPERTIES OF PURE NITRIC ACID

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I. INTRODUCTION

Nitric acid has been for many years one of the most important commercial acids. By far the greatest amount of the acid has been employed for industrial purposes in the form of relatively dilute aqueous solutions containing up to 70 per cent HNO_3.

Recent advances in the field of chemical technology have created an increasing demand for highly concentrated nitric acid, due particularly to the development of binary liquid rocket fuels. The problems associated with the production, handling, and storage of highly concentrated solutions of nitric acid have in turn resulted in a need for reliable data on the physicochemical properties of such solutions and, especially, of the pure acid.

An examination of the scientific literature on nitric acid indicates that most of the earlier determinations of its properties were carried out on impure or decomposed samples. Unfortunately, modern texts and reference manuals continue to report obsolete values, some over a century old.

It is the purpose of this report to collect, evaluate, and present the "best" values of the various physicochemical properties of analytically pure nitric acid. The scarcity of the data has made it necessary to extend the study to nitric acid containing up to 1 per cent impurities, the exact concentration being stated whenever possible. Early values of the properties have been presented only when believed to be pertinent. Excellent reviews of the earlier data prior to 1935 are to be found in Gmelin's *Handbuch der anorganischen Chemie* and Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry*.

Whenever possible, the data have been obtained from the original research report published by the investigator. When the report was not available the information was obtained from abstracting journals. In many cases, determinations of given physical properties were reported chronologically in order to show the vintage of the data cited in various reference manuals.

II. PREPARATION OF NITRIC ACID

Pure liquid nitric acid decomposes at temperatures above its freezing point ($-41.59°C$.) according to the overall equation:

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$
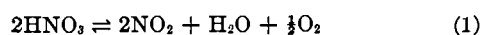
where NO_2 represents an equilibrium mixture of nitrogen dioxide and nitrogen tetroxide. At room temperature the rate of decomposition is rapid enough for the colorless pure acid to acquire in a few hours a yellow tinge indicative of oxides of nitrogen. The vapors of nitric acid are believed to undergo also photochemical decomposition.

Owing to this instability, special precautions must be taken in order to prepare analytically pure acid. The following methods have been used on a laboratory scale.

A. FROM ALKALI NITRATES AND SULFURIC ACID

Pure nitric acid can be prepared by treating anhydrous sodium nitrate (67) or potassium nitrate (106) with 100 per cent sulfuric acid. The reaction is carried out in the absence of air in an all-glass apparatus shielded from light. The operating temperature is kept at 0°C. or below, in order to avoid the decomposition of the nitric acid. Under these conditions, the reaction can be expressed by the equation:

$$H_2SO_4 + KNO_3 \rightleftharpoons HNO_3 + KHSO_4 \qquad (2)$$

The nitric acid formed is removed from the reaction mixture by vacuum distillation and collected in a receiver cooled below its freezing point. The product is a white, crystalline solid, which melts to form a colorless liquid. Acid analyzing 100.00 ± 0.05 per cent HNO_3 has been prepared in this manner.

B. BY THE DISTILLATION OF CONCENTRATED NITRIC ACID

Concentrated nitric acid is distilled with two to three volumes of 95–100 per cent sulfuric acid (preferably the latter) under reduced pressure in an all-glass still. The distillation is carried out at temperatures around 0°C. and repeated two to three times. The distillate is collected and stored at a temperature of 0°C. or below. This method has been used by many investigators to produce 100 per cent nitric acid (9, 10, 11, 23, 28, 42, 60, 91, 110, 126, 127, 144, 181, 204, 206).

Earlier workers distilled the mixture of nitric and sulfuric acids above room temperature. Under these circumstances the product acquires a yellowish color due to the oxides of nitrogen formed by the decomposition of the nitric acid. It is possible to remove the oxides and obtain a colorless acid by passing a stream of dry air (42, 144, 181, 206) or ozonized oxygen (206) through

the distillate. However, it is doubtful if water, which is also formed by the decomposition of the acid, can be quantitatively removed by this method.

Potier (161) has recently described an apparatus for the preparation of pure nitric acid by distillation of the commercial acid under atmospheric pressure. The density of his product was somewhat higher than that reported from other sources for pure nitric acid (see Section III,I), so that the purity of the product is questionable.

C. BY FRACTIONAL CRYSTALLIZATION OF CONCENTRATED NITRIC ACID

Küster and Münch (118) attempted to prepare pure nitric acid by fractional crystallization of 98.5 per cent acid. The highest concentration attained was 99.67–99.79 per cent HNO_3. The product was a white crystalline solid which formed a straw-colored liquid when melted. This led the investigators to believe that pure nitric acid is stable only below its freezing point. Actually, pure nitric acid can be kept at 0°C. for many hours without visible signs of decomposition.

More recently, Biltz and Hülsmann (18) reported the preparation of a sample melting between −41.0°C. and −42.5°C. by similar methods, starting with colorless, chlorine-free 99 per cent nitric acid.

D. BY OTHER METHODS

Creighton (41) produced 99 per cent nitric acid from a 71 per cent aqueous solution of nitric acid by electrolysis, in the anode section of a diaphragm cell. The operating temperature ranged from 5°C. to 10°C.

Attempts to obtain 100 per cent nitric acid by fortifying highly concentrated nitric acid with excess nitrogen pentoxide and subsequently diluting it with the required amount of water have not been successful (78, 127, 141, 206).

III. PHYSICAL PROPERTIES OF NITRIC ACID

A. MOLECULAR STRUCTURE

The analysis of electron diffraction patterns (136) and the microwave spectrum (142) indicate that the molecule of nitric acid in the gas phase is planar. Structural constants obtained by these methods are presented in table 1. For comparison, the bond distances and angles derived from the x-ray diffraction study of single crystals of nitric acid (130) are included. The dimensions shown for the gaseous molecule were calculated assuming the O—H bond length to be 0.96 A. and the N—O—H angle to be 90°. These values, though reasonable, were assumed by Maxwell and Mosley (136) for the sake of expediency and have been accepted without experimental evidence in more recent publications (37, 130, 142).

The microwave data were supplemented by the N—O bond length (1.203 A.) measured from the microwave

spectrum of nitryl chloride (136) to permit the other dimensions of nitric acid to be calculated. A completely independent set of bond lengths and angles requires data from the isotopically substituted molecules.

From the dependence of the Stark effect components for the 0_{00}-1_{01}, 0_{00}-1_{11}, and 2_{12}-2_{11} transitions on the electric field, the molecular dipole moment of the nitric acid molecule is found to be 2.16 Debyes (142).

The microwave dimensions confirm the suggestion of Cohn, Ingold, and Poole (37) that the O—N—O angle is closer to 135° than the 130° value found by electron diffraction. For a symmetric or nearly symmetric rotor, the relative intensities of the P, Q, and R branches in the infrared spectrum are known approximately for various orientations of the vibrational dipole moment changes with respect to the axes of the principal moments of inertia (7). The greater O—N—O angle is more consistent with the observed band shapes and assignments in the infrared spectrum of nitric acid vapor (37). This choice of the larger O—N—O angle

TABLE 1

Structural constants of the nitric acid molecule

Structural Constant	Electron Diffraction	Microwave Spectrum	X-ray Diffraction
N—O length (A.)	1.22 ± 0.02		1.24 ± 0.025
N—OH length (A.)	1.41 ± 0.02	1.44	1.30 ± 0.025
O—N—O angle (degrees)	130 ± 5	137.83	134 ± 3.5
O—N—OH angle (degrees)	115 ± 2.5		113 ± 5
Principal moments of inertia (a.m.u. A.²)			
Ia		38.854	
Ib		41.780	
Ic (⊥molecular plane)		80.747	

implies that the intermediate moment of inertia, I_b, makes an angle of about 30° with the N—OH bond.

No quantitative approximations to the electronic structure of the nitric acid molecule using valence models have been published, but some interpretations have been advanced on qualitative grounds. Kortüm proposed resonance among the structures (114)
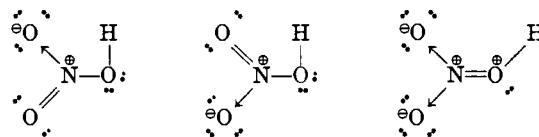
from a consideration of the electronic absorption spectra of the acid, its salts, and derivatives. The third structure is of minor importance because of the unlikely electron configuration at the double bond (adjacent charge rule) (159). Even though intramolecular hydrogen bonding is not represented, the structures depicted for the two nitrogen–oxygen bonds are consistent with bond lengths, Raman spectra, and infrared spectra (37, 92).

From studies of the surface tension and parachor of

liquid nitric acid (193) association of the molecules was inferred, the dimers having the structure
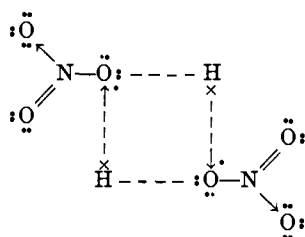
where the dashed arrow connotes the "singlet linkage" and the dotted line "½ electrovalence." The agreement between observed and calculated values for the parachor can only be fortuitous, because the choice of monomer structure, bond types in the dimer, and scale of atomic parachor values is somewhat arbitrary.

Any valence model for nitric acid vapor must account for the large O—N—O angle and the high barrier to rotation about the N—OH bond. Both these facts may be explained by intramolecular hydrogen bonding (37). To be complete, the model must also reflect changes in dimensions and molecular spectra with phase transitions.

B. CRYSTAL STRUCTURE

According to Luzzati (130), the crystal unit cell of nitric acid contains sixteen molecules of HNO_3 and has the dimensions $a = 16.23 \pm 0.05$, $b = 8.57 \pm 0.03$, $c = 6.31 \pm 0.01$ A. The group symmetry is $P_{2_1/a} - C_{2h}^5$ in the monoclinic system, with the angle $\beta = 90°$. The density calculated from these values, which were obtained at the freezing point of the acid ($-41.6°C.$), is 1.895 g. cm.$^{-3}$

The molecular dimensions for crystalline nitric acid reported in table 1 are weighted averages of the bond lengths and angles of the four molecules in the arbitrarily chosen asymmetric unit. Luzzati (130) suggests that twinning and disordering occur in the crystals, owing to the positions of the hydrogen atoms. There is no evidence, however, of any frozen-in disorder in the heat capacity data for solid nitric acid (67). Although a detailed comparison of the dimensions of nitric acid in the gaseous and crystalline states is unjustified because of the uncertainties in the data, the 0.1 A. decrease in N—OH bond length on freezing is too large to be dismissed on these grounds. This shortening has been attributed to intermolecular hydrogen bonds in the crystals (37, 130, 131).

C. FREEZING POINT

The data prior to 1935 are of historical interest only. The freezing points obtained by Forsythe and Giauque (67), Dunning and Nutt (58), Kay and Stern (106), and Antipenko, Beletskaya, and Krylova (4) are in very good agreement (see table 2). Of the three values, that reported by Forsythe and Giauque—namely $-41.59°C.$ —is considered the best.

TABLE 2

Freezing point of nitric acid

Freezing Point	Observers	Date	Reference
°C.			
−47*	Berthelot	1877	(12)
−45	Veley and Manley	1898	(205)
−42	Erdmann	1902	(62)
−41.2	Küster and Kremann	1904	(117)
−41.3	Küster and Münch	1905	(118)
−41.1	Mishchenko	1929	(144)
−41.0†	Biltz and Hülsmann	1932	(18)
−41.5	Briner, Süsz, and Favarger	1935	(23)
−41.59‡	Forsythe and Giauque	1942	(67)
−41.62 ± 0.05	Dunning and Nutt	1951	(58)
−41.8	Potier	1953	(162)
−41.60 ± 0.05	Kay and Stern	1954	(106)
−41.6 ± 0.1	Antipenko, Beletskaya, and Krylova	1958	(4)

* Bertholet called the acid freezing at this temperature "hydrated nitric acid."

† Biltz and Hülsmann reported freezing points varying between −41.0°C. and −42.5°C. for different samples of nitric acid. They could find no difference in the density of these samples.

‡ Determined calorimetrically.

D. BOILING POINT

The thermal instability of nitric acid makes an accurate determination of its normal boiling point very difficult. For this reason experimentally determined values of the boiling point are open to question.

Egan (59) calculated the fugacity of pure nitric acid from the thermodynamic data of Forsythe and Giauque (67) and, on the assumption that the fugacity at a pressure of 1 atm. is equal to the vapor pressure, obtained a boiling point of 84°C. The writers recalculated the fugacity, using more recent heat capacity data for nitric acid vapor (155), and obtained in a similar manner a boiling point of 84.1°C. Since the fugacity of the vapor at 1 atm. pressure would be expected to be somewhat less than 1 atm., the true boiling point would be slightly lower than 84.1°C. The experimental value of 82.6 ± 0.2°C., reported by Potier (165), may be reasonably close to the true value (see table 3).

TABLE 3

Normal boiling point of nitric acid

Boiling Point	Observers	Date	References
°C.			
86*	Berthelot	1877	(12)
83	Berl and Samptleben	1922	(10)
87†	Taylor	1925	(96, 198)
83	Berl and Saenger	1929	(11)
84‡	Egan	1945	(59)
85.3 (756 mm.)	Miskidzh'yan, Trifonov, and Balandina	1949	(149)
82.6 ± 0.2	Potier	1953	(165)
84.1‡	Stern, Mullhaupt, and Kay	1959	

* Berthelot called the acid having a normal boiling point of 86°C. "hydrated nitric acid." His "anhydrous nitric acid," with a boiling point of about 50°C., is presumably nitrogen pentoxide.

† Obtained by extrapolation of available vapor pressure data.

‡ Calculated.

TABLE 4

Heat of vaporization of nitric acid

Temperature	Heat of Vaporization	Observers	Date	Reference
°C.	cal. mole⁻¹			
20	9350*	Wilson and Miles	1940	(212)
	9426†	Wilson and Miles	1940	(212)
	7800*	Taylor	1925	(198)
25	9355‡	Forsythe and Giauque	1942	(67)
75	7900*	Pascal	1921	(157)
80	7500*	Taylor	1925	(198)
86	7584*	Pascal	1921	(157)
	7250*§	Berthelot	1877	(12)

* From vapor pressure data. † Average calorimetric value.
‡ Calculated from the calorimetric value of Wilson and Miles (212).
§ Temperature not given.

E. HEAT OF FUSION

Berthelot (12) determined the heat of fusion of nitric acid in 1877 but described his experiments as imperfect. His value of 601 cal. mole⁻¹ is still quoted in standard reference texts. The value 2503 ± 2 cal. mole⁻¹, determined calorimetrically by Forsythe and Giauque (67), is considered to be the most reliable.

F. HEAT OF VAPORIZATION

The heats of vaporization reported for the higher temperatures are questionable, while the value of 7800 cal. mole⁻¹ cited by Taylor for 20°C. can definitely be rejected. The calorimetrically measured heat of vaporization of 9426 cal. mole⁻¹ at 20°C. (212) appears to be the most reliable.

G. HEAT CAPACITY

Mishchenko (120) has reported values of the specific heat of pure liquid nitric acid in the temperature range

TABLE 5

Heat capacity of nitric acid

Temperature	Heat Capacity, C_p	Temperature	Heat Capacity, C_p
°K.	cal. deg.⁻¹ mole⁻¹	°K.	cal. deg.⁻¹ mole⁻¹
15	0.677	120	11.09
20	1.238	130	11.47
25	1.934	140	11.92
30	2.740	150	12.37
35	3.609	160	12.81
40	4.468	170	13.27
45	5.193	180	13.72
50	5.855	190	14.20
55	6.463	200	14.70
60	7.012	210	15.25
65	7.522	220	15.82
70	7.988	230	16.46
75	8.419	240	26.70
80	8.825	250	26.65
85	9.187	260	26.59
90	9.510	270	26.51
95	9.794	280	26.42
100	10.06	290	26.33
110	10.56	300	26.24

0°C. = 273.10°K.

from 2.53°C. to 60.11°C. which were obtained by the extrapolation of data for aqueous solutions of known concentration to 100 per cent HNO₃.

The heat capacity of pure nitric acid was carefully measured calorimetrically by Forsythe and Giauque (67) in the temperature range 15–231.51°K. (solid state) and 231.51–300°K. (liquid state). Their results are given in table 5. The accuracy of the values is reported to be of the order of 3 per cent at 15°K., 1 per cent at 20°K., and 0.1 per cent above 35°K.

The extrapolated values of Mishchenko agree to within about 0.5 per cent with the data in table 5 at comparable temperatures.

The heat capacity in the ideal gaseous state at 1 atm. pressure between 298.16°K. and 500°K. has been computed by Palm and Kilpatrick (155), using the recent spectroscopic measurements of Cohn, Ingold, and Poole (37) and of Fréjacques (72). The results of this computation are presented in table 22.

The heat capacities of the liquid and vapor can be expressed conveniently by empirical equations. The equation for the liquid,

$$C_p(l) = 25.64 + 1.427 \times 10^{-2}T - 4.090 \times 10^{-5}T^2 \quad (3)$$

represents the data in table 5 between 230°K. and 300°K. to better than 0.05 per cent. The equation for the vapor,

$$C_p(g) = 2.88 + 4.047 \times 10^{-2}T - 2.407 \times 10^{-5}T^2 \quad (4)$$

represents the data in table 22 (with the contributions of internal rotation included) to better than 0.1 per cent. In both equations the heat capacity is expressed in calories degree⁻¹ mole⁻¹ and the temperature in degrees Kelvin.

Egan (59) has reported similar relations, but his equation for the heat capacity of nitric acid vapor is incorrect.

H. VAPOR PRESSURE

In 1925 Taylor (198) reviewed critically all the then existing data on the vapor pressure of nitric acid and its aqueous solutions. The vapor pressure values reported in the *International Critical Tables* (96) are based on this study. Subsequent measurements indicate that Taylor's values are low.

The writers, using the thermodynamic data of Forsythe and Giauque (67) for the liquid and the more recent data of Palm and Kilpatrick (155) for the vapor, calculated the vapor pressure of nitric acid from free energy–temperature relations assuming that, at a given temperature, the vapor pressure is equal to the fugacity (see Section V,C). This assumption is satisfactory at the lower pressures. At pressures near 1 atm. the fugacity would be expected to be a few per cent lower. Nevertheless, the vapor pressures of nitric acid computed by this method are believed to be more

reliable than the values determined experimentally, especially at the higher temperatures. A similar calculation by Egan (59) is not recommended, being based on obsolete data (see also Section III,G).

The authors' data agree within 1 per cent with the experimental vapor pressure of Wilson and Miles (212), and within about 4 per cent with other recent measurements below 25°C., including those of Vandoni (201) (14.1 mm. of mercury at 0°C.) and of Vandoni and Laudy (202) (46.28 mm. of mercury at 20°C.), not reported in table 6.

I. DENSITY

1. Liquid density at vapor pressure

The density of nitric acid containing 0.04 per cent nitrogen dioxide has been determined most recently

TABLE 6

Vapor pressure of nitric acid

Tem-pera-ture	Vapor Pressure						
	Taylor (198)	Berl and Saenger (11)	Klemenc and Rupp (111)	Wilson and Miles (212)	Lloyd and Wyatt (123)	Potier (163, 164)	Stern, Mull-haupt, and Kay
°C.	mm. Hg	mm. Hg	mm. Hg	mm. Hg	mm. Hg	mm. Hg	mm. Hg
−10	—	—	—	—	6.93*	—	—
0	11	14.0	14.9	14.7	14.0*	14.15	14.6
5	15	19.6	—	20.1	—	19.76	—
10	22	26.5	—	27.1	26.26	26.52	27.2
12.5	—	—	31.5	—	—	—	—
15	30	35.5	—	36.2	—	35.6	—
20	42	47.3	—	48.0	47.0*	47.5	48.1
25	57	61.0	62.1	62.9	—	—	—
30	77	77.4	—	—	—	—	81.4
40	133	—	—	—	—	—	132
50	215	—	—	—	—	—	207
60	320	—	—	—	—	—	313
70	460	—	—	—	—	—	461
80	625	—	—	—	—	—	660
90	820	—	—	—	—	—	922
100	—	—	—	—	—	—	1261
Boiling point.	760 (87°C.)	760 (83°C.)	—	—	—	—	760 (84.1°C.)

* Interpolated.

between −30°C. and 50°C. by Antipenko, Beletskaya, and Krylova (4), who expressed their results by the equation

$$d \text{ (g. cm.}^{-3}) = 1.5492 - 0.00183t \text{ (°C.)} \tag{5}$$

The estimated error was within ±0.003 g. cm.$^{-3}$ between 0°C. and 50°C., and within ±0.0006 g. cm.$^{-3}$ between −30°C. and 0°C. These results are in excellent agreement with the measurements of Stern and Kay (190), who reported the density of the pure acid between 1°C. and 32°C. as

$$d \text{ (g. cm.}^{-3}) = 1.5492 - 0.00182t \text{ (°C.)} \tag{6}$$

with an accuracy of ±0.0001 g. cm.$^{-3}$ Both equations can be employed with equal confidence in the stated

TABLE 7

Density of nitric acid

Comparison between equation 6 and the literature

Tem-pera-ture	Density from Equa-tion 6	$\Delta d = d_{eq.6} - d_{lit}$					
		Mish-chenko (144)	Klemenc and Rupp (111)	I.C.T. (95)	Mason, Petker, and Vango (133)	Lee and Millen (121)	Antipenko, Beletskaya, and Krylova (4)
°C.	g.cm.$^{-3}$						
−20	1.5856*	—	—	—	—	+0.004	−0.0002
−10	1.5674*	—	—	—	—	+0.003	−0.0002
0	1.5492*	+0.0013	+0.0013	—	0.000	—	0.0000
5	1.5401	+0.0010	—	−0.0001	—	—	0.0000
10	1.5310	+0.0006	—	0.0000	—	—	0.0000
15	1.5219	+0.0004	—	+0.0002	—	—	+0.0001
20	1.5128	—	—	−0.0001	—	—	+0.0002
25	1.5037	—	+0.0019	−0.0003	0.000	—	+0.0002
30	1.4946	—	—	−0.0006	—	—	+0.0002
35	1.4855*	—	—	—	—	—	+0.0003
40	1.4764*	—	—	—	−0.001	—	+0.0004

* Extrapolated.

temperature ranges. Density values calculated from the latter are compared with other data reported in the literature in table 7.

2. Liquid density at pressures higher than the vapor pressure

The specific volume of liquid nitric acid at pressures higher than the vapor pressure has been determined by Reamer, Corcoran, and Sage (173). Their results, expressed as densities, are shown in table 8. The acid sample upon which the measurements were made contained less than 0.5 per cent impurities. The standard error was stated to be ±0.055 g. cm.$^{-3}$, and the standard deviation from smoothed curves was ±0.0025 g. cm.$^{-3}$

3. Density of solid nitric acid

Because of the inconsistencies in the data of Biltz, Hülsmann, and Eickholz, only Luzzati's value for the density of solid nitric acid appears to be reliable (see table 9).

TABLE 8

Density of liquid nitric acid at pressures higher than the vapor pressure

Pressure	Density		Pressure	Density	
	21.1°C.	37.8°C.		21.1°C.	37.8°C.
atm.	g. cm.$^{-3}$	g. cm.$^{-3}$	atm.	g. cm.$^{-3}$	g. cm.$^{-3}$
13.6	1.5124	1.4833	153.1	1.5327	1.5000
27.2	1.5147	1.4859	170.1	1.5344	1.5016
40.8	1.5170	1.4874	187.1	1.5361	1.5029
54.4	1.5190	1.4894	204.1	1.5377	1.5042
68.1	1.5213	1.4910	238.2	1.5405	1.5063
85.1	1.5241	1.4930	272.2	1.5432	1.5081
102.1	1.5264	1.4948	306.2	1.5454	1.5094
119.1	1.5286	1.4967	340.2	1.5470	1.5100
136.1	1.5308	1.4983			

TABLE 9

Density of crystalline nitric acid

Temperature	Density	Observers	Date	Reference
°C.	g. cm.⁻³			
−41.6	1.895*	Luzzati	1950	(129)
−96	1.841†	Biltz, Hülsmann, and Eickholz	1935	(19)
−195	1.883	Biltz, Hülsmann	1932	(18)
	1.901†	Biltz, Hülsmann, and Eickholz	1935	(19)
−273	1.90‡	Biltz and Hülsmann	1932	(18)

* Calculated from x-ray data.
† Values obtained from *Gmelin's Handbuch der anorganischen Chemie*, the original paper not being available.
‡ Extrapolated.

J. COEFFICIENT OF CUBICAL EXPANSION

The mean coefficient of cubical expansion of solid nitric acid is reported to be 3.3×10^{-4} deg.⁻¹ in the temperature range from −96°C. to −195°C. and 1.7×10^{-4} deg.⁻¹ in the temperature range from −195°C. to −272°C. (80). These data are questionable, being based on the measurements of Biltz, Hülsmann, and Eickholz (19).

K. COMPRESSIBILITY OF LIQUID

The coefficient of compressibility, β, defined as

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \tag{7}$$

has been calculated for liquid nitric acid, using the specific volume data determined by Reamer, Corcoran, and Sage (173). The results are given in table 10.

A value of 32.2×10^{-6} atm.⁻¹ at 0°C. and for the pressure range from 1 to 32 atm. is cited for the coef-

TABLE 10

Coefficient of compressibility of nitric acid*

Pressure	Coefficient of Compressibility $\beta \times 10^6$	
	21.1°C.	37.8°C.
atm.	atm.⁻¹	atm.⁻¹
13.6	155.4	—
27.2	130.6	110.4
40.8	116.1	95.5
54.4	107.6	86.4
68.1	100.5	80.7
85.1	93.3	76.3
102.1	86.8	71.9
119.1	80.9	67.6
136.1	75.6	63.5
153.1	70.6	59.2
170.1	65.8	55.1
187.1	61.4	50.1
204.1	57.4	46.2
238.2	50.7	37.3
272.2	45.0	29.1
306.2	40.0	19.4

* The acid is stated to contain less than 0.5 per cent (by weight) of impurities.

ficient of compressibility of nitric acid in some recent texts. This value is based on the measurements of Colladon and Sturm (38), published in 1827, and refers to dilute nitric acid. A compressibility of 338×10^{-6} atm.⁻¹ at 20.3°C. and in the pressure range from 1 to 32 atm., reported without reference in the *Handbook of Chemistry and Physics* (86), may conceivably have originated from the same source.

L. VELOCITY OF SOUND IN NITRIC ACID

The velocity of sound in pure nitric acid is reported in the *International Critical Tables* (99) as 1425 meters sec.⁻¹ at 16°C. based on the experimental work of Schmidt (186). Schmidt's paper was not available for review.

M. SURFACE TENSION

The surface tension of pure nitric acid has been determined between 0°C. and 40°C. by Miskidzh'yan and

TABLE 11

Surface tension of nitric acid

Temperature	Surface Tension	Observers	Date	Reference
°C.	dynes cm.·			
0	43.56	Miskidzh'yan and Trifonov	1947	(147)
20	41.15	Miskidzh'yan and Trifonov	1947	(147)
	40.58	Taketa	1953	(193)
22.5	40.30	Taketa	1953	(193)
25	39.99	Taketa	1953	(193)
27.5	39.67	Taketa	1953	(193)
30	39.34	Taketa	1953	(193)
40	37.76	Miskidzh'yan and Trifonov	1947	(147)

Trifonov (147) and evaluated by Taketa (193) by extrapolation of measurements with solutions containing 65.15–99.77 per cent HNO_3. Their results are reported in table 11.

Older measurements by Aston and Ramsey (5) were carried out with 99.8 per cent nitric acid containing excess nitrogen dioxide. Their values are about 4 per cent lower than those of the Russian investigators, which are the most reliable.

N. ELECTRICAL CONDUCTIVITY

The specific conductance of nitric acid has been determined by many investigators but, as shown in table 12, the agreement is very unsatisfactory.

The older data of Veley and Manley (206), of Saposhnikov (183, 184), and of Berl and Saenger (11) need not be taken too seriously, while the recent measurements of Duboz (57) are completely out of line with those of other investigators. The acid used by Miskidzh'yan and Trifonov (148) appears to have suffered some decomposition. The measurements of Taylor, Lynne, and Follows (197), of Taylor and Follows (196), and of Taylor, Baker, and Lynne (195) may have been affected

by impurities (194). The precision of their data is of the order of ± 6 per cent, rather than ± 1 to 2 per cent as claimed; at higher temperatures (not reported in table 12) the precision is expected to be even lower. The most reliable values seem to be those of Lee and Millen (121) and of Robertson, Mason, and Sage (180) at the lower temperatures.

The discrepancy among the data reported by various investigators could be attributed to the fact that the specific conductance of nitric acid and solutions in the vicinity of 100 per cent HNO_3 is sensitive to the presence of small amounts of water and nitrogen dioxide, which influence the self-ionization of the acid (Section IV).

All measurements are consistent in showing that the temperature dependence of the specific conductance is very small.

O. THERMAL CONDUCTIVITY

Van der Held and Van Drunen (200) studied the thermal conductivity of a number of inorganic acids and found a linear dependence of the thermal conductivity on concentration. A linear extrapolation of their data yields the value of 0.21 kcal. m.$^{-1}$ hr.$^{-1}$ deg.$^{-1}$, or 5.8×10^{-4} cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$, for the thermal conductivity of 100 per cent nitric acid at 17.2°C.

A thermal conductivity of 0.295 kcal. m.$^{-1}$ hr.$^{-1}$ deg.$^{-1}$ at 20°C. was obtained by a similar extrapolation of the data reported by Riedel (178) for dilute solutions of nitric acid. In view of the extrapolations used, no "best" value can be recommended.

P. VISCOSITY

The data reported in the literature for the viscosity of pure nitric acid are given in table 13. In addition to these data a value of 9.753×10^{-3} poises at 20°C. has been calculated by Bingham and Stone (20) from the data of Graham (82, 83). The latter claimed that the most concentrated nitric acid used in his measurements contained 0 per cent H_2O, a statement which was interpreted by Bingham and Stone as meaning 100 per cent HNO_3. However, the low specific gravity of 1.5046 at 15°C. of this acid indicates the presence of substantial amounts of impurities and for this reason the accuracy of the above value of the viscosity is questionable.

Bingham and Stone (20) employed an acid analyzing 99.2 per cent HNO_3 and 0.07 per cent NO_2. Their viscosity data have been corrected to 100 per cent HNO_3. The values given in the *International Critical Tables* (97) are stated to be based on the measurements of Graham (82, 83) and of Bingham and Stone (20), a correction having been applied whenever possible for the failure of the viscometer to obey Poisseuille's law exactly. The acid used by Taylor, Lynne, and Follows (197) contained from 0.05 to 0.2 per cent nitrogen tetroxide and probably also traces of nitrogen pentoxide

TABLE 12
Specific conductivity of nitric acid

Temperature	Specific Conductance $K \times 10^2$	Observers	Date	References
°C.	ohm^{-1}			
-20	3.40	Lee and Millen	1956	(121)
-10	3.68	Lee and Millen	1956	(121)
0	2.893	Veley and Manley	1898	(206)
	2.9700*, 3.2194†	Miskidzh'yan and Trifonov	1947	(148)
	3.279	Naumova	1949	(151)
	3.558	Taylor, Lynne, and Follows	1951	(197)
	3.593	Taylor and Follows	1951	(196)
	3.77	Robertson, Mason, and Sage	1952	(180)
	2.62	Duboz	1952	(57)
10	3.653	Taylor, Lynne, and Follows	1951	(197)
	2.62	Duboz	1952	(57)
15	4.118	Veley and Manley	1898	(206)
	3.678	Taylor, Lynne, and Follows	1951	(197)
18	5.0‡	Berl and Saenger	1929	(11)
	3.703	Taylor, Lynne, and Follows	1951	(197)
25	4.79	Saposhnikov	1905	(183, 184)
	3.1712†	Miskidzh'yan and Trifonov	1947	(148)
	3.4724	Naumova	1949	(151)
	3.744, 3.704, 3.735	Taylor, Lynne, and Follows	1951	(197)
	3.734	Taylor and Follows	1951	(196)
	3.865, 3.300, 3.730	Taylor, Baker, and Lynne	1951	(195)
25.4	2.43	Duboz	1952	(57)
30	4.217	Veley and Manley	1898	(206)
	3.690	Taylor, Lynne, and Follows	1951	(197)

* After 3 hr.
† After 6 days.
‡ By extrapolation from conductivities of nitric acid–nitrogen pentoxide solutions.

and water. Miskidzh'yan and Trifonov (146) and Naumova (151) purified commercial nitric acid by vacuum distillation with sulfuric acid, according to a method described by Mishchenko (144), and obtained a colorless product which was stated to be 100 per cent nitric acid.

The agreement between the different viscosity measurements is not good. In many cases the experimental

TABLE 13
Viscosity of liquid nitric acid

Temperature	Viscosity $\eta \times 10^3$	Observers	Date	Reference
°C.	poises			
0	12.23	Miskidzh'yan and Trifonov	1947	(146)
	11.00	Naumova	1949	(151)
	10.92	Mason, Petker, and Vango	1955	(133)
10	10.37	Bingham and Stone	1923	(20)
	10.3*	International Critical Tables	1929	(97)
20	8.780	Bingham and Stone	1923	(20)
	8.98*	International Critical Tables	1929	(97)
	9.46	Miskidzh'yan and Trifonov	1947	(146)
24.9	7.61	Briner, Süss, and Favarger	1935	(23)
25	7.33†	Taylor, Lynne, and Follows	1951	(197)
	7.46	Mason, Petker, and Vango	1955	(133)
40	6.798	Bingham and Stone	1923	(20)
	6.80*	International Critical Tables	1929	(97)
	7.15	Miskidzh'yan and Trifonov	1947	(146)
	6.17	Mason, Petker, and Vango	1955	(133)

* Reported as relative viscosities and converted to c.g.s. units using the viscosity of water at the stated temperatures (97).
† Extrapolated from viscosity data of mixtures of nitric acid and nitrogen pentoxide.

procedures have not been described in enough detail to make possible the selection of the best values with any degree of certainty. From an examination of the available data and of the work of Chanukvadze (27) on the nitric acid–water system up to 99.5 per cent HNO_3, it appears that the values of Briner, Süsz, Favarger (23), of Naumova (151), and of Mason, Petker, and Vango (133) are the most representative of pure nitric acid.

The values of 22.75×10^{-3} and 17.70×10^{-3} poises at 0° and 10°C., respectively, given by Pagliani and Oddone (154) for the viscosity of 100 per cent nitric acid, are often quoted but appear to be out of line with the data of other investigators.

Friend and Hargreaves (75) have expressed the temperature dependence of the viscosity of nitric acid between 18°C. and 70°C. by the equation:

$$\log \eta \times 10^3 = -0.9004 + 550.0/T \qquad (8)$$

where η is in poises and T in degrees Kelvin. The acid decomposed extensively during the viscosity measurements. The composition was not stated, but the acid appears to have contained excess nitrogen dioxide and possibly also water.

Q. MAGNETIC PROPERTIES

1. Specific and molar susceptibilities

Nitric acid is a diamagnetic substance. With the exception of a few of the earlier measurements, the values of the specific and molar susceptibility of nitric acid as reported by different investigators are presented chronologically in table 14.

The more recent determinations of Pascault and Chédin (158) and of Kido (107) are in satisfactory agreement and are believed to represent the most reliable values of the diamagnetic susceptibility of nitric acid.

TABLE 14

Specific and molar susceptibilities of nitric acid

The reported data refer to ambient temperature

Specific Susceptibility $x \times 10^6$	Molar Susceptibility $\chi_{mol} \times 10^6$	Observers	Date	Reference
c.g.s.m. units	*c.g.s.m. units*			
−0.283*	−17.85	Pascal	1910	(156)
−0.278*	−17.54	Cabrera, Jimeno, and Marquina	1916	(25)
−0.306	−19.3*	Shaffer and Taylor	1926	(187)
−0.189 ± 1.1%	−12*†	Decker	1926	(51)
−0.313	−19.8*	Kido	1932	(107)
−0.319*	−20.1‡	Kido	1932	(107)
−0.316§	−19.9*	Pascault and Chédin	1950	(158)

* Calculated from χ_{mol} or χ, respectively.

† The original value given by Decker is in error by a factor of 10^3.

‡ χ_{mol} taken to be the same as $\chi_{NO_3^-}$, assuming $\chi_{H^+} = 0$. $\chi_{NO_3^-}$ was evaluated from the linear dependence of the susceptibility of some alkali nitrates on the number of electrons of the cations.

§ Determined with pure nitric acid. All other data in table 14 were obtained with nitric acid solutions.

A specific susceptibility of -0.467×10^{-6} c.g.s.m. at 22°C. is listed for liquid nitric acid in the *International Critical Tables* (98) and stated to be based on the work of Endo (61). This value appears questionable.

2. Birefringence (Cotton–Mouton effect)

Krishnan and Raman (116) have estimated the constant of magnetic birefringence (Cotton–Mouton constant, c_m) of 100 per cent nitric acid to be 7.0×10^{-14} c.g.s.m. at about 16°C. for light of wavelength $\lambda = 0.578 \ \mu$, based on the measurements of Cotton and Mouton (40) on nitric acid solutions. It was assumed that the magnetic birefringence of water is negligible.

The *International Critical Tables* (100) list a relative constant of birefringence

$$\gamma_m \equiv 100 \left(\frac{C_{HNO_3}}{C_{C_6H_5NO_2}} \right)_m = 2.5 \qquad (9)$$

at 15.5°C. and for $\lambda = 0.578 \ \mu$. Taking 2.53×10^{-12} for the magnetic birefringence of nitrobenzene at the same wavelength and approximately the same temperature (40), $c_m = 6.3 \times 10^{-14}$ c.g.s.m. is obtained for nitric acid. This value is also based on the work of Cotton and Mouton (40) and refers to acid of density 1.49 g. cm.$^{-3}$, corresponding to about 90 per cent nitric acid.

3. Anisotropy

The magnetic anisotropy of nitric acid has been estimated from the constant of birefringence (Cotton–Mouton constant) (116) to be

$$\chi^{\parallel} - \chi^{\perp} = -5.3 \times 10^{-6} \text{ c.g.s.m.} \qquad (10)$$

where $\chi^{\parallel}$ and $\chi^{\perp}$ are the molar susceptibilities along and perpendicular to the axis, respectively.

This value is in good agreement with the observed diamagnetic anisotropy of crystals of potassium and of sodium nitrates, which has been attributed to the nitrate ion (116).

R. OPTICAL PROPERTIES

1. Index of refraction

The index of refraction of nitric acid is reported as a function of temperature in table 15.

The value of $n_D^{16.4} = 1.397$ cited in the *International Critical Tables* (94) without a reference is undoubtedly based on the measurements of Brühl (24). Of the data in table 15, only those of Miskidzh'yan and Trifonov (147) and of Miskidzh'yan, Trifonov, and Balandina (149) were obtained with pure nitric acid.

The index of refraction of the acid was determined also as a function of wavelength by Brühl (24) and by Lühdemann (126), but their measurements may have been affected by impurities.

TABLE 15

Index of refraction of nitric acid

Temperature	Index of Refraction n_D	Observers	Date	Reference
°C.				
5	1.4030	Miskidzh'yan and Trifonov	1947	(147)
14.2	1.3972	Veley and Manley	1902	(207)
16.4	1.3969*	Brühl	1897	(24)
18.5	1.3958*	Brühl	1897	(24)
23.7	1.4011†	Zecchini	1905	(216)
24	1.3970	Miskidzh'yan, Trifonov, and Balandina	1949	(149)
35	1.3910	Miskidzh'yan and Trifonov	1947	(147)

* Refers to >99 per cent HNO_3.
† Refers to 99.31 per cent HNO_3.

2. Ultraviolet spectrum

The ultraviolet absorption of nitric acid has been examined in the wavelength range 2400–3300 A. Early studies (89, 187, 209) presented conflicting data, probably due to difficulties in obtaining the pure acid. The recorded spectra are characterized by continuous absorption in the range 2500–3300 A. Jones and Thorn (105) found an absorption maximum at 2565 A., having a molar extinction coefficient of 11.1, while Dalmon (30) has reported the values 2575 A. and 9.5 for the corresponding quantities.

For the vapor of the pure acid, continuous absorption has been found in the region 2980–2520 A., with a maximum located at 2620 A. (90). A later study showed the absorption in the vapor to be the same as in the liquid acid, except for a more distinct band (47). In the solid, at temperatures down to that of liquid air, this band appears as two. Below liquid-air temperature and down to 20°K., four bands were found in the same region.

Evidence from Raman spectra, electrical conductivity, and cryoscopic studies led to the identification of the absorbing species in the ultraviolet near 2570 A. as molecular nitric acid and nitrogen pentoxide (47, 105). However, these species participate in ionic equilibria in the system water–nitric acid–nitrogen pentoxide (see Section IV), yielding nitronium and nitrate ions at compositions near 100 per cent HNO_3. From a study of this system, it was suggested (47) that the nitronium ion might be responsible for some of the absorption at 2565 A. Since the nitrate ion is a relatively weak absorber with a maximum at 3020 A., it would not contribute appreciably to the maximum for the pure acid. Chédin (30) compared Dalmon's spectra with Raman intensities and vapor pressures for the system nitric acid–water and interpreted the ultraviolet absorption of these solutions in terms of equilibria involving molecules of water, nitric acid monohydrate, nitric acid trihydrate, nitric acid, nitrate ions, and solvated hydrogen ions. Within the limits of error in his calculations, the ultraviolet spectrum of 100 per cent nitric acid could

be attributed solely to HNO_3 molecules. It was concluded that the amounts of nitronium and nitrate ions arising from self-ionization were probably too small to affect the spectrum. However, the absorption of the nitronium ion recently observed in solutions of nitrogen pentoxide in sulfuric acid rises very sharply without a maximum from 3150 A. to shorter wavelengths (52). The molal extinction coefficient increases from 0.03 at 3150 A. to 8.5 at 2650 A.; at 2575 A. one can estimate the relative values for the extinction coefficients of nitronium ion and pure nitric acid, compared on the same concentration basis, to be in the ratio of at least three to one. These data indicate that nitronium ions and, to a lesser degree, nitrate ions do contribute to the absorption of 100 per cent nitric acid between 3300 and 2400 A. The spectrum at 2575 A. and shorter wavelengths of nitric acid molecules will be somewhat different from the band observed in 100 per cent nitric acid.

3. Raman and infrared spectra

The Raman scattering of liquid nitric acid has been observed by many investigators (1, 2, 3, 8, 28, 29, 31, 43, 44, 45, 53, 92, 93, 108, 134, 135, 140, 168, 169, 170, 171, 175, 176, 188, 191, 208, 213, 214), usually in the course of research on aqueous solutions of the acid. The literature prior to 1950 was examined critically by Ingold and Millen (92) as part of their own research. Table 16 contains the Raman frequencies and assignments adopted by them for the fundamental vibrational modes.

Only two thorough analyses of the vibrational spectrum of the vapor below 3600 cm.$^{-1}$ have been published (37, 72, 73), both employing infrared absorption. The frequencies and assignments from the more complete study by Cohn, Ingold, and Poole (37) are shown in table 16.

The most recent determination of the infrared spectrum of liquid nitric acid (132) was obtained as part of a search for infrared absorption bands due to the nitronium ion. Of the earlier papers, those of Fréjacques (72, 73) are most important; Freymann and Freymann (74) were handicapped by the presence of nitrates dissolved in their samples from contact with the cell windows, and Bethell and Sheppard (16, 17) did not attempt any discussion of assignments. In the cases where bands were recorded, by Fréjacques and by Marcus and Fresco, the frequencies agree well, and averages are reported in tables 16 and 18. In table 18 the assignments also follow Cohn, Ingold, and Poole.

The vibrational frequencies for solid nitric acid were obtained in Raman scattering experiments by Simon and Höppner (188) and from infrared absorption measurements by Bethell and Sheppard (16, 17), but in neither case were assignments proposed. In the Raman photographs scattering by the nitrate ion and the glass

cell make the results difficult to interpret. The interpretation of the infrared spectrum is also complicated, because 90 per cent nitric acid (estimated by Marcus and Fresco) was used instead of the pure acid. Where the bands for solid nitric acid can be assigned with reasonable certainty by comparing frequencies with those for liquid and vapor, these values appear in tables 16 and 18.

The assignments given in the tables are founded on an interpretation of the relative intensities and degrees of polarization of the Raman bands, as well as a comparison with frequencies of similar molecules. These arguments were confirmed and developed further in an analysis of infrared band shapes, frequency shifts on deuteration, and relative intensities of Raman and infrared bands. In these discussions, a molecular model was assumed in which the hydrogen atom is considered to vibrate against a heavy, rigid frame. For the internal motions of this frame, the planar nitric acid molecule is treated as a four-atom structure (O_2NO') with C_{2v} symmetry. The OH group is represented by a single mass unit O' and the N—O' band is taken as the C_2 axis.

Fréjacques (72, 73) revived the older assignment by Mathieu and Massignon (134, 135) of the class A_1 frequencies. In this interpretation ν_3 (680 cm.$^{-1}$) was attributed principally to the N—OH stretching vibration, while ν_2 (886 cm.$^{-1}$ in the vapor) was identified chiefly with the deformation of the NO_2 group. Such a view implies a stiffer nitryl group with the hydroxyl radical more loosely attached than is the case for the model described above. By relating the frequency shifts of the 886 cm.$^{-1}$ band to properties expected for the NO_2 deformation mode, Fréjacques tried to demonstrate the plausibility of the assignment. The increase from 886 to 922 cm.$^{-1}$ on liquefaction of nitric acid was attributed to the formation of hydrogen bonds at the

NO_2 group, and the subsequent increase to 956 cm.$^{-1}$ with dilution to 40 per cent HNO_3 was explained by the formation of a monohydrate structure of the form
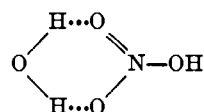
Dodd, Rolfe, and Woodward (56) have suggested that the approximate constancy of frequency within each of three sets in the series nitryl fluoride, nitric acid, nitryl chloride (two sets are definitely identified as NO_2 stretching motions) lends support to this argument.

The frequency increase discussed by Fréjacques would also be expected in the N—OH stretching vibration, because the N—OH bond would become stronger as intermolecular hydrogen bonds form at the expense of the intramolecular linkages. As nitric acid is diluted with water, it is reasonable to expect the N—OH stretching frequency to approach the value for the symmetric stretching vibration of the nitrate ion; similarly, the NO_2 deformation frequency should approach that of the symmetric bending mode of the ion. The assignment scheme of table 16 is more consistent with these ideas than the arguments of Fréjacques. If the deformation frequency did change because of hydrogen bonding in the structure shown above, then an even more prominent shift should appear in the bending frequency of the attached water molecule. A constant value for this mode (1639 cm.$^{-1}$) has been reported (132) in the range 80–12 per cent HNO_3, where it was observed. The trend in frequencies cited by Dodd, Rolfe, and Woodward is not sufficiently pronounced to be unambiguously interpreted. Because of the presence of hydrogen bonding in nitric acid and its absence in the nitryl halides, one may expect variation, not con-

TABLE 16

Fundamentals of the nitric acid vibrational spectrum

No.	Symmetry and Assignment	Vapor	Liquid		Solid	
		Infrared	Raman	Infrared	Raman	Infrared
		cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
ν_1	A₁ NO₂ stretch	1320 (s, o)*	1300 (s, P)*	1304 (s)*	1245 (s)*	1317 (s)*
ν_2	A₁ N—OH stretch	886 (s, q)	925 (s, P)	922 (s)	987 (w)	948 (m)
ν_3	A₁ NO₂ bend	—	680 (m, P)	690 (m)†	—	—
ν_4	B₂ NO₂ stretch	1710 (s)	1675 (m, D)	1672 (s)	—	1670 (s)
ν_5	B₂ N—OH bend	583 (m, q)	610 (m, D)	—	—	—
ν_6	B₁ out-of-plane bend	765 (m, q)	(767)‡	768 (m)	779 (w)	775 (w)
ν_7	A′ O—H stretch	3560 (m)	3400 (br)	3380 (m)	—	3226 (br)
ν_8	A′ O—H bend	1335 (s, q)	—	(1340)§	—	—
ν_9	A′ O—H torsion	465 (s, Q)	480 (w)¶	—	—	—

* Intensity: s = strong, m = medium, w = weak.
  Band shape: br = broad, o = no Q branch, q = weak Q branch, Q = strong Q branch.
  Polarization: P = polarized, D = depolarized.
† Observed only by Marcus and Fresco (132) on solutions of 90–70 per cent HNO_3.
‡ Calculated from first overtone.
§ Calculated from combination band.
¶ Observed by Redlich and Nielsen only (175).

stancy, in a series of molecules for a given vibration frequency. For these reasons, the assignments adopted by Ingold and Millen (92) and Cohn, Ingold, and Poole (37) are preferred. In addition, their view is more consonant with the existence of a hydronium-ion structure in the acid solution, for which there is spectroscopic evidence (65).

A study of the infrared absorption in nitryl chloride led Ryason and Wilson (182) to propose interchanging the assignments for frequencies ν_3 and ν_6 of nitric acid. More recently Dodd, Rolfe, and Woodward (56) examined the infrared and Raman spectra of nitryl fluoride, reconfirming the assignments by Ingold and Millen for these modes in nitric acid. The out-of-plane bending mode in these molecules is the only one in its symmetry class, so that the observed band has unique properties. In the infrared the fundamental is intense, exhibiting a strong Q branch, but in the Raman it is weak if visible at all. The first overtone is Raman active and is polarized. Except in the case of Raman data, which were not available to any extent for nitryl chloride, the above properties have been observed for ν_6 in nitric and deuteronitric acids, nitryl fluoride, and nitryl chloride, so that the identification of ν_6 with the out-of-plane bending mode is established.

For deuteronitric acid, only the infrared absorption by the vapor (37) and the Raman scattering by the liquid (8, 175) have been published; the frequencies are catalogued in table 17 according to the assignments of table 16.

The overtone and combination frequencies below 3400 cm.$^{-1}$ were recorded in studies of the vibrational fundamentals, and references for the bands in this range have already been given. For the band in nitric acid vapor at 1206 cm.$^{-1}$ the assignment $\nu_6 + \nu_9$ (132) has been retained instead of $2\nu_5$ (73), because the shift of band frequency in deuteronitric acid indicates that a hydrogen vibration is involved. In the infrared spectrum of liquid nitric acid two bands at 2600 cm.$^{-1}$ and at 2615 cm.$^{-1}$ were assigned as $\nu_2 + \nu_4$ (132) and $2\nu_1$ (73). On the basis of values observed for the fundamentals either assignment may be correct. The average of the frequencies is listed in table 18 as $\nu_2 + \nu_4$, according to the choice of Marcus and Fresco (132), and the band reported by them at 2690 cm.$^{-1}$ is labeled $2\nu_1$. Although the frequencies obtained in solid nitric acid were not all identified by Bethell and Sheppard (17), a consistent assignment can be made by comparing frequencies with the values for vapor and liquid.

Above 3400 cm.$^{-1}$ the observed bands have been interpreted in terms of overtones and combinations of hydrogen vibrations. These frequencies were all measured by infrared absorption before the fundamentals were reported in the infrared. For the vapor, the first and second overtones (reported by Jones (104) and by Badger and Bauer (6), respectively) extrapolate to a

TABLE 17

Raman and infrared frequencies of deuteronitric acid

Number	Symmetry and Assignment	Vapor Infrared	Liquid Raman
		cm.$^{-1}$	cm.$^{-1}$
ν_1	A$_1$ NO$_2$ stretch	1313 (s, q)*	1300 (s)*
ν_2	A$_1$ N—OH stretch	888 (s, q)	915 (s)
ν_3	A$_1$ NO$_2$ bend	—	670 (m)
ν_4	B$_2$ NO$_2$ stretch	1685 (s)	1645 (m)
ν_5	B$_2$ N—OH bend	543 (m, q)	580 (m)
ν_6	B$_1$ out-of-plane bend	764 (m, Q)	(767)†
ν_7	A' O—H stretch	2627 (m, Q)	2470 (br)
ν_8	A' O—H bend	1014 (s, q)	—
ν_9	A'' O—H torsion	(365)‡	370 (w)§
$\nu_6 + \nu_9$		1114	—
$2\nu_6$		—	1535
$\nu_1 + \nu_4$		2980	—

* Intensity: s = strong, m = medium, w = weak.
  Band shape: br = broad, o = no Q branch, q = weak Q branch, Q = strong Q branch.
  Polarization: P = polarized, D = depolarized.
  † Calculated from $2\nu_6$.
  ‡ Calculated from $\nu_6 + \nu_9$.
  § Observed only by Redlich and Nielsen (175).

fundamental having a frequency of 3550 cm.$^{-1}$, very close to the observed value (3560 cm.$^{-1}$). The series is easily represented by an energy expression employing only a second-degree anharmonic term. In the case of the liquid, the analysis is not as satisfactory, probably because water was present in some samples and because hydrogen-bonding effects are more pronounced in the liquid. Kinsey and Ellis (109) observed bands in concentrated nitric acid at 6800, 9900, and 12800 cm.$^{-1}$ that they identified as overtones in an anharmonic series extrapolating to a calculated frequency of 3500 cm.$^{-1}$ for the O—H stretching fundamental. Bands recorded at 4720 and 8000 cm.$^{-1}$ were explained as combination tones of members of the O—H stretching series and a fundamental observed in the Raman effect. If the assignment of the 4720 cm.$^{-1}$ band is correct, then the

TABLE 18

*Overtone and combination frequencies of nitric acid*

| Assignment	Vapor Infrared	Liquid Raman	Liquid Infrared	Solid Infrared
	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
$\nu_6 + \nu_9$	1206	—	—	—
$2\nu_3$	—	1360	—	—
$2\nu_6$	—	1535	1538	—
$\nu_2 + \nu_4$	2585	—	2608	—
$2\nu_1$	2627	—	2690	~2790
$\nu_1 + \nu_4$	3000	—	3000	~3070
$2\nu_4$	3390	—	—	—
$\nu_7 + \nu_8$	—	—	4720*	—
$2\nu_7$	6945	—	6800*	—
$2\nu_7 + \nu_8$	—	—	8000*	—
$3\nu_7$	10170	—	{ 9900*	—
			9832	
$4\nu_7$	—	—	12800*	—

* Observed in concentrated nitric acid.

value in the infrared of the Raman active frequency is 1340 cm.$^{-1}$ Although the O—H deformation fundamental of nitric acid has been definitely identified only in the vapor, 1340 cm.$^{-1}$ is about the value expected for the liquid. This assignment is consistent with the assignments of table 16 and the fact that hydrogen bending modes do not usually exhibit the spectacular shifts often observed for the stretching vibrations with phase changes or dilution. From this value of ν_8 and the combination frequency 8000 cm.$^{-1}$, the first overtone of the O—H stretching mode is estimated to be 6660 cm.$^{-1}$, compared with the band at 6800 cm.$^{-1}$ proposed by Kinsey and Ellis. Dalmon and Freymann (49) have observed a band at 9832 cm.$^{-1}$, which was attributed to the second overtone of the O—H stretching vibration in dimers for the acid. The doublet structure, decrease in intensity with dilution, and disappearance of the band at 80 per cent acid concentration were cited as evidence for this conclusion. Using a simple, two-constant energy expression as above, one calculates 6657 cm.$^{-1}$ for $2\nu_7$ and 12904 cm.$^{-1}$ for $4\nu_7$ from the values $\nu_7 = 3380$, $3\nu_7 = 9832$ cm.$^{-1}$ The comparatively poorer fit of the band at 6800 cm.$^{-1}$ might arise from the distortion of the observed band shape by the overlap of combination or overtone bands of the water in the Kinsey and Ellis samples.

IV. SELF-IONIZATION OF NITRIC ACID

The large electrical conductivity of pure nitric acid had led early investigators to suggest that this compound is extensively self-ionized. In 1924 Walden (210) suggested that concentrated nitric acid should be regarded as an amphoteric electrolyte, dissociating according to the equation:

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \rightleftharpoons OH^- + NO_2^+ \qquad (11)$$
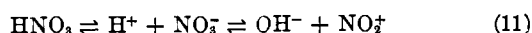
Hantzsch attributed the high conductivity of pure nitric acid to the formation of complex ions

$$[NO(OH)_2^+][NO_3^-] \text{ or } [N(OH)_3^{++}][NO_3^-]_2$$
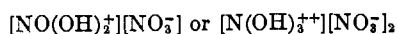
which he called "nitronium nitrate" and later "nitracidium nitrate," in equilibrium with the ester-like "pseudo-acid" NO_2OH (87, 88, 89). These earlier theories are no longer accepted, being based on incomplete or partially faulty experimental data.

According to modern views, the self-ionization of nitric acid results from a self-dehydration, as shown by the equation

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O \qquad (12)$$
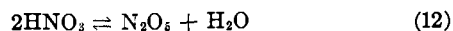
Nitrogen pentoxide is completely dissociated in nitric acid solutions at low temperatures into stably solvated nitronium (NO_2^+) and nitrate (NO_3^-) ions, while the water exists mainly as a solvated molecular species. The complete self-ionization of nitric acid can consequently be expressed, apart from solvation, by the equation:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (13)$$
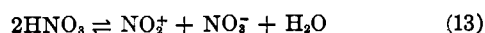
The equilibrium constant for this process, defined in terms of mole fractions and activity coefficients

$$K_s = \frac{(x_{NO_2^+})(x_{NO_3^-})(x_{H_2O})(\gamma_\pm)(\gamma_{H_2O})}{(x_{HNO_3})^2(\gamma_{HNO_3})^2} \qquad (14)$$

was calculated by Lee and Millen (121) for several temperatures using cryoscopic and conductance data (see table 19).

While the mechanism of the total self-ionization of nitric acid is due, principally, to self-dehydration, about 10–15 per cent of the process could be attributed to the autoprotolysis

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \qquad (15)$$
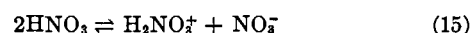
The extensive evidence available in favor of the former mechanism of self-ionization has been discussed in detail by Gillespie, Hughes, and Ingold (79) and by Dunning and Nutt (58), in conjunction with their cryoscopic studies of nitric acid in the presence of additives. Their discussions and the conclusions reported by other investigators in subsequent papers are summarized below.

(i) The nitronium and nitrate ions have been identified in the Raman spectrum of pure nitric acid by the weak lines at 1400 cm.$^{-1}$ and 1050 cm.$^{-1}$, respectively (92). A nitronium ion fundamental at 2360 cm.$^{-1}$ has

TABLE 19

Equilibrium constant for self-ionization of nitric acid

| Temperature	10^5K	Reference
°C.		
−40	2.44	Dunning and Nutt (58)
−20	1.602	Lee and Millen (121)
−10	0.930	Lee and Millen (121)
+25	0.280	Taylor, Lynne, and Follows (197)

been observed in the infrared spectrum of a sample of liquid nitric acid 18.4 μ thick (132). The only spectral effect resulting from the addition of 6 per cent by weight of nitrogen pentoxide to nitric acid solutions consists in the superposition of the lines of the nitronium and nitrate ions on the normal Raman spectrum of the acid (92). At the same time, the absence of the known frequencies of molecular nitrogen pentoxide demonstrates its complete dissociation into these ions.

The formation of ions upon the addition of nitrogen pentoxide to nitric acid is also confirmed by the corresponding large increase in the electrical conductivity of the acid.

Nuclear spin resonances of the nitrogen nucleus in nitronium ions, nitrate ions, and nitric acid exhibit chemical shifts relative to the resonance frequency for undissociated nitrogen pentoxide (153). For solutions of nitrogen pentoxide in nitric acid, the N^{15} resonance

recorded by Ogg and Ray (153) showed a single line at the average of the resonance frequencies for nitronium and nitrate ions and for nitric acid, indicating the presence of extremely rapid chemical exchange between these three species.

(*ii*) Evidence for the presence of water in analytically anhydrous nitric acid has been obtained by Chédin and Fénéant (32), who have identified two very weak bands in the Raman spectrum of pure nitric acid, at 2980 and 3550 cm.$^{-1}$, as belonging to a hydrogen-bond solvate of water. The ionization of water in nitric acid solutions, which could take place according to the equation

$$HNO_3 + H_2O \rightleftharpoons NO_3^- + H_3O^+ \qquad (16)$$
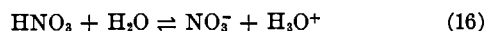
occurs only to a small extent. This has been substantiated by the observations that the electrical conductivity of nitric acid solutions containing as much as 8–10 per cent by weight of water is smaller than that of the pure acid (47, 180, 206) and that the intensity of the Raman line at 1050 cm.$^{-1}$, identifying the nitrate ion in the spectrum of nitric acid, remains practically unchanged upon addition of up to 10 per cent by weight of water (28, 172, 174).

The equilibrium expressed by the equation

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (13)$$
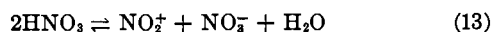
can be reversed by the addition of the products, which also confirms the proposed mechanism of self-ionization (28, 92).

(*iii*) The nitric acidium ion ($H_2NO_3^+$) has not been detected in the Raman spectrum of nitric acid. However, addition of sulfuric or perchloric acid suppresses the self-ionization of nitric acid, possibly owing to the reaction

$$HNO_3 + HClO_4 \rightleftharpoons H_2NO_3^+ + ClO_4^- \qquad (17)$$
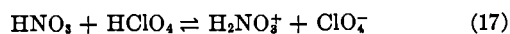
The nitric acidium ion thus formed would repress the autoprotolysis (58). Hughes, Ingold, and Reed (91) have shown that the autoprotolysis is a necessary step in the kinetics of nitronium-ion formation. On the other hand, the shape of the N^{14} spin resonance line for the nitronium ion in solutions of nitric and sulfuric acids was interpreted by Ogg and Ray (153) as evidence that the ion existed as NO_2^+, not $H_2NO_3^+$.

(*iv*) The products of self-ionization are strongly solvated, as indicated by the following evidence: The hydration of nitrogen pentoxide dissolved in pure nitric acid involves a highly endothermal step (35), which can be attributed to the desolvation of strongly solvated ions. The addition of up to 23 per cent of nitrogen pentoxide to nitric acid has only a negligible effect on the total vapor pressure (11), a behavior suggesting that the ionic species formed by the dissociation of

nitrogen pentoxide are strongly solvated and do not associate easily in the stated concentration range.

The solvation of the nitrate ion is evidenced by the large exothermic heat of solution of sodium or potassium nitrate dissolved in nitric acid, which is of the order of 6 kcal. mole^{-1} (35). Chédin and Vandoni (36) were able to show that the formation of a stable hydrogen-bonded complex of the form $(NO_3^-) \cdot (HNO_3)_2$ could quantitatively account for the lowering of the vapor pressure of nitric acid by potassium nitrate. In agreement with this view, compounds of nitric acid with ammonium or alkali metal nitrates, having the general formulas $MNO_3 \cdot HNO_3$ and $MNO_3 \cdot 2H_2O$, have been described in the literature. Changes observed in the Raman spectrum of nitric acid upon addition of sodium or potassium nitrate have been ascribed to the formation of hydrogen bonds of the type —OH$\cdots$O$^-$ (33). Gillespie, Hughes, and Ingold (79) have accepted the value of 2 for the solvation number of the nitrate ion proposed by Chédin and Vandoni and assigned the same solvation number to the nitronium ion in order to account for the configuration of their freezing-point diagram.

The solvation of water in nitric acid has been demonstrated by similar arguments (32, 34, 35).

The partial vapor pressure of water over nitric acid–water solutions is very small at concentrations up to 20 per cent by weight of water. The solution of water in nitric acid is a strongly exothermal process, involving about 4 kcal. mole.$^{-1}$ Finally, when water is added to nitric acid, the high-frequency OH band at 3400 cm.$^{-1}$ in the Raman spectrum of nitric acid is replaced by a group of several bands. These spectral modifications are almost identical with those occurring upon addition of alkali nitrates to pure nitric acid and suggest the formation of a stable hydrogen-bonded solvate. The exact composition of this solvate has not been unambiguously determined. The freezing-point data of Gillespie, Hughes, and Ingold (79) indicate the formation of a complex having the formula $(H_2O) \cdot (HNO_3)_2$, while Chédin, Fénéant, and Vandoni (34) reported the complex to be a monohydrate, $(H_2O) \cdot (HNO_3)$. Since the data of Gillespie, Hughes, and Ingold have been obtained for solutions containing from 0 to 5 per cent by weight of water and those of the latter investigators refer to solutions containing from 5 to 20 per cent of water, the proposed compositions of the water–nitric acid complex are not necessarily contradictory (79).

Chédin (28) has suggested that the equilibrium

$$2(H_2O) \cdot (HNO_3) \rightleftharpoons (H_2O) \cdot (HNO_3)_2 + H_2O \qquad (18)$$
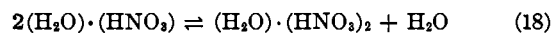
is established in concentrated solutions of nitric acid. At concentrations below 85 per cent HNO_3 the equilibrium is strongly displaced to the left.

Recently, Lloyd and Wyatt (124, 125) tested the rigor of the assumptions made in earlier studies of

TABLE 20

Entropy of nitric acid

Contributions	Entropy
	cal. deg.$^{-1}$ mole^{-1}
0–15°K., Debye extrapolation	0.243
15–231.51°K., graphical integration	19.443
Entropy of solid at melting point (231.51°K.)	19.686
Fusion	10.812
231.51–298.1°K., graphical integration	6.688
Entropy of liquid at 298.1°K. and 62.9 mm.Hg	37.19
Vaporization at 298.1°K. and 62.9 mm.Hg	31.38
ΔS for compressing the gas from 62.9 mm.Hg to 1 atm.	−4.95
Entropy of gas at 298.1°K. and 1 atm. (Third Law)	63.62

0°C = 273.10°K.

nitric acid as a solvent. The vapor pressure and cryoscopic data for nitric acid solutions can be interpreted satisfactorily in terms of ideal solutions in which the solutes are assigned fixed solvation numbers. But, for the analysis of the heats of solutions in nitric acid, these authors believe that neither fixed solvation numbers nor complete dissociation of nitrogen pentoxide in nitric acid is a valid assumption. In addition, the presence of undissociated nitrogen pentoxide molecules in nitric acid solutions and the increase in their concentration with temperature have been suggested in kinetic studies of the thermal decomposition of nitric acid (discussed in detail in a later section).

V. THERMODYNAMIC PROPERTIES OF NITRIC ACID

A. ENTROPY

1. Entropy of nitric acid in the solid, liquid, and vapor phases

Forsythe and Giauque (67) have calculated the absolute entropy of pure nitric acid from calorimetric data. The results are summarized in table 20.

TABLE 21

Itemized contributions to the entropy of nitric acid vapor at 298.1°K.

Contributions	Entropy
	cal. deg.$^{-1}$ mole^{-1}
Translational	38.35
Rotational	23.35
Vibrational, ν = 465 cm.$^{-1}$	0.75
583 cm.$^{-1}$	0.47
680 cm.$^{-1}$	0.33
765 cm.$^{-1}$	0.24
886 cm.$^{-1}$	0.15
1320 cm.$^{-1}$	0.03
1335 cm.$^{-1}$	0.03
1710 cm.$^{-1}$	0.00
3560 cm.$^{-1}$	0.00
Total calculated entropy	63.70
Entropy from thermal data	63.62

2. Comparison of entropy of nitric acid vapor calculated from calorimetric and spectroscopic data

The entropy of nitric acid vapor at 298.1°K. has recently been computed by Cohn, Ingold, and Poole (37) from their spectroscopic measurements, neglecting anharmonicity and gas imperfection. The results are given in table 21. The agreement is within the accuracy of the calorimetric determinations.

The entropy contribution of the hydrogen twisting vibration (465 cm.$^{-1}$) is somewhat uncertain, owing to the neglect of its large anharmonicity. A more accurate value of 0.67 cal. deg.$^{-1}$ mole^{-1} is obtained from the difference between the calorimetric and the calculated entropies, the contribution of the hydrogen twisting vibration being excluded from the latter value. Thus, a corresponding potential barrier of 10.2 kcal. mole^{-1}, restricting the rotation of the hydroxyl group around the N—O bond in the gas molecules, was computed by

TABLE 22

Thermodynamic functions of nitric acid

Ideal gaseous state at 1 atm.

T	$\dfrac{-(F° - H_0°)}{T}$		$\dfrac{(H° - H°)}{T}$		$S°$		$C_p°$	
	A	B	A	B	A	B	A	B
°K.	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}	cal. deg.$^{-1}$ mole^{-1}
298.16	53.99	54.22	8.92	9.46	62.90	63.68	11.42	12.80
300	54.05	54.28	8.93	9.48	62.97	63.75	11.46	12.86
325	54.77	55.05	9.15	9.77	63.91	64.81	12.01	13.49
350	55.45	55.78	9.37	10.05	64.82	65.83	12.53	14.09
375	56.11	56.48	9.60	10.34	65.71	66.82	13.04	14.67
400	56.73	57.16	9.83	10.63	66.56	67.79	13.52	15.21
425	57.34	57.82	10.06	10.92	67.39	68.73	13.98	15.74
450	57.92	58.45	10.29	11.20	68.21	69.65	14.42	16.22
475	58.48	59.06	10.52	11.48	68.99	70.53	14.83	16.66
500	59.03	59.66	10.74	11.74	69.77	71.40	15.22	17.10

A = contributions of translations, overall rotations, and vibrations.
B = includes contributions of internal rotation.

Cohn, Ingold, and Poole (37). A potential barrier of this order of magnitude could be produced by internal hydrogen bonding in the gas molecules, as originally suggested by Forsythe and Giauque (67). The same conclusions were reached by Palm and Kilpatrick (155).

B. THERMODYNAMIC PROPERTIES OF GASEOUS NITRIC ACID

Palm and Kilpatrick (155) have calculated the thermodynamic properties of gaseous nitric acid between 298.16°K. and 500°K., based on recent determinations of its vibrational spectrum. The fundamental frequencies used in this calculation have been presented in Section V,A,2. Although there is disagreement (Section III,R,3) in the assignment of some of the vibrational bands, statistical mechanical calculations made with the data will not be materially affected. The results are summarized in table 22.

Thermodynamic functions previously computed by Forsythe and Giauque (67) agree with the data presented in table 22 within 1 cal. deg.$^{-1}$ mole^{-1}.

C. THERMODYNAMIC FUNCTIONS OF VAPORIZATION

The authors have calculated the enthalpy of vaporization, the standard free energy of vaporization, and the fugacity of nitric acid as a function of temperature, using the thermal data of Forsythe and Giauque (67) and the heat capacities for the vapor obtained by Palm and Kilpatrick (155) from spectroscopic data. The enthalpy and free energy are reported below in terms of convenient analytical expressions; the functions are given in calories per mole and the temperature in degrees Kelvin.

1. Enthalpy

For the temperature range from 0°C. to 100°C. (0°C. = 273.16°K.)[1], the standard enthalpy of vaporization can be expressed by the equation

$$\Delta H^\circ_{vap.} = 14,744 - 22.759T + 1.3100 \times 10^{-2}T^2 + 5.6116 \times 10^{-6}T^3 \quad (19)$$

TABLE 23

Standard free-energy change and equilibrium constant for the vaporization of pure nitric acid and the fugacity of pure nitric acid

T	ΔF°	K	f
°C.	cal. mole^{-1}	atm.	mm. Hg
0	2144	0.0192	14.6
10	1873	0.0358	27.2
20	1607	0.0633	48.1
30	1346	0.107	81.4
40	1089	0.174	132
50	836	0.272	207
60	587	0.412	313
70	341	0.606	461
80	99	0.868	660
90	−139	1.213	922
100	−375	1.659	1261

2. Free energy

The standard free energy of vaporization can be expressed by the equation

$$\Delta F^\circ_{vap.} = 14,744 - 170.02T + 22.759T \ln T - 1.3100 \times 10^{-2}T^2 - 2.0858 \times 10^{-6}T^3 \quad (20)$$

and is valid in the same temperature range.

3. Equilibrium constant and fugacity

The equilibrium constant, K, for the vaporization process

$$HNO_3(l) = HNO_3(g) \quad (21)$$
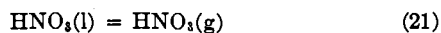
[1] A correction was applied to the data of Forsythe and Giauque, who used a slightly different temperature scale (0°C. = 273.10°K.).

TABLE 24

Heat of formation of nitric acid

$\Delta H^\circ_{298.1}$	References
cal. mole^{-1}	
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3(l)$	
−41,610	Thomsen (199)
−41,600	Berthelot (12)
−41,349	Forsythe and Giauque (67, 68, 69)
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3$ (aq. $a = 1$)	
−49,320	Forsythe and Giauque (67, 68, 69)
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3(g)$	
−31.994	Forsythe and Giauque (67, 68, 69)

has been calculated from the standard free energy of vaporization. The equilibrium constant is, in this case, equal to the fugacity of the pure acid.

In table 23 are listed values for the thermodynamic functions in the range from 0°C. to 100°C. Egan's earlier calculation is not recommended because of his use of obsolete data (see Section III,G).

D. HEAT OF FORMATION

The earlier determinations of Thomsen and Berthelot are of historical interest only. It is interesting that the agreement with the more recent determination of Forsythe and Giauque is quite good (see table 24).

E. FREE ENERGY OF FORMATION

The free energies of formation of gaseous, liquid, or aqueous nitric acid from its elements in their standard reference states were obtained by Lewis and Randall (122) and Krase (115) from equilibrium measurements, while Forsythe and Giauque (67, 68, 69) used absolute entropies and heats of reaction based on careful calorimetric determinations (see table 25).

TABLE 25

Free energy of formation of nitric acid

$\Delta F^\circ_{298.1}$	References
cal. mole^{-1}	
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3(l)$	
−19,030	Forsythe and Giauque (67, 68, 69)
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3$ (aq. $a = 1$)	
−26,500	Lewis and Randall (122)
−26,345	Forsythe and Giauque (67, 68, 69)
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g)$ $= HNO_3(g)$	
−18,210	Lewis and Randall (122)
−18,560	Krase (115)
−17,554	Forsythe and Giauque (67, 68, 69)

As will be noted, the differences in the values are not great. However, the values given by Forsythe and Giauque[2] are considered the most reliable.

VI. Stability of Nitric Acid

A. THERMAL DECOMPOSITION

1. Early work

The thermal decomposition of nitric acid was apparently first studied by Scheele (185), who stated that nitric acid vapor passing through a heated tube decomposes to form nitrogen dioxide and oxygen. If the tube is white-hot, the products of decomposition are nitrogen and oxygen.

Mitscherlich (150) reported that the decomposition takes place according to the stoichiometry

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$
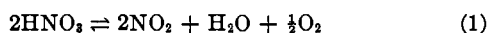
which was confirmed by Carius (26), Berthelot (13, 14, 15), Reynolds and Taylor (177) and represents also the view held at present. Carius determined the degree of decomposition of the acid at various temperatures from vapor density measurements and found it to be 100 per cent at 256°C. (26); this result is reasonably consistent with more recent data. The earlier investigators did not differentiate between the decomposition in the liquid and the vapor phases.

Braham and Gatehouse (22) and Böttger (21) believed that nitrogen and nitrous oxide were produced in addition to nitrogen dioxide, water, and oxygen when nitric acid was heated. The former erroneously stated that pure nitric acid is not decomposed by heat.

Berthelot (13, 14, 15) and Reynolds and Taylor (177) found that the rate of decomposition at room temperature is very slow, equilibrium being reached only after many months. A statement by the latter investigators that the decomposition of the pure acid occurs only after an induction period of about one month has not been confirmed. Berthelot regarded reaction 1 as essentially irreversible, but this opinion was shown to be incorrect (177). Reynolds and Taylor also observed that very large decomposition pressures could develop when nitric acid was enclosed in sealed tubes, and were the first to recognize from this behavior the difficulty of storing highly concentrated acid in air-tight containers for longer periods of time.

2. Kinetics of decomposition in the vapor phase

It is generally accepted at present that the decomposition of nitric acid vapor can be represented by the overall equation

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

with the equilibrium

$$2NO_2 \rightleftharpoons 2NO + O_2 \qquad (22)$$
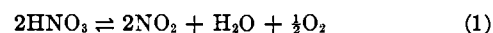
superimposed on that of equation 1.

No agreement exists between different investigators as to the mechanism of decomposition. Fréjacques (71, 73) studied the kinetics of reaction 1 between 260°C. and 475°C. and at pressures up to a few centimeters of mercury. He found that the initial stage of the decomposition was second order with respect to nitric acid and largely homogeneous even at the lower temperatures (95 per cent at 300°C.). Fréjacques suggested that the rate-determining step is

$$2HNO_3 \rightarrow N_2O_5 + H_2O \qquad (12)$$

followed by the decomposition of nitrogen pentoxide according to the Ogg mechanism (152). Nitric oxide formed by reaction 22 is immediately oxidized to nitrogen dioxide by an intermediate, NO_3, and appears as a product only when its rate of formation becomes faster than that of the intermediate. The rate of decomposition of the acid is affected by the appearance of nitric oxide, and can be expressed by the relation:

$$-\frac{d[HNO_3]}{dt} = k_a[HNO_3]^2 + k_b[NO][HNO_3] \qquad (23)$$

The second-order rate constant, k_a, is given as a function of temperature by the equation

$$k_a = 1.5 \times 10^{14} \exp\left(-\frac{33,500}{RT}\right) \text{ liter mole}^{-1} \text{ min.}^{-1} \qquad (24)$$

the experimental energy of activation being 33.5 kcal. mole.$^{-1}$ Above 400°C. the rate and energy of activation are slightly higher. The products of reaction 1 and nitrogen have no influence on the initial rate of decomposition.
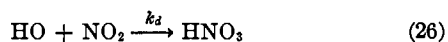
Johnston, Foering, Tao, and Messerly (101) and, later, Johnston, Foering, and Thompson (102) disagreed with some of the above results. The former studied the decomposition of nitric acid vapor between 100°C. and 465°C., while the latter examined the reaction at 400°C. in some detail. Both groups used nitrogen as carrier gas at 1 atm. total pressure, the partial pressures of the acid varying from 0.1 to about 2 cm. of mercury. According to these investigators, the decomposition is entirely homogeneous only above 400°C., while below 300°C. it is essentially heterogeneous. In the homogeneous range, the reaction was first order with respect to nitric acid; the initial rate was inhibited by nitrogen dioxide and unaffected by the other reaction products,

water vapor and oxygen, or by nitrogen or carbon dioxide. In the presence of an excess of reducing agents, such as nitric oxide, carbon monoxide, hydrogen, methane, and benzene, the rate was first order in nitric acid, zero order with respect to reducing agent, and of the same magnitude as the initial rate of decomposition of nitric acid. There was no evidence of any bimolecular reaction between acid and reducing agent, as found by Fréjacques in the case of nitric oxide.
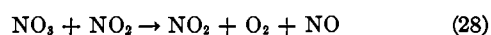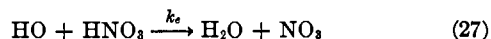
To explain the first-order reaction, Johnston, Foering, Tao, and Messerly suggested that nitric acid decomposes according to the equation

$$HNO_3 \xrightarrow{k_e} HO + NO_2 \tag{25}$$
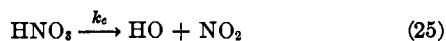
while the work of Johnston, Foering, and Thompson indicated a reversal of this step

$$HO + NO_2 \xrightarrow{k_d} HNO_3 \tag{26}$$

possibly followed by the reactions

$$HO + HNO_3 \xrightarrow{k_e} H_2O + NO_3 \tag{27}$$

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO \tag{28}$$

$$NO_3 + NO \rightarrow 2NO_2 \tag{29}$$

By making the steady-state assumption for the hydroxyl radical, Johnston, Foering, and Thompson obtained the rate equation

$$-\frac{d[HNO_3]}{dt} = 2k_c[HNO_3] \frac{1}{1 + (k_d/k_e) [NO_2]/[HNO_3]} \tag{30}$$

in agreement with an empirical fit of the data. Further evidence for this mechanism was found in that the rate constant k_c increased with increasing concentration of inert gas (102, 103) and, at low pressures, with that of reactant (103), as required by the Lindemann mechanism for a unimolecular reaction such as 25.

Johnston, Foering, and Thompson tried to reconcile the discrepancy between the results of Fréjacques on one hand and those of Johnston, Foering, Tao, and Messerly and themselves on the other by suggesting that, since Fréjacques did not use carrier gas, his experiments were performed at pressures low enough to fall in the second-order region of the unimolecular reaction 25. The disagreement concerning the effect of nitric oxide and the values of the activation energy was removed by the work of Johnston, Foering, and White (103). These investigators observed at very low pressures side reactions involving nitric oxide and water, which were not found at 1 atm. total pressure; furthermore, inhibition by nitrogen dioxide did not follow under these conditions the linear relationship with $(NO_2)/(HNO_3)$ of equation 30. The mechanism responsible for these effects was not determined, but could involve nitrous acid as an intermediate. The low energy of activation found by Fréjacques was attributed by

Johnston, Foering, and White to severe self-cooling at the higher temperatures, caused by the endothermicity of reaction 1.

Below 250°C. reaction 1 is largely heterogeneous (60, 101), but its mechanism is not understood. The rate of reaction, which is extremely slow in this temperature range, is retarded by two of the products, nitrogen dioxide and water vapor, but not by oxygen (101). The energy of activation is about 5 kcal. mole⁻¹ (101). The order of reaction was found to change from a higher to a lower value, at times decreasing to zero; only part of the initial rate data was first order (60, 101). Changes from a positive order to a negative one were also noted in plain reaction cells, but not in cells containing glass powder. Ellis and Murray (60), who made this interesting observation, suggested that heterogeneous and homogeneous reactions occur simultaneously in the plain cells: the rate of the heterogeneous reaction decreases with time owing to wall poisoning, while that of the homogeneous reaction increases, perhaps owing to catalysis by decomposition products.

3. Kinetics of decomposition in the liquid phase

The decomposition of nitric acid in the liquid phase proceeds by the same stoichiometry as in the gas phase (70, 179)

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2 \tag{1}$$
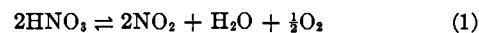
with the fast equilibrium

$$2NO_2 \rightleftharpoons N_2O_4 \tag{31}$$

being established simultaneously. The reaction is homogeneous and much faster than in the gas phase at comparable temperatures (179).

The mechanism of the liquid-phase decomposition is still a matter of conjecture. According to Franck and Schirmer (70) the rate of reaction between 40°C. and 80°C. is proportional to the concentration ratio $(HNO_3)^2/(H_2O)$ and thus, by virtue of equilibrium 12, to the concentration of nitrogen pentoxide resulting from the self-dehydration of the acid. This behavior suggested that the first-order decomposition of nitrogen pentoxide is the rate-determining step in the decomposition of nitric acid. Franck and Schirmer supported this conclusion by pointing out that the energy of activation and temperature dependence of the latter reaction were in agreement with the corresponding values for the decomposition of the pentoxide. However, the activation energy of about 24 kcal. mole⁻¹ reported by these authors for nitric acid agrees well only with activation energy for the decomposition of nitrogen pentoxide in the gas phase and in inert solvents (50, 63) but is significantly lower than the value of 28.3 kcal. mole⁻¹ found when the pentoxide was dissolved in nitric acid (64). Even higher energies of activation, up

to 38.7 kcal. mole^{-1}, were reported by other investigators (39). Franck and Schirmer were also not aware of the self-ionization of nitric acid and did not consider its possible effect on the mechanism.

Robertson, Mason, and Corcoran (179) studied the liquid-phase decomposition of the pure acid between 54°C. and 88°C. and the effect of various additives on this reaction. They found that the initial rate was increased by ammonium nitrate and nitrogen pentoxide, and decreased by nitrogen tetroxide, potassium nitrate, potassium bisulfate, sulfuric acid, nitrosylsulfonic acid (NOHSO$_4$), chloric acid, and water. Water was the most effective inhibitor on both a molal and a weight basis. An examination of the possible ionic equilibria in the presence of additives led to the conclusion that the rate-determining step in the decomposition of nitric acid involved the first-order decomposition of nitrogen pentoxide, as postulated by Franck and Schirmer. Since the pentoxide dissociates in nitric acid, it was not possible to distinguish experimentally between the rate expressions

$$-\frac{d[HNO_3]}{dt} = k_f[N_2O_5] \tag{32}$$

and

$$-\frac{d[HNO_3]}{dt} = k_\theta[NO_2^+][NO_3^-] \tag{33}$$

The apparent energy of activation was 32 kcal. mole^{-1} for the pure acid.

The Franck and Schirmer mechanism was also favored by Tait, Happe, Sprague, and Cordes (192), who showed that their rate measurements at 65°C. and 70°C. could be explained if, respectively, 3.2 and 5.4 per cent of the nitrogen pentoxide from the self-dissociation of nitric acid were in molecular form. However, Cordes, Fetter, and Happe (39) studied more recently the decomposition of liquid nitric acid between 55°C. and 75°C. and the effect of the additives water, nitrogen tetroxide, potassium nitrate, nitronium fluorosulfonate (NO$_2$FSO$_3$), and potassium fluorosulfonate (KFSO$_3$) on the rate of decomposition at 65°C. Contrary to the observations of Robertson, Mason, and Corcoran, nitrogen tetroxide had no effect on the initial rate. Cordes, Fetter, and Happe found the nitrogen pentoxide hypothesis inadequate to account for their results; they proposed a more complex ionic mechanism and an alternative free-radical mechanism, neither of which proved to be entirely satisfactory. Further work, perhaps by spectroscopic techniques, is required to elucidate this problem.

It is interesting to note that none of the above additives is able to prevent extensive decomposition of the acid during long storage periods under ordinary conditions. The use of oxidants appears to be more promising for this purpose, and it is reported that the addition of 1 per cent of lead dioxide will keep highly concentrated nitric acid colorless for over fifteen days at ambient temperatures (73).

B. PHOTOCHEMICAL DECOMPOSITION

Very little information is available on the photolysis of nitric acid. The reaction appears to have been investigated first by Scheele (185) in 1777, who reported that acid of specific gravity of not less than 1.4 is decomposed by sunlight, whereupon oxygen is evolved and the liquid acquires a yellow color. Gay-Lussac (76), Fiedler (66), and Peake (160) confirmed these results.

According to Berthelot (13, 14, 15), the products of the photochemical decomposition are identical to those obtained by thermal decomposition. The reaction proceeds in stages, the first products being nitrous acid and oxygen, followed by a combination of the former with excess nitric acid to produce water and nitrogen dioxide.

Berthelot, and Reynolds and Taylor (177), believed that the photochemical decomposition of nitric acid occurs only in the vapor phase. However, Simon and Höppner (188) have observed the formation of gas bubbles in crystals of pure nitric acid and nitric acid monohydrate when irradiated with light of wavelength 5358 A. Zintl (188) has also noted the evolution of gas from monohydrate crystals exposed to x-rays. It would seem from these observations that nitric acid crystals may also decompose photochemically.

When nitric acid is sealed in tubes, the decomposition pressure developed upon exposure to light is a function of the relative volume of liquid enclosed and independent of the shape and the size of the tube. The pressure, which is due mainly to oxygen, increases with increasing relative volume of liquid until a maximum is reached (177), then decreases and approaches zero for completely filled tubes (22, 177). An interpretation of this apparent reversal of the photochemical decomposition is difficult, owing to the uncontrolled conditions under which the experiments were performed. A comparison with the equilibrium pressures obtained at corresponding temperatures and vapor-to-liquid ratios by thermal decomposition of the acid indicates that the systems studied did not reach thermodynamic equilibrium. The attainment of photostationary states is also not evident.

Reynolds and Taylor have tentatively explained these pressure relations in isochoric systems as due to a competition between the photochemical decomposition of certain (undefined) molecular species present in the vapor and the recombination of the products to form nitric acid in the liquid, or both liquid and vapor. When a large proportion of liquid is present, the recombination becomes relatively greater than the decomposition, and this results in a decrease in the decomposition pressure.

C. THERMODYNAMICS AND VOLUMETRIC BEHAVIOR
AT PHYSICOCHEMICAL EQUILIBRIUM

The free-energy change and equilibrium constant of the reaction

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$
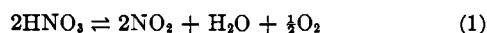
in the gas phase have been determined by Forsythe and Giauque (67, 68, 69) from thermal measurements. Their results are given in table 26.

The equilibrium constant for the gas-phase reaction 1 has also been determined by Jones (104) in the temperature range from 70°C. to 120°C., using an infrared absorption method. The results agree within experimental error with those of Forsythe and Giauque. From the data of the latter investigators, Ellis and Murray (60) calculated the degree of decomposition of nitric acid vapor and found it to be 100 per cent at about 200°C. and a pressure of 1 atm.

The thermodynamic functions for reaction 1 in the liquid phase have not been measured, to the best knowledge of the authors. The volumetric behavior of this reaction in the liquid and gas–liquid regions has been investigated by Reamer, Corcoran, and Sage (173) and by Kay and Stern (106), and the reversibility of the reaction was demonstrated. Reamer, Corcoran, and Sage measured the specific volume of nitric acid at physical and chemical equilibrium between 88°C. and 170°C. and at pressures up to 340 atm. Kay and Stern determined the relation between temperature, equilibrium pressure, and ratio of gas volume to total volume between 76°C. and 125°C. and up to 109 atm. A summary of their data is given in table 27. Specific volumes of the heterogeneous gas–liquid system at physicochemical equilibrium are somewhat higher than those reported by Reamer, Corcoran, and Sage (173) in the same pressure and temperature range. The disagreement can be attributed to the effect of a trace of

TABLE 26

Free-energy change and equilibrium constant for the reaction
$$H_2O(g) + 2NO_2 + \tfrac{1}{2}O_2 = 2HNO_3(g)$$
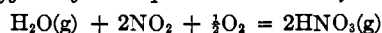
$$\Delta H_0^\circ = -19{,}998 \text{ cal. mole}^{-1}$$

T	$\dfrac{\Delta(F^\circ - H_0^\circ)}{T}$	$\Delta F^\circ/T$	ΔF°	K
°K.	cal. deg.$^{-1}$mole^{-1}	cal. deg.$^{-1}$mole^{-1}	cal.mole^{-1}	atm.$^{-3/2}$
273	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}

0°C. = 273.10°K.

TABLE 27

Relation between equilibrium pressure, gas-to-total volume ratio (V^g/V), and specific volume of nitric acid at physicochemical equilibrium between 76°C. and 125°C.

Equilibrium Pressure	V^g/V	Specific Volume	V^g/V	Specific Volume	V^g/V	Specific Volume
	76°C.		85°C.		95°C.	
atm.		cm.^{3} g.$^{-1}$		cm.^{3} g.$^{-1}$		cm.^{3} g.$^{-1}$
13.6	0.690	2.140	0.726	2.407	0.780	3.020
20.4	0.558	1.491	0.590	1.616	0.637	1.816
27.2	0.460	1.240	0.487	1.322	0.525	1.429
40.8	0.319	1.006	0.340	1.041	0.368	1.103
54.4	0.229	0.8859	0.245	0.9108	0.264	0.9527
68.1	0.169	0.8172	0.180	0.8378	0.193	0.8671
81.7	0.125	0.7779*	0.133	0.7972*	0.143	0.8134
95.3	0.092	—	0.098	—	0.105	0.7829*
108.9	0.066*	—	0.069*	—	0.074	—
	105°C.		115°C.		125°C.	
13.6	0.846	4.216	0.934	7.167	—	—
20.4	0.694	2.239	0.774	2.854	0.867	5.074
27.2	0.573	1.616	0.642	1.903	0.726	2.426
40.8	0.401	1.171	0.445	1.279	0.511	1.453
54.4	0.288	0.9951	0.319	1.058	0.364	1.144
68.1	0.209	0.9002	0.234	0.9433	0.266	1.001
81.7	0.153	0.8415	0.171	0.8740	0.195	0.9165
95.3	0.111	0.8066	0.123	0.8297	0.141	0.8615
108.9	0.078	—	0.085*	0.8003*	0.098	0.8241

* Extrapolated.

water (of the order of 0.5 per cent) in the acid used by the latter investigators, which is known to influence markedly the volumetric behavior at low values of V^g/V.

The magnitude of the pressures developed by pure nitric acid at physicochemical equilibrium is striking, especially when compared to its vapor pressure at comparable temperatures, and illustrates the difficulty of storing such acid under isochoric conditions. The high pressures are due to the very low solubility of one of the decomposition products, oxygen, in the solution of the other products and nitric acid.

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