Lawrence Berkeley National Laboratory

Recent Work

Title

IONIZATION OF STRONG ELECTROLYTES. IX. PROTON MAGNETIC RESONANCE IN THE
TERNARY SYSTEM HNO₃-DNO₃-H₂O D₂O

Permalink

<https://escholarship.org/uc/item/49j2z789>

Author

Merbach, A.

Publication Date

1966-11-01

University of California

Ernest O. Lawrence
Radiation Laboratory

IONIZATION OF STRONG ELECTROLYTES. IX. PROTON
MAGNETIC RESONANCE IN THE TERNARY SYSTEM HNO_3 - DNO_3 - H_2O - D_2O

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract W-7405-eng-48

IONIZATION OF STRONG ELECTROLYTES. IX. PROTON MAGNETIC
RESONANCE IN THE TERNARY SYSTEM $\text{HNO}_3\text{-DNO}_3\text{-H}_2\text{O-D}_2\text{O}$

A. Merbach

November 1966

IONIZATION OF STRONG ELECTROLYTES. IX. PROTON MAGNETIC
RESONANCE IN THE TERNARY SYSTEM HNO_3 - DNO_3 - H_2O - D_2O

A. Merbach*

Inorganic Materials Research Division,
Lawrence Radiation Laboratory
University of California, Berkeley, California

Abstract

Nuclear magnetic resonance (NMR) was previously established as a reliable method for the determination of the degree of dissociation. The proton magnetic resonance shift has been measured in the full range of the ternary system HNO_3 - DNO_3 - H_2O - D_2O . The two nitric acids are about equally strong at 32°C, but at 0° deuterionitric acid is weaker, at 63° stronger than HNO_3 .

---

* Present address: Institut de Chimie Minérale et Analytique, Université de Lausanne, Switzerland.

The system $\text{HNO}_3\text{-DNO}_3\text{-H}_2\text{O}$ is a ternary system because of the instantaneous exchange of D and H in an aqueous solution. Since the usefulness of the NMR-method for investigating dissociation has been fully established^{1,2}, it is interesting to compare the strength of HNO_3 and DNO_3 . Moreover, there appears to be a possibility that a complete investigation of nitric and other light and heavy acids may lead to further progress regarding the structure of the hydrogen ion³.

Substances

Anhydrous nitric acid was prepared by vacuum distillation from a mixture with sulfuric acid. For the small amounts required, more efficient but also more complicated equipment⁴ presents no advantage.

Deuteronitric acid was prepared by the method developed by Redlich and Nielsen⁵. Nitrogen tetroxide is oxidized to the pentoxide by means of ozone and under proper precautions combined with heavy water. Any traces of nitrogen oxides, formed during the reaction or later, are easily removed by means of ozone.

The content of acid in the anhydrous acid and in stock solutions was determined by weight titration with sodium hydroxide solution and methyl red. The primary standard was a freshly distilled solution of hydrochloric acid; its acidity was determined by precipitating and weighing silver chloride. All weights were corrected for buoyancy. The accuracy obtained was about 0.01%.

---

¹ Hood, Redlich and Reilly, J. Chem. Phys. 22, 2067 (1954).

² G. C. Hood and C. A. Reilly, J. Chem. Phys. 32, 127 (1960).

³ cf. A. J. Kresge and A. L. Allred, J. Amer. Chem. Soc. 85, 1541 (1963).

⁴ A. Potier, Ann. Fac. Sci. Univ. de Toulouse, Sér. 4, 20, 1 (1956).

⁵ O. Redlich and L. E. Nielsen, J. Amer. Chem. Soc. 65, 654 (1943).

Measurement

A spectrometer A-60 (Varian Associates) equipped with a variable temperature probe (V-6058) was used for the proton magnetic resonance determinations. The side-band technique applied to this instrument leads to a precision of about 0.001 ppm.

The high sensitivity of the chemical shift of our solutions to temperature made it necessary to develop a technique of temperature measurements which would give consistent results to within $\pm 0.2^\circ\text{C}$ ⁶. A capillary filled with a mixture of water, methanol, and hydrochloric acid exhibits two sharp resonance lines. The chemical shift between these two lines is strongly, and approximately linearly, dependent on the sample temperature. This technique has the advantage that, after calibration, one can measure the sample temperature at precisely the same region of the sample which furnishes the shift signal. The technique is independent of the sample spinning rate and the flow of nitrogen used to control the sample temperature.

Freshly boiled water was used as an external reference. The water and the temperature reference solution were contained in two separate capillaries (1 mm), both placed in a standard 5 mm NMR tube.

Bulk Susceptibility

Since an external reference is used, the chemical shift δ is obtained from the resonance field strength H of the solution and the field H_0 for water by means of a correction term g defined by the relation

---

⁶ R. W. Duerst and A. Merbach, Rev. Scient. Instr. 36, 1896 (1965).

$$s = (H_0/H - 1) \cdot 10^6 + g. \quad (1)$$

The term g is given⁷ by the "bulk susceptibilities", namely, the volume magnetic susceptibilities χ and χ_0 of the acid solution and water, according to

$$g = (2\pi/3)(\chi - \chi_0) \cdot 10^6. \quad (2)$$

For HNO_3 , measurements of the (gram) magnetic susceptibility⁸ κ and available data⁹ for the density d furnish the volume susceptibility

$$\chi = \kappa \cdot d. \quad (3)$$

The results of Pacault and Chédin were represented as a function of the weight fraction (gram HNO_3 per gram of solution) by

$$10^6 \kappa = -0.7184 + 0.465 w - 0.0676 w^2 + 0.0038 w^3 \quad (4)$$

with a standard deviation of 0.002.

For deuterionitric acid and mixed solutions an estimate of the correction term g can be based on the assumption that the molal susceptibility, i.e., the product

$$\chi \cdot V$$

of the volume susceptibility and the volume V of one mole of the solution is independent of the deuterium fraction r . Observed data¹⁰ confirm this theoretically plausible assumption for water. The ratio of the molal

⁷ cf. C. Lussan, J. Chim. Phys. 60, 1100 (1965).

⁸ A. Pacault and J. Chédin, Mém. Soc. Chim. 180, 766 (1950).

⁹ P. Pascal, Nouveau Traité de Chimie Minérale, tome I, 814 and tome X, 468-470 (1956).

¹⁰ Ibid. tome I, 822 (1956).

volumes V'_O of H_2O and V''_O of D_2O is

$$V'_O/V''_O = 0.9973 \quad (5)$$

at $25^\circ C$; the corresponding ratio for HNO_3 and DNO_3 is⁵

$$V'_1/V''_1 = 0.9974 \quad (6)$$

For the molal volume V of a mixture with a D-fraction r and the volume V' of a light mixture of the same acid concentration one will assume

$$V/V' = 1 - r + r/0.9974 = 1 + 0.0026 r. \quad (7)$$

The assumption of independence of the molal susceptibility of the isotopic composition leads to the relation

$$\chi V = \chi' V' \quad (8)$$

between the molal susceptibility χV of a solution and the value $\chi' V'$ for the corresponding light solution.

A first approximation following from (5) to (8) would be

$$\chi = \chi' V'/V = \chi'/(1 + 0.0026 r). \quad (9)$$

A second approximation, that may be slightly better, is obtained with the aid of measurements of V'_O/V''_O as a temperature function¹¹. The data are represented by

$$V'_O/V''_O = 0.99406 + 0.1081 \cdot 10^{-3} t + 0.783 \cdot 10^{-6} t^2 \quad (10)$$

with a standard deviation of 0.0001. We assume that the value (6) for V'_1/V''_1 is independent of the temperature. We introduce the mole fraction x of acid ($HNO_3 + DNO_3$) and obtain instead of (9) the result

$$\chi = \chi'/[1 - r + r(1-x) V''_O/V'_O + 1.0026 rx]. \quad (11)$$

The differences between (9) and (11) do not exceed $0.006 \cdot 10^{-6}$.

---

¹¹ T.-L. Chang and L.-H. Tung, Nature, 163, 737 (1949).

Relation (11) was used for the computation of g .

Results

The observed proton magnetic resonance shifts s , corrected for the susceptibility of the medium by addition of g , are shown in Table I as a function of the D-fraction ($D/[D+H]$), the mole fraction of acid ($\text{HNO}_3 + \text{DNO}_3$), and the temperature.

Parabolic interpolation of s with respect to the temperature furnished the values at 0° , 32° and 63°C , given in Tables II ($x < 0.5$) and III ($x > 0.5$).

Upper Range. If the shifts in the upper range are plotted against Gutowsky's variable

$$p = 3x/(2-x) \quad (12)$$

the accuracy of the linear relation between s and p in the region $0.6 < x < 0.95$ is remarkable. In a previous paper of this series¹, the linearity was interpreted as indicating the completeness of the reaction

Denoting by s_2 and s_3 the specific proton shifts for the monohydrate H_3NO_4 and the dimer $(\text{HNO}_3)_2$, respectively, one finds for solutions containing less than one H_2O for one HNO_3

$$s = 0.5 (s_3 - s_2) p + 1.5 s_2 - 0.5 s_3 \quad (14)$$

This interpretation is now confirmed by the present, more precise, data.

It is also extended to deuteronic acid solutions.

But there are minor deviations near $x = 0.5$ and $x = 1.0$. Near the equimolal composition, a small part of the acid is dissociated into ions. Its influence on s can be obtained from an approximate algebraic

representation of the shifts derived for $x < 0.5$. The contribution of the ions is given by

$$C = B_1 [1 + 0.49 p (B_2 - p)(3 - p)] / [1 + B_3 (B_2 - p)^2] - B_1 / (1 + B_3 B_2^2). \quad (15)$$

The coefficients B_1 , B_2 , B_3 depend on the temperature and D-fraction according to

$$B_1 = 0.2626 (1 - 0.642 \cdot 10^{-2} t + 0.144 r + 0.149 r^2) \quad (16)$$

$$B_2 = 0.7493 (1 - 0.063 \cdot 10^{-2} t - 0.063 r + 0.046 r^2) \quad (17)$$

$$B_3 = 24.76 (1 - 0.231 \cdot 10^{-2} t - 0.120 r) . \quad (18)$$

Near $x = 1$, the shift increases sharply beyond the linear relation (14). It is known that in nitric acid above $x = 0.95$ dissociation according to

occurs to the extent of a few per cent. But this reaction would require a lowering of s below (14) rather than an increase beyond it since the specific shift s_3 for the dimer is higher than s_2 for the monohydrate. It is possible that the nitronium ion NO_2^+ is so strongly paramagnetic that its influence on the bulk susceptibility causes the excess over (14). However, in this case one would expect a very large broadening of the resonance peak, contrary to observation. More plausible is therefore the interpretation that the increase is due to polymerization of the acid beyond the dimer at $x > 0.95$.

Empirically the excess above (14) is represented by

$$E = 0.133 / [0.01 + (3.214 - p - 0.00021 r [63 - t])^2] - 0.002 . \quad (20)$$

In interpreting the resonance data, one always wishes to refer the shift of a solution to water of the same D-fraction while the experimental data refer to pure H_2O . The shift of heavy water has been measured

and represented by the "water function"

$$W = - 0.019 r (1 + 0.017 t) . \quad (21)$$

The algebraic representation of the shifts for $x > 0.5$ is now given by

$$s = A_1 + A_2 p - W + C + E . \quad (22)$$

The functions W , C and E are given by (15) to (18), (20) and (21). The coefficients A_1 and A_2 are

$$A_1 = 1.5s_2 - 0.5s_3 = 2.669(1 - 5 \cdot 10^{-5}t + 0.084 r - 71 \cdot 10^{-5}rt) \quad (23)$$

$$A_2 = 0.5(s_3 - s_2) = 1.428(1 + 61 \cdot 10^{-5}t - 0.011 r + 33 \cdot 10^{-5}rt) . \quad (24)$$

The differences Δs of the observed data and the values computed according to (22) are shown in Table III.

The specific shift s_2 of the monohydrate H_3NO_4 is found to be

$$s_2 = A_1 + A_2 = 4.097 + 74 \cdot 10^{-5}t + 0.208 r - 143 \cdot 10^{-5}rt . \quad (25)$$

This relation is used in the computation of the degrees of dissociation.

For HNO_3 at 25° one obtains $s_2 = 4.115$. The first investigation¹ estimated $s_2 = 4.25$, well within the limits of error. The estimate $s_2 = 3.55$ of a later study² depends in part on results for Raman intensities.

Similarly we obtain from (23) and (24)

$$s_3 = A_1 + 3A_2 = 6.953 - 250 \cdot 10^{-5}t + 0.176 r - 48 \cdot 10^{-5}rt \quad (26)$$

or, for HNO_3 at 25° , $s_3 = 6.890$ while the older measurement¹ gave $s_3 = 7.00$ in good agreement.

The representation of s by (22) is theoretically sound and the number of empirical parameters will be considered to be ample. Nevertheless the standard deviation 0.032 is considerably larger than the estimated experimental error, roughly ten times as large.

Lower Range. An extensive effort to find an algebraic representation for the lower range ($x < 0.5$) was unsuccessful. The limiting slopes

$$s_1 = \lim_{p \rightarrow 0} ds/dp \quad (27)$$

were found graphically. They are satisfactorily represented by

$$s_1 = 10.17 + 3.23 r + 0.82 \cdot r^{10} + (3.02 - 1.54 r - 1.70 r^2) \cdot 10^{-2} t. \quad (28)$$

The previously¹ derived relation for the degree of dissociation α

$$s/p = s_1 \alpha + s_2 (1-\alpha) \quad (29)$$

permits the computation of α since s_1 and s_2 are given by (28) and (25). The results for α for the three temperatures, for the whole range of r , and for $x < 0.5$ are shown in Table II. The results for HNO_3 are in satisfactory agreement with earlier data^{1,2,12}.

For a comparison of the results for HNO_3 with earlier data², and for the comparison of HNO_3 and DNO_3 , Figures 1 to 3 show the deviation function

$$F = \alpha - 1 + 2x \quad (30)$$

as a function of x for three temperatures (diagrams of α would not be sufficiently sensitive to show the deviations). The curves must be lower than the straight line shown at the left end since $\alpha < 1$, and higher than the line shown at the right end since $\alpha > 0$.

At 0° , DNO_3 is much weaker than HNO_3 , but at 63° , the values of α for HNO_3 have dropped appreciably more than for DNO_3 . At 32° the strength of the two acids is about equal, as predicted by Halpern¹³.

Equation (29) is based on the assumption that the specific shift s_1

---

¹² Young, Maranville and Smith, in "Structure of Electrolytic Solutions" edited by W. J. Hamer (John Wiley & Sons, New York 1959), p. 35.

¹³ O. Halpern, J. Chem. Phys. 3, 456 (1935).

of the hydrogen ion does not change with the concentration of the acid. Results obtained for perchloric acid, to be presented in the next paper of this series, appear to indicate that s_1 varies with the degree of hydration of the hydrogen ion. This question and a more detailed analysis of the dissociation of nitric acid will be discussed in a later paper of this series.

Acknowledgements

This work was performed under the auspices of the United States Atomic Energy Commission at the Lawrence Radiation Laboratory of the University of California. The author sincerely appreciates the invitation of the Inorganic Materials Research Division of the Lawrence Radiation Laboratory to carry out this investigation, and the support extended to him. Further financial support from the "Stiftung für Stipendien auf dem Gebiete der Chemie, Zürich, Switzerland" is gratefully acknowledged.

I should like to thank Dr. Otto Redlich for suggesting the problem and for numerous valuable discussions. I should also like to thank Dr. C. M. Sederholm and Dr. R. W. Duerst for very helpful discussions and criticism.

TABLE I
SUSCEPTIBILITY CORRECTION AND CORRECTED SHIFTS

D-fraction r	Mole fraction of acid x	Temp °C	g ppm	s ppm	Temp °C	g ppm	s ppm	Temp °C	g ppm	s ppm
0.000	0.0125	0.5	0.003	0.196	33.1	0.006	0.213	62.7	0.007	0.225
0.000	0.0264	0.9	0.009	0.409	33.1	0.016	0.443	62.1	0.019	0.468
0.000	0.0409	0.8	0.014	0.633	33.3	0.025	0.689	61.7	0.031	0.715
0.000	0.0562	0.9	0.020	0.866	33.2	0.033	0.931	62.4	0.042	0.971
0.000	0.0760	0.7	0.028	1.173	33.3	0.044	1.240	62.4	0.058	1.279
0.000	0.1014	0.8	0.039	1.545	33.1	0.059	1.613	62.1	0.074	1.636
0.000	0.117	0.5	0.046	1.752	33.1	0.068	1.814	62.2	0.083	1.824
0.000	0.1331	1.2	0.054	1.951	33.0	0.077	2.002	62.2	0.092	2.004
0.000	0.1481	1.3	0.062	2.233	32.9	0.086	2.173	62.5	0.103	2.167
0.000	0.1636	1.1	0.074	2.583	33.0	0.099	2.391	61.8	0.118	2.373
0.000	0.1790	1.3	0.088	2.923	33.0	0.115	2.621	61.7	0.135	2.586
0.000	0.1954	1.5	0.106	3.243	32.8	0.134	2.859	61.9	0.157	2.811
0.000	0.2114	1.5	0.127	3.543	33.0	0.157	3.089	60.4	0.175	3.032
0.000	0.2274	1.3	0.145	3.823	32.9	0.221	3.575	61.9	0.242	3.507
0.000	0.2434	1.5	0.169	4.093	32.9	0.256	3.783	61.6	0.277	3.724
0.000	0.2594	1.5	0.223	4.243	33.0	0.299	4.039	60.9	0.318	4.005
0.000	0.2754	2.0	0.268	4.474	33.0	0.322	4.791	60.4	0.408	4.792
0.000	0.2914	1.7	0.363	4.724	33.0	0.415	5.063	60.5	0.431	5.077
0.000	0.3074	1.7	0.387	5.013	33.0	0.428	5.236	63.6	0.445	5.253
0.000	0.3234	0.7	0.399	5.176	32.4	0.455	5.657	63.2	0.471	5.686
0.000	0.3394	0.5	0.426	5.539	32.7	0.476	6.047	63.5	0.491	6.094
0.000	0.3554	0.5	0.445	5.771	32.7	0.476	6.047	61.1	0.501	6.339
0.000	0.3714	2.5	0.458	6.024	33.1	0.487	6.291	61.0	0.515	6.748
0.000	0.3874	1.5	0.473	6.226	33.0	0.501	6.709	63.3	0.525	7.140
0.000	0.4034	0.6	0.481	7.008	32.7	0.510	7.099	66.2	0.020	0.545
0.000	0.4194	0.5	0.509	0.487	33.1	0.017	0.521	66.5	0.038	0.065
0.000	0.4354	0.6	0.018	0.884	33.2	0.030	0.937	66.5	0.065	1.507
0.000	0.4514	0.8	0.031	1.424	32.9	0.048	1.488	66.3	0.082	1.929
0.000	0.4674	0.6	0.044	1.859	33.0	0.066	1.939	66.2	0.104	2.304
0.000	0.4834	0.7	0.062	2.243	32.9	0.086	2.344	63.5	0.129	2.640
0.000	0.4994	0.8	0.082	2.523	33.0	0.109	2.697	63.4	0.164	2.993
0.000	0.5154	0.5	0.111	3.111	33.0	0.141	3.075	62.5	0.199	3.312
0.000	0.5314	0.6	0.147	3.443	33.0	0.179	3.409	60.8	0.276	3.813
0.000	0.5474	1.3	0.223	3.723	32.9	0.256	3.888	60.3	0.313	4.045
0.000	0.5634	1.5	0.262	4.117	32.8	0.294	4.097	62.3	0.348	4.276
0.000	0.5794	1.2	0.298	4.704	32.8	0.329	4.312	61.6	0.380	4.533
0.000	0.5954	1.0	0.334	4.526	32.9	0.363	4.557	61.5	0.410	5.027
0.000	0.6114	1.8	0.381	5.003	32.7	0.412	5.053	61.3	0.444	5.570
0.000	0.6274	1.9	0.421	5.483	33.1	0.449	5.551	62.3	0.462	6.140
0.000	0.6434	0.5	0.435	5.754	31.7	0.464	5.827	62.4	0.515	6.444
0.000	0.6594	0.5	0.447	6.021	32.1	0.477	6.101	62.0	0.532	7.122
0.000	0.6754	0.4	0.453	6.319	32.1	0.489	6.407	65.0	0.011	0.237
0.000	0.6914	0.8	0.481	7.011	32.2	0.507	7.095	64.9	0.034	0.666
0.000	0.7074	0.3	0.005	0.301	32.8	0.009	0.316	65.3	0.035	0.666
0.000	0.7234	0.2	0.012	0.624	33.0	0.020	0.653	64.9	0.051	1.252
0.000	0.7394	0.8	0.017	0.878	32.7	0.028	0.914	65.0	0.060	1.475
0.000	0.7554	1.0	0.024	1.225	32.7	0.039	1.263	65.4	0.074	1.775
0.000	0.7714	0.5	0.028	1.435	32.7	0.045	1.470	65.4	0.094	2.037
0.000	0.7874	0.5	0.044	1.775	32.0	0.057	1.802	65.1	0.095	2.327
0.000	0.8034	1.0	0.046	2.066	32.1	0.067	2.074	65.1	0.127	2.155
0.000	0.8194	1.0	0.058	2.403	32.3	0.081	2.392	60.4	0.147	2.564
0.000	0.8354	1.5	0.118	3.385	33.1	0.147	3.303	61.0	0.234	3.651
0.000	0.8514	1.3	0.154	3.726	32.9	0.186	3.630	60.4	0.256	4.055
0.000	0.8674	1.3	0.181	3.904	33.1	0.214	3.809	61.2	0.282	4.282
0.000	0.8834	1.3	0.213	4.179	32.8	0.275	4.124	63.9	0.351	4.758
0.000	0.8994	1.6	0.283	4.337	32.7	0.314	4.317	63.9	0.421	5.157
0.000	0.9154	0.7	0.305	4.456	32.4	0.339	4.462	63.5	0.454	5.454
0.000	0.9314	0.7	0.322	4.596	32.4	0.362	4.624	63.3	0.481	5.946
0.000	0.9474	0.8	0.353	4.763	32.4	0.392	4.801	63.2	0.522	7.122
0.000	0.9634	0.6	0.386	5.088	32.4	0.415	5.144	63.3	0.543	7.122
0.000	0.9794	0.6	0.409	5.365	32.4	0.438	5.432	63.3	0.564	7.122
0.000	0.9954	0.6	0.436	5.827	32.3	0.465	5.907	63.2	0.582	7.122
0.000	0.9814	0.9	0.475	6.999	32.4	0.506	7.085	62.9	0.071	1.879
0.000	0.9974	1.1	0.011	0.670	33.0	0.018	0.677	62.9	0.082	2.175
0.000	0.9834	0.8	0.020	1.225	33.0	0.033	1.230	62.8	0.091	2.374
0.000	0.9994	0.9	0.026	1.502	33.1	0.042	1.505	62.8	0.113	2.707
0.000	0.9854	0.5	0.036	1.931	33.1	0.055	1.920	62.6	0.124	2.858
0.000	0.9914	0.8	0.046	2.278	32.6	0.067	2.241	62.6	0.163	3.260
0.000	0.9974	0.6	0.053	2.510	32.4	0.076	2.461	63.6	0.199	3.581
0.000	0.9834	0.5	0.069	2.903	32.4	0.094	2.820	64.0	0.271	4.008
0.000	0.9994	0.7	0.078	3.073	32.5	0.104	2.985	64.0	0.318	4.255
0.000	0.9854	0.6	0.111	3.572	32.4	0.140	3.443	63.5	0.379	4.688
0.000	0.9914	0.8	0.148	3.920	32.3	0.179	3.775	63.8	0.401	4.979
0.000	0.9974	0.7	0.215	4.380	32.3	0.248	4.155	64.3	0.420	5.092
0.000	0.9834	0.6	0.264	4.318	32.2	0.296	4.367	64.3	0.445	5.403
0.000	0.9994	1.0	0.331	4.707	32.2	0.360	4.724	64.1	0.473	5.822
0.000	0.9854	0.8	0.353	4.865	32.4	0.382	4.897	64.1	0.487	6.151
0.000	0.9914	0.7	0.374	5.049	32.4	0.403	5.095	63.8	0.519	7.128
0.000	0.9974	0.6	0.399	5.232	31.9	0.427	5.393			
0.000	0.9834	0.6	0.427	5.747	32.2	0.456	5.820			
0.000	0.9994	0.8	0.441	6.021	32.4	0.471	6.105			
0.000	0.9854	1.0	0.476	7.015	32.4	0.503	7.096			

TABLE II

LOW RANGE: CORRECTED SHIFT (INTERPOLATED FOR 0°, 32°, 63°C) AND DEGREES OF DISSOCIATION

D-Fraction	Mole Fraction of Acid	Shift			Degree of Dissociation		
		0°	32°	63°	0°	32°	63°
0.000	0.0125	0.196	0.212	0.226	1.033	1.012	0.996
0.000	0.0264	0.407	0.442	0.469	0.967	0.984	0.993
0.000	0.0409	0.631	0.687	0.716	0.985	0.977	0.990
0.000	0.0562	0.863	0.929	0.971	0.964	0.940	0.970
0.000	0.0760	1.171	1.233	1.280	0.951	0.901	0.840
0.000	0.1014	1.543	1.613	1.636	0.911	0.847	0.765
0.000	0.1171	1.751	1.813	1.824	0.871	0.798	0.710
0.000	0.1331	1.948	2.001	2.004	0.825	0.745	0.656
0.000	0.1481	2.131	2.173	2.166	0.788	0.704	0.616
0.000	0.1686	2.361	2.391	2.371	0.743	0.647	0.560
0.000	0.1930	2.611	2.622	2.584	0.667	0.579	0.495
0.000	0.2214	2.862	2.869	2.809	0.567	0.504	0.426
0.000	0.2541	3.117	3.090	3.025	0.501	0.421	0.351
0.000	0.3448	3.608	3.577	3.503	0.276	0.228	0.184
0.000	0.3966	3.806	3.784	3.720	0.170	0.140	0.110
0.000	0.4672	4.040	4.039	4.001	0.053	0.042	0.029
0.321	0.0280	0.486	0.520	0.543	1.008	1.003	0.972
0.321	0.0506	0.883	0.935	0.964	1.007	0.990	0.944
0.322	0.0834	1.432	1.487	1.507	0.960	0.918	0.855
0.322	0.1136	1.898	1.939	1.932	0.896	0.836	0.758
0.323	0.1482	2.329	2.344	2.310	0.782	0.712	0.633
0.324	0.1837	2.707	2.698	2.641	0.671	0.601	0.536
0.325	0.2311	3.114	3.076	2.994	0.534	0.458	0.402
0.326	0.2855	3.467	3.412	3.310	0.392	0.338	0.284
0.329	0.3967	3.931	3.883	3.806	0.159	0.135	0.109
0.330	0.4590	4.116	4.084	4.039	0.051	0.051	0.038
0.662	0.0163	0.301	0.315	0.327	0.920	0.911	0.896
0.666	0.0332	0.624	0.652	0.668	0.967	0.972	0.981
0.669	0.0468	0.876	0.915	0.931	0.958	0.963	0.940
0.673	0.0658	1.223	1.262	1.269	0.939	0.933	0.894
0.676	0.0781	1.434	1.469	1.476	0.912	0.897	0.860
0.680	0.0988	1.775	1.802	1.792	0.867	0.844	0.797
0.685	0.1175	2.065	2.074	2.040	0.823	0.788	0.732
0.690	0.1416	2.402	2.393	2.333	0.759	0.719	0.657
0.685	0.2405	3.388	3.307	3.181	0.489	0.443	0.389
0.682	0.2947	3.730	3.633	3.496	0.360	0.321	0.277
0.679	0.3342	3.907	3.812	3.578	0.274	0.243	0.207
0.673	0.4283	4.180	4.126	4.028	0.106	0.093	0.076
0.668	0.4945	4.337	4.318	4.252	0.019	0.016	0.007
0.998	0.0305	0.670	0.677	0.677	0.981	0.980	0.965
0.998	0.0568	1.224	1.230	1.218	0.954	0.956	0.957
0.998	0.0711	1.501	1.505	1.485	0.921	0.922	0.900
0.998	0.0953	1.931	1.921	1.878	0.853	0.845	0.815
0.998	0.1163	2.279	2.242	2.175	0.798	0.778	0.741
0.998	0.1319	2.511	2.462	2.373	0.755	0.732	0.689
0.998	0.1614	2.904	2.821	2.706	0.673	0.642	0.599
0.998	0.1773	3.074	2.987	2.857	0.623	0.595	0.551
0.998	0.2311	3.574	3.444	3.278	0.482	0.450	0.408
0.998	0.2861	3.923	3.777	3.586	0.353	0.325	0.288
0.998	0.3860	4.386	4.157	4.009	0.180	0.149	0.130
0.998	0.4645	4.316	4.367	4.264	0.044	0.051	0.040

TABLE III.

HIGH RANGE: CORRECTED SHIFTS s (INTERPOLATED FOR 0°, 32°, 63°C) AND DEVIATIONS Δs (OBSERVED - CALCULATED)

D-Fraction r	Mole Fraction of Acid x	0°C		32°C		63°C	
		s	Δs	s	Δs	s	Δs
0,000	0,6504	4,740	+0,018	4,790	+0,031	4,790	-0,001
0,000	0,7053	5,011	+0,023	5,062	+0,031	5,077	+0,003
0,000	0,7367	5,174	+0,022	5,235	+0,036	5,253	+0,008
0,000	0,8080	5,586	+0,026	5,656	+0,040	5,686	+0,017
0,000	0,8671	5,971	+0,029	6,046	+0,042	6,093	+0,028
0,000	0,9012	6,206	+0,021	6,289	+0,038	6,341	+0,025
0,000	0,9528	6,621	+0,020	6,707	+0,032	6,750	+0,003
0,000	0,9928	7,006	-0,041	7,097	-0,030	7,140	-0,065
0,332	0,5221	4,302	+0,010	4,313	+0,017	4,275	-0,027
0,334	0,5833	4,523	-0,004	4,557	+0,012	4,541	-0,023
0,337	0,6992	5,004	-0,024	5,051	-0,011		
0,341	0,7908	5,478	-0,049	5,550	-0,023	5,570	-0,017
0,339	0,8352	5,752	-0,047	5,828	-0,023	5,867	-0,035
0,338	0,8737	6,020	-0,035	6,101	-0,011	6,150	-0,019
0,336	0,9132	6,318	-0,023	6,407	+0,002	6,465	-0,002
0,333	0,9849	7,008	+0,006	7,095	+0,018	7,135	-0,015
0,662	0,5415	4,455	+0,026	4,462	+0,035	4,420	-0,007
0,656	0,5876	4,595	0,000	4,623	+0,020	4,599	-0,015
0,650	0,6322	4,761	-0,018	4,801	+0,006	4,789	-0,022
0,638	0,7077	5,086	-0,049	5,144	-0,017	5,153	-0,034
0,629	0,7624	5,364	-0,059	5,432	-0,026	5,454	-0,038
0,614	0,8387	5,825	-0,051	5,907	-0,017	5,946	-0,024
0,582	0,9789	6,996	+0,018	7,084	+0,035	7,122	+0,003
0,998	0,5856	4,705	+0,041	4,724	+0,064	4,689	+0,032
0,998	0,6324	4,864	+0,009	4,897	+0,037	4,880	+0,014
0,998	0,6780	5,048	-0,014	5,095	+0,020	5,092	+0,004
0,998	0,7381	5,331	-0,034	5,394	+0,006	5,408	-0,002
0,998	0,8130	5,745	-0,046	5,820	-0,007	5,852	-0,010
0,998	0,8553	6,019	-0,042	6,104	0,000	6,150	+0,004
0,998	0,9687	7,012	+0,065	7,096	+0,084	7,128	+0,052

MUB-13072

Figure 1. Deviation Function F for 0°C ($\circ \text{HNO}_3$, $\bullet \text{HNO}_3$ Hood and Reilly, $\square \text{DNO}_3$).

MUB-13071

Figure 2. Deviation Function F for 32°C ($\circ$ HNO₃, $\bullet$ HNO₃ Hood and Reilly at 25°, $\square$ DNO₃).

MUB-13073

Figure 3. Deviation Function F for 63°C ($\circ$ HNO_3 , $\bullet$ HNO_3 Hood and Reilly at 70° , $\square$ DNO_3).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.