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IONIZATION OF STRONG ELECTROLYTES XI.
THE MOLECULAR STATES OF NITRIC ACID AND PERCHLORIC ACID

O. Redlich, R. W. Duerst and A. Merbach

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IONIZATION OF STRONG ELECTROLYTES XI.
THE MOLECULAR STATES OF NITRIC ACID AND PERCHLORIC ACID

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January 1968

Abstract

Recent proton magnetic measurements in the ternary systems HNO_3-DNO_3-water and $HClO_4$-$DClO_4$-water partly confirm older data and furnish new information of the molecular states of the acids, on hydration and solvation of the hydrogen ion, and the distribution of H in deuterated acids between the ion and water. The dissociation constants of HNO_3 and DNO_3 between 0 and 25° are derived from the measurements.

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1. Introduction

More than fifty years after Arrhenius, the investigation of the dissociation of strong electrolytes led to quantitative results. The results reported in the preceding ten papers of this series[1-10], the precise work of Young[11-16] and his coworkers, and results of later

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(1) O. Redlich and J. Bigeleisen, J. Amer. Chem. Soc. 65, 1883 (1943).

(2) O. Redlich, E. K. Holt and J. Bigeleisen, J. Amer. Chem. Soc. 66, 13 (1944).

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(11) T. F. Young, Record of Chem. Progress, 12, 81 (1951).

(12) A. A. Krawetz, Thesis, University of Chicago (1955).

(13) T. F. Young and L. A. Blatz, Chem. Revs. 44, 93 (1949).

(14) T. F. Young, L. F. Maranville and H. M. Smith, in "The Structure of Electrolytic Solutions", W. J. Hamer, Ed. (John Wiley & Sons, Inc., New York, 1959) p.35.

(15) D. E. Irish, B. McCarroll and T. F. Young, J. Chem. Phys. 39, 3436 (1963).

(16) E. L. Gasner, Thesis, University of Chicago (1965).

authors[17-24] have furnished definite information of the molecular state of strong acids.

In the present discussion previous results on nitric acid and perchloric acid are interpreted and revised. For some time it had been clear that only measurements extended over the whole concentration range up to the anhydrous acids[1-4,8-10] could furnish a satisfactory basis of interpretation. The extension to DNO_3 and $DClO_4$ was desirable because the great influence of deuterium substituion on proton magnetic resonance[25,26] promised new information on the molecular state.

Two recent papers[9,10] reported proton magnetic resonance shifts, obtained within a few ppb for about 80 solutions of each of the two acids between 0 and 65°C. These data lead to definite conclusions concerning

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(17) P. M. Vollmar, J. Chem. Phys. 39, 2236 (1963).

(18) R. E. Hester and R. A. Plane, Inorg. Chem. 3, 769 (1964).

(19) K. Heinziger and R. E. Weston, Jr., J. Chem. Phys. 42, 272 (1965).

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(22) D. E. Irish and G. E. Walrafen, J. Chem. Phys. 46, 378 (1967).

(23) J. T. Miller and D. E. Irish, Can. J. Chem. 45, 147 (1967).

(24) A. K. Covington and T. H. Lilley, Trans. Faraday Soc. 63, 1749 (1967).

(25) A. J. Kresge and A. L. Allred, J. Am. Chem. Soc. 85, 1541 (1963).

(26) V. Gold, Proc. Chem. Soc. 1963, 141.

the states of the acids in the whole ternary fields. Yet the information does not appear to be fully exhausted and further conclusions beyond the present discussion may be expected.

2. Deuterium Substitution

Various peculiar features of the influence of deuterium substitution have been discovered during the examination of the data.

21. High Concentrations

In some concentration ranges the influence of deuterium substitution is very strong, in others it is negligible. The difference is characteristic.

The shifts of anhydrous $HClO_4$ and $DClO_4$ are equal[10] within the narrow limits of experimental error. What is called "shift of $DClO_4$" here is actually the shift of the proton in $DClO_4$ containing 0.2% $HClO_4$. The independence of the shift of the D-fraction means that the replacement of $HClO_4$ by $DClO_4$ in the environment of the proton does not affect the shift of proton. The result is good evidence for the monomeric state of the anhydrous acid since a replacement of H-bonds by D-bonds would be expected to change the internal field at least by a small amount.

The nuclear magnetic resonance (NMR) of nitric acid depends strictly linearly on Gutowsky's variable[27]

$$p = 3x/(2-x) \qquad (2.1)$$

in the mole fraction range $0.6 < x < 0.95$. The linear coefficient A_2

(27) H. S. Gutowsky and A. Saika, J. Chem. Phys. 21, 1688 (1953).

is represented[9] as a function of the isotopic atom fraction

$$r = D/(H+D) \tag{2.2}$$

and the temperature t by

$$A_2 = 1.428 - 0.016r + (0.087 + 0.047r)\cdot 10^{-2}t \ . \tag{2.3}$$

The linearity was interpreted as an indication of the stoichiometric completeness of the reaction

$$(HNO_3)_2 + 2H_2O = 2H_3NO_4 \ . \tag{2.4}$$

The dependence of A_2 on r is zero at 38°C and hardly more than the errors of observation and smoothing at other temperatures.

The dependence on r of the specific shifts s_2 of H_3NO_4 and s_3 of $(HNO_3)_2$, as given later in equations (3.4) and (3.5), is slightly higher but still rather small.

These results suggest some general conclusions: The proton-deuterium distribution between uncharged molecules is nearly uniform. The interaction of non-bonded molecules is not appreciably affected by the isotopic substitution.

The results are in accord with the molecular interpretation given.

22. Hydration and Dissociation

Deuterium substitution greatly increases the shift for the lower range ($x < 0.5$) of both acids and also for the upper range of perchloric acid. These are the solutions containing hydrogen ion in large concentrations. Earlier authors[25,26] have already concluded from the observed ratio

$$k = s_{11}/s_{10} \tag{2.5}$$

of the limiting slopes s_{11} of $DClO_4$, and s_{10} of $HClO_4$ that the proton has a strong preference for the ion over water. This conclusion,

confirmed also by Heinziger and Weston[28], is now corroborated by more extensive experimental data of high precision.

A survey of the data now available for the lower range shows several peculiar features of the shifts. The ratio s/p is shown as a function of the mole fraction x of the acid in Figures 1-3 for nitric acid and in Figures 10-12 for perchloric acid. The curves of s/p show an approach to a horizontal limiting tangent at x=0 for HNO_3 at 0°C (Figure 1), hardly at 25°C (Figure 2) and not at all at 65° (Figure 3). The steepness of the approach increases with the deuterium content

$$r = D/(H+D)$$

and the temperature.

For $HClO_4$ the horizontal approach extends at all temperatures from x=0 to almost x=0.1. Deuteration has the same effect as for nitric acid.

The interpretation is based on the preference of H for the hydrogen ion and on incomplete dissociation. The concentration independence of s/p in dilute $HClO_4$ means that the acid is here completely dissociated and that the contribution of each ion does not change. The deuterated perchloric acid is of course also completely dissociated but with increasing ion concentration the H content of each ion decreases from its limiting value at x=0. The magnitude of this effect is influenced by the degree of hydration.

This effect, conspicuously isolated in dilute perchloric acid, is noticeable in HNO_3 at 0°C. It is swamped by the influence of incomplete dissociation at 65°C. In the deuterated nitric acids both effects are

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(28) K. Heinziger and R. E. Weston, Jr., J. Phys. Chem. 68, 744 (1964).

superimposed at all concentrations.

The combined influence of both effects will be quantitatively derived in the next section for later application to both acids.

23. The Dependence of the Shift on the Isotopic Composition and the Acid Concentration

The concentrations (better: numbers of moles per stoichiometric mole of solution) of the species hydrogen ion, undissociated molecule, water without regard to substitution will be called

$$y_1 \cdots H_{2m+1}O_m^+; \quad y_2 \cdots H_3NO_4; \quad y_3 \cdots H_2O \; . \tag{2.6}$$

They can be expressed by the mole fraction x of the acid and the degree of dissociation α as

$$y_1 = \alpha x; \quad y_2 = (1-\alpha)x; \quad y_3 = 1-2x-(m-1)\alpha x \; . \tag{2.7}$$

We assume that the ratio H/D has the same value ϕ for the undissociated molecule and for water; its limit for infinite dilution is

$$\lim_{x=0} \phi = (1-r)/r \; . \tag{2.8}$$

The deviation of ϕ from this limiting value is a measure of the non-uniformity of the H/D distribution between ions and molecules.

The ratio H/D is higher for the hydrogen ion. Abbreviating

$$q = 2m+1 \tag{2.9}$$

we may write the exchange reaction as

$$H_pD_{q-p}O_m^+ + H_2O = H_{p+1}D_{q-p-1}O_m^+ + HOD \; . \tag{2.10}$$

We adopt the usual assumption that no distinction need be made for the H/D ratio of various species of water. The concentration of an ion $H_pD_{q-p}O_m^+$ will be denoted by h_p. The exchange equilibrium (2.10) is then determined by the H/D ratio ϕ for all uncharged molecules, the

equilibrium constant k, and appropriate statistical factors. The result corresponding to the reaction (2.10) is a recursion formula

$$h_{p+1} = h_p \cdot k\phi(q-p)/(p+1) \tag{2.11}$$

which can be used to express all concentrations h_p by the concentration h_o of $D_qO_m^+$ with the aid of the binomial coefficients $\binom{q}{p}$:

$$h_1 = h_o \cdot k\phi q \tag{2.12}$$

$$h_p = h_o \cdot (k\phi)^p \binom{q}{p} . \tag{2.13}$$

One obtains for the total ion concentration

$$y_1 = \alpha x = \sum_{p=0}^{q} h_p = h_o(1+k\phi)^q \tag{2.14}$$

and for the total H-content of all ions

$$\sum_{p=1}^{q} p\, h_p = h_o \cdot qk\phi(1+k\phi)^{q-1} = y_1 qk\phi/(1+k\phi) . \tag{2.15}$$

For the determination of the unknown variables h_o, α, ϕ we need, in addition to (2.14), two more relations. One is a material balance. The fraction (1-r) represents the concentration of H divided by the concentration of H+D. Since the H/D ratio of the uncharged molecules is ϕ, their H/(H+D) ratio is $\phi/(1+\phi)$ so that the proton content of the molecules is $(3y_2+2y_3)\phi/(1+\phi)$. The overall H/(H+D) ratio is then, with the aid of (2.15),

$$1-r = [y_1 qk\phi/(1+k\phi) + (3y_2+2y_3)\phi/(1+\phi)]/(2-x) \tag{2.16}$$

or, in view of (2.7),

$$(1-r)(2-x) = \alpha xqk\phi/(1+k\phi) + (2-x-\alpha xq)\phi/(1+\phi) . \tag{2.17}$$

The degree of dissociation α and the distribution ratio ϕ follow from this equation and the observed shifts. Conventionally the specific

shifts s_{10} for the hydrogen ion and s_2 for the undissociated acid are defined in such a manner that the contributions to the shift in HNO_3 solution are

$$\alpha p \cdot s_{10} = 3\alpha x s_{10}/(2-x) \quad \text{and} \quad (1-\alpha)p \cdot s_2 = 3(1-\alpha)xs_2/(2-x), \quad (2.18)$$

respectively. In isotopically mixed solutions these terms are to be multiplied by the H/(H+D) ratio, namely, $k\phi/(1+k\phi)$ for the ions and $\phi/(1+\phi)$ for the molecules. In addition, the total hydrogen content (2-x) in (2.16) is to be replaced by the H content, namely, (1-r)(2-x). The shift is therefore represented for isotopically mixed solutions by

$$s = 3x[\alpha s_{10}k\phi/(1+k\phi) + (1-\alpha)s_2\phi/(1+\phi)]/[(1-r)(2-x)] \ . \quad (2.19)$$

Equations (2.17) and (2.19) can be used for an explicit representation of α. Replacing x by (2.1) we obtain from (2.17)

$$\alpha = 3(1+k\phi)(1-r-r\phi)/[pq\phi(k-1)] \quad (2.20)$$

and from (2.19)

$$\alpha = [s(1-r)/p\phi - s_2/(1+\phi)]/[ks_{10}/(1+k\phi) - s_2/(1+\phi)] \ . \quad (2.21)$$

From these two relations one obtains a quadratic equation in ϕ, so that ϕ and also α can be expressed by the observed quantities s_{10}, s_2, k, p, r and q. The results for perchloric acid, to be discussed later, furnish a basis for a crude estimate of q as a function of the temperature t(°C), namely,

$$q = 4.3 + 0.01\ t. \quad (2.22)$$

But the automatic computation following this procedure gave widely discrepant values for α from (2.20) and (2.21). Finally, the solution of these equations was enforced by choosing a set of values for ϕ close to the limiting value (2.8), computing the values α' and α'' according to

the two equations, and interpolating the results for $\alpha'=\alpha''$.

The reason for the peculiar behavior lies in (2.20). This relation is a material balance connecting the H/D distribution of the hydrogen ion and of the uncharged molecules. It becomes meaningless in various boundary cases: (a) for x=0; (b) for $\alpha'=0$; (c) for r=0. In other words, it loses its meaning whenever ϕ approaches the limiting value (2.8). Actually ϕ is always close to the limiting value and therefore the information furnished by (2.20) is not very strong. But it is not negligible, especially for r=1.

For the limiting value (2.8) of ϕ, equation (2.21) becomes

$$\alpha = (s/p-s_2)/(s_1-s_2) \tag{2.23}$$

with

$$s_1 = s_{10}/(1-r+r/k) \; . \tag{2.24}$$

Equation (2.23) is the relation proposed for the light acid by Gutowsky and Saika[27]. Equation (2.24) may be written, in view of (2.5),

$$1/s_1 = (1-r)/s_{10}+r/s_{11} \tag{2.25}$$

and thus establishes a simple relation for the dependence of the limiting slope

$$s_1 = \lim_{p=0} (ds/dp) \tag{2.26}$$

on the isotopic composition r.

For completely dissociated solutions we have $\alpha=1$. In this case the quadratic equation resulting from (2.20) and (2.21) can be solved in the usual manner. Now one can represent s/p as calculated functions of r and x for complete dissociation. These functions are represented in Figures 1-3 and 10-12 as broken lines.

3. Nitric Acid

The relations of the preceding section permit an exhaustive analysis of the experimental data[9] obtained for HNO_3-DNO_3-water in the lower range ($x < 0.5$).

31. Degree of Dissociation

The experiences gained in the interpretation of the results for perchloric acid led to a revision of the limiting slopes s_1 (mole fraction x=0) of the shifts observed for nitric acid. The shifts s for $HClO_4$ in paper X of this series denoted the observed values referred to an H_2O-D_2O mixture of the same deuterium fraction r as that of the acid solution. But in paper IX on HNO_3, the observed shifts, called s' in the following, were referred to pure H_2O. In the present discussion, s will be referred to the H_2O-D_2O mixture. By means of the "water function"

$$W = -0.019r\ (1+0.017t) \tag{3.1}$$

one obtains

$$s = s'-W\ . \tag{3.2}$$

Through a mistake of the senior author, W was subtracted in equation (22) of paper IX while it should have been added. The equations (23), (25) and (26) are therefore to be corrected and should read

$$A_1 = 1.5s_2 - 0.5s_3 = 2.669 - 0.013\cdot10^{-2}t + 0.262r - 0.124\cdot10^{-2}rt \tag{3.3}$$

$$s_2 = A_1 + A_2 = 4.097 + 0.074\cdot10^{-2}t + 0.246r - 0.077\cdot10^{-2}rt \tag{3.4}$$

$$s_3 = A_1 + 3A_2 = 6.953 + 0.248\cdot10^{-2}t + 0.215r + 0.017\cdot10^{-2}rt. \tag{3.5}$$

The limiting slopes s_{10} of HNO_3 and s_{11} of DNO_3 have been obtained by graphical extrapolations of the revised values of s/p (Figures 1,2) at 0°, 25° and 65°C. The new results are

$$s_{10} = 100/(9.755 - 3.28\cdot10^{-2}t + 1.38\cdot10^{-4}t^2) \tag{3.6}$$

$$s_{11} = 100/(6.534 - 0.79\cdot10^{-2}t). \tag{3.7}$$

The limiting slopes s_1 for intermediate isotopic mixtures follow from (2.25). They are the end points of the calculated functions (broken lines) in Figures 1-3. The observed and calculated values are shown in Table I. The differences do not exceed 0.30. Although all values have been obtained by extrapolation, inspection of Figures 1-3 shows that the discrepancies are slightly larger than to be expected.

Table I. Limiting Slopes for HNO_3

r	0	0.32		0.67		1.00
		obs.	calc.	obs.	calc.	
0°C	10.25	11.70	11.42	12.84	13.14	15.30
25°	11.08	12.54	12.26	13.62	13.85	15.79
65°	12.185	13.57	13.29	14.62	14.80	16.61

The degrees of dissociation α have been computed from (2.20) and (2.21) by the method described in Section 23. The results for intermediate isotopic compositions have been corrected for the discrepancies shown in Table I. The degrees of dissociation shown in Table II supersede the results in Table II of a preceding paper[9] of this series.

The deviation function

$$F = \alpha - 1 + 2x \tag{3.8}$$

is shown in Figures 4-6. It allows a very sensitive representation of the observed values. The variation of α with the isotopic composition is well within the range of experimental errors at 65°C, and not much larger at lower temperatures. The strong decrease of the dissociation with increasing temperature is immediately seen in a comparison of the diagrams in Figures 4-6.

Table II. Degrees of Dissociation of Nitric Acid

D-fraction r	Mole fraction of acid x	Degree of dissociation 0°C	25°C	65°C
0	0.0125	1.017	.991	.975
0	.0264	0.982	.965	.943
0	.0409	.973	.962	.909
0	.0562	.952	.926	.880
0	.0760	.939	.893	.829
0	.1014	.899	.843	.755
0	.1171	.859	.797	.700
0	.1331	.814	.747	.649
0	.1481	.778	.706	.606
0	.1686	.723	.650	.551
0	.1930	.658	.585	.486
0	.2214	.579	.510	.418
0	.2541	.494	.428	.344
0	.3448	.272	.233	.180
0	.3966	.168	.143	.107
0	.4672	.052	.044	.028
0.3209	.0280	.984	.975	.952
.3213	.0506	.971	.948	.900
.3219	.0834	.928	.884	.809
.3224	.1136	.872	.813	.717
.3231	.1482	.767	.701	.601
.3238	.1837	.665	.597	.501
.3248	.2311	.534	.471	.385
.3261	.2855	.396	.345	.273
.3285	.3967	.163	.140	.106
.3300	.4590	.065	.055	.038
.6624	.0163	1.000	.990	.986
.6659	.0332	0.995	.974	.934
.6688	.0468	.977	.951	.900
.6730	.0658	.960	.921	.845
.6757	.0781	.936	.888	.811
.6804	.0988	.899	.842	.751
.6847	.1176	.862	.795	.691
.6904	.1416	.807	.734	.624
.6849	.2405	.547	.475	.378
.6817	.2948	.410	.350	.272
.6792	.3342	.316	.268	.204
.6728	.4283	.125	.106	.076
.6677	.4945	.024	.020	.009
.9977	.0305	1.000	.981	.935
.9977	.0568	0.976	.941	.868
.9977	.0711	.953	.913	.832
.9977	.0953	.904	.853	.757
.9977	.1163	.864	.799	.694
.9977	.1319	.829	.761	.648
.9977	.1614	.760	.684	.570
.9977	.1773	.713	.640	.527
.9977	.2311	.573	.501	.398
.9977	.2861	.432	.371	.284
.9977	.3860	.229	.178	.131
.9977	.4645	.055	.058	.040

32. Dissociation Constant

The derivation of the dissociation constant

$$K_c = a_2'/[(1-\alpha)\beta' c] \qquad (3.9)$$

by means of the activity a_2' of the solute, the activity coefficient β' of the undissociated molecule, and the concentration c (moles of solute per liter) has been discussed in the first paper[1] of this series. As in the preceding paper[10], a definition based on the mole fraction x and the corresponding activities

$$K_2 = a_2/[(1-\alpha)\beta_2 x a_1] \qquad (3.10)$$

is preferred because the use of the volume concentration c is inconvenient for precise measurements over a wider temperature range. The standard states and the relation

$$K_c = 55.51\ K_2 \qquad (3.10)$$

have been discussed before[10].

The activities have been derived over the entire concentration range by Mr. W. E. Gargrave[29].

The results for log $(K_2\beta_2)$ at 0°, 25° and 65°C for r=0 and r=1 are shown in Figures 7 and 8.

The extrapolations to x=0 appear to be quite reasonable and furnish the results given in Table III.

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(29) O. Redlich, W. E. Gargrave and W. D. Krostek, UCRL-17694, July 1967; Ind. Eng. Chem. Fundamentals, in print.

Table III. Dissociation Constant K for Nitric Acid

t°C	HNO_3	DNO_3
0	35	48
25	20	25
65	10	10

It has been predicted by Lewis and Schutz[30] and by Halpern[31] that deuteration will reduce the dissociation constants of weak acids but the change will become smaller with increasing strength. More than thirty years ago we found[32] for water the value 0.16 for the ratio heavy/light K_c''/K_c', a value well confirmed since by several authors. This may be considered to be the lower end of the scale of acid strength. The values found now for the upper end of the scale in Table III are nearly equal for HNO_3 and DNO_3, in good accord with the theoretical predictions.

33. Comparison With Previous Results

Young, Maranville and Smith[14] showed the good agreement between Raman intensities and NMR data. Moreover, they calculated dissociation constants from conductivities measured by A. A. Noyes and Eastman[33] at 218 and 306°C. The curve in Figure 9 represents the relation

$$\log K_c = 6.557 - 320.88/T - 0.01359\ T \qquad (3.12)$$

which they obtained as the result of their Raman intensities between

(30) G. N. Lewis and P. W. Schutz, J. Am. Chem. Soc. 56, 1913 (1934).

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

(32) E. Abel, E. Bratu and O. Redlich, Z. physik. Chem. (A) 173, 353 (1935).

(33) A. A. Noyes and G. W. Eastman, Carnegie Inst. of Washington Publ. no. 63, 239. A. A. Noyes, ibid. 333 (1907).

0 and 50°C and the conductivities of Noyes and Eastman.

The usefulness of these data, obtained at a time when available experimental tools were not highly developed, is as remarkable as the critical and sober clarity of Noyes' conclusions.

On the whole the agreement between various authors is quite satisfactory. Our present results for HNO_3 are lower at 0° and 25°C than all earlier data. The difference may be mainly due to the change in the extrapolation procedure; the new method of extrapolating in a diagram of log (Kβ) against x_2 rather than c definitely appears to be better (see Figure 7).

4. Perchloric Acid

The considerable differences in the molecular states of nitric and perchloric acids have been pointed out in previous papers of this series.

It has been pointed out before that the diagrams of s/p immediately express the strong dissociation of perchloric acid and the weaker dissociation of nitric acid.

The second difference appears in the upper range. The shifts of nitric acid are not much changed by deuterium substitution, those of perchloric acid are.

41. Hydration in the Lower Range

In view of the strength of perchloric acid it makes sense to investigate hydration and H-preference of the hydrogen ion under the simplifying assumption of complete dissociation. Accordingly we introduce

$$\alpha = 1 \tag{4.1}$$

into (2.20) and (2.21), and solve for s/p, assuming various values of q. The calculations are based on the limiting slopes, which are now represented by

$$s_{10} = 100/(11.507 - 2.444\cdot10^{-2}t + 0.335\cdot10^{-4}t^2)$$

$$s_{11} = 100/(7.189 - 0.203\cdot10^{-2}t - 0.248\cdot10^{-4}t^2) .$$

It is seen from Figures 10-12 that the calculated limiting slopes for intermediate isotopic mixtures, as given by the extrapolation of the broken lines or also by (2.25), are in very good agreement with the observed results.

In the whole range the quality of the agreement of calculated lines and observed data is not much influenced by the choice of q. The relation (2.22) is therefore only a crude estimate. The resulting hydration number m (equation 2.9) runs from 1.6 to 2. Since it has been obtained by fitting the data over a range of moderate concentrations, the low values are not unreasonable. They are not incompatible with the usually assumed limiting value m=4 for low concentrations. The slight increase of the hydration number with the temperature is not in contradiction with our general knowledge since the hydration number is the result of a balance between the strength of hydrogen bonds in the ion and in water. A higher bonding enthalpy change for the ion is not at all unlikely.

The comparison of the observed data with the calculated curves in Figures 10-12 furnishes a very satisfactory confirmation of the model assumed for the hydrogen distribution in Section 2. Deviations for mole fractions approaching 0.5 are to be expected in view of incomplete dissociation and concentration dependence of q. Corresponding refinements

of the model obviously could be introduced; but it may be questioned whether such formal refinements make sense.

42. Solvation in the Upper Range

The strong increase of the shift on deuteration in the upper range ($x > 0.5$, $p > 1$ in Figure 1 of the preceding paper[10]) causes a serious difficulty in the interpretation. There cannot be any doubt that the shifts near p=3 reflect the complete dissociation of water in the acid

$$H_2O + HClO_4 = H_3O^+ + ClO_4^- \quad (4.2)$$

Consequently the extrapolation of the limiting slope

$$\lim_{p=3} ds/dp \quad (4.3)$$

back to p=1 (Figure 1 of the cited paper) should give the shift value for a fictitious solution consisting only of H_3O^+ and ClO_4^-, i.e., the specific shift σ_1 of the hydronium ion H_3O^+. The steeper slope of the shift curve near p=3 of $DClO_4$ compared with $HClO_4$ would be explained by the H-preference of H_3O^+ over $HClO_4$.

The difficulty of this interpretation, which we had adopted before, results from the observation that the shift s for deuterated acids in part of the upper range is higher than σ_1. Even if the H-distribution ratio is extremely in favor of the ion over the acid molecule, and even if water were completely dissociated in the whole range from p=1 to 3, the shift could not exceed the value σ_1 of a solution containing only H_3O^+ as shift-producing species. Incomplete dissociation and a finite H-distribution ratio would lower this upper limit.

This seeming contradiction is explained by solvation of the hydrogen

ion. For a solvate

$$(H_3O \cdot n\ HClO_4)^+$$

the specific shift τ_n lies still on the straight line obtained by back extrapolation of (4.3) to a certain value x_n of the acid mole fraction. This value is the mole fraction in which the fictitious solutions consists only of $(H_3O \cdot n\ HClO_4)^+$ and ClO_4^-. The computation furnishes the data of Table IV obtained by linear interpolation between p=1; σ_1=6.056 and p=3; s_2=5.759.

Table IV. Specific Shifts of Hypothetical Solvates (65°C)

n	x_n	p_n	τ_n
0	0.5	1	6.056=σ_1
1	0.667	1.5	5.982
3	0.8	2	5.908

The actual specific shift of H_3O^+ must be appreciably higher, even higher than $\bar{\sigma}_1$ = 7.150 (65°C), the value derived previously for the specific shift for H in D_3O^+. A revision of the estimate of the degree of dissociation α in the middle range should be based on a solvate but since the values τ_n do not differ much from σ_1, no appreciable changes of the numerical results should be expected.

The surprising steepness of the limiting slope of $DClO_4$ near p=3 is now explained by H-preference of the ion in exactly the same manner as the steepness of the slope at low concentration.

A minor observation fits in very well with this interpolation. The shift curves for $HClO_4$ (Figure 13) show a slight hump and dip. Inflexion points are seen at x = 0.88 (65°C) and 0.85 (25°C). This

irregularity, occurs on approach of the range where, on dilution, not enough molecules $HClO_4$ are available for hydrogen bonding with the ion. The solvate therefore should gradually change into the hydrate. The measurements on deuterated acids do not define the shift curves in sufficient detail for the discovery of an inflexion point.

5. Conclusions

Long ago it was emphasized by Hantzsch and other authors that perchloric acid is one of the most strongly dissociated acids. The first crudely quantiative Raman intensities were presented in the second paper[2] of this series. The great difference in the molecular states of nitric acid and perchloric acid was pointed out; the complete dissociation of water in nearly anhydrous solutions was also recognized in 1944.

Nuclear magnetic resonance[3,8] furnished more information over the whole range of $HClO_4$. But the interpretation by means of the model that had been successful for nitric acid failed here. This was soon pointed out in a personal communication by T. F. Young, quoted by Hood and Reilly[8] in 1960 on the basis of Gasner's Raman measurements[16]. The reason for the failure was mentioned by Hood and Reilly: The specific shift of the hydrogen ion varies with its hydration and therefore with the acid concentration. The variation is small compared with the influence of incomplete dissociation for nitric acid but not for perchloric acid. Heinziger and Weston[19] arrived at similar results as Young and Gasner. Wynne-Jones[20] and Covington[21,24] and their coworkers repeated measurements of the earlier authors and presented more criticism than information.

The two preceding papers of this series and the present one resulted from the conclusion that not endless repetition of earlier measurements

in a limited, easily accessible concentration range but only new determinations over the whole range and extension to DNO_3 and $DClO_4$ could further elucidate the molecular state of the acids. The work on HNO_3-DNO_3-water furnished a welcome confirmation of the older results and new information on DNO_3. The work on $HClO_4$-$DClO_4$-water confirmed and extended earlier results[25,26,28] on the distribution of H between ions and water, and furnished information on the hydration and solvation of the hydrogen ion.

The results of this series are believed to justify our leading guideline: To gather full experimental information in a whole field and then to discuss the data in view of the currently available theoretical principles. The collection of complete information is much more helpful than the provision for a bare minimum amount of data required for the criticism of some model.

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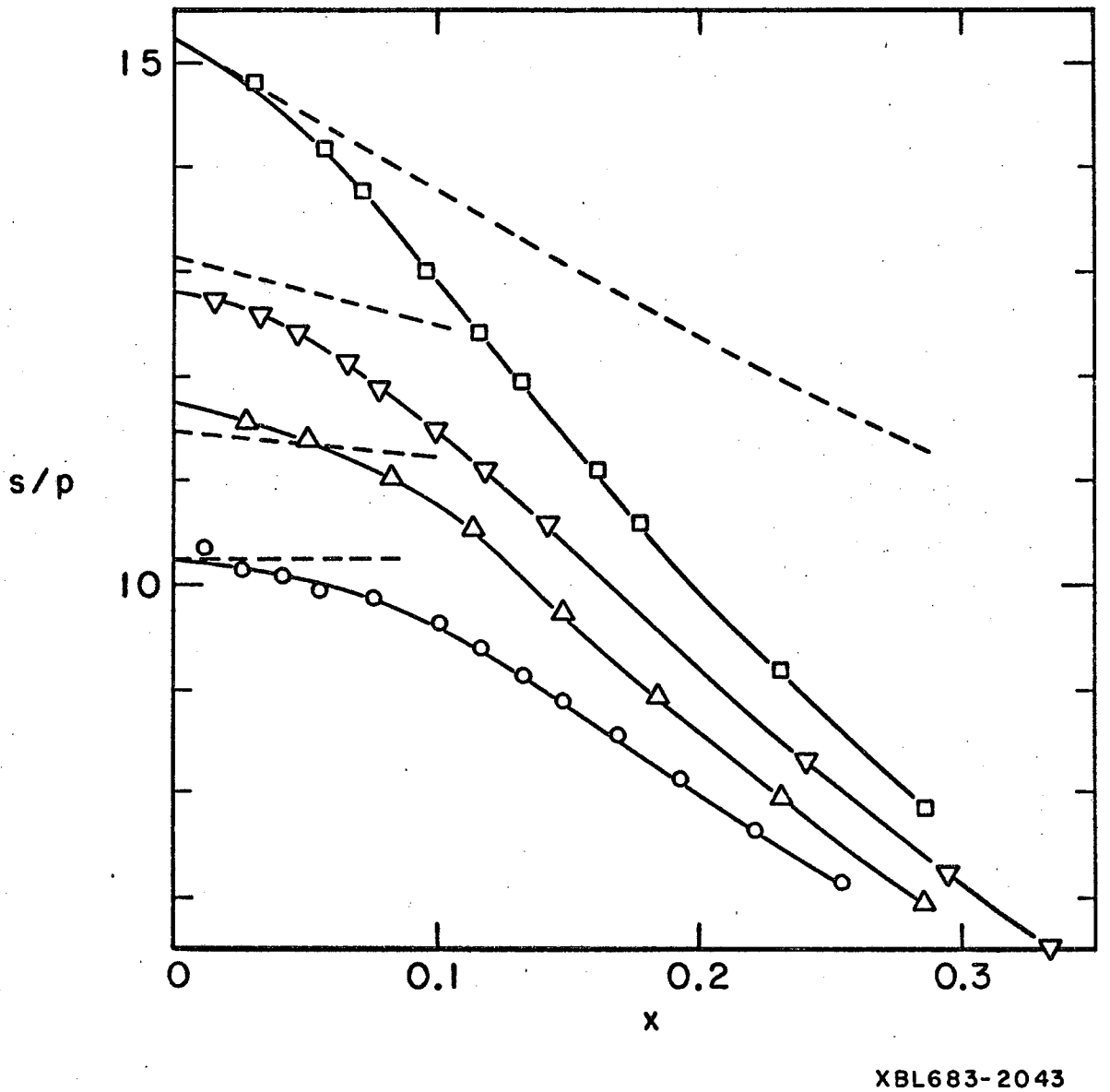

Fig. 1 Nitric acid, s/p at moderate concentrations

○ r = 0
△ r = 0.32
▽ r = 0.67
□ r = 1

The broken lines are calculated. 0°C, q = 4.3.

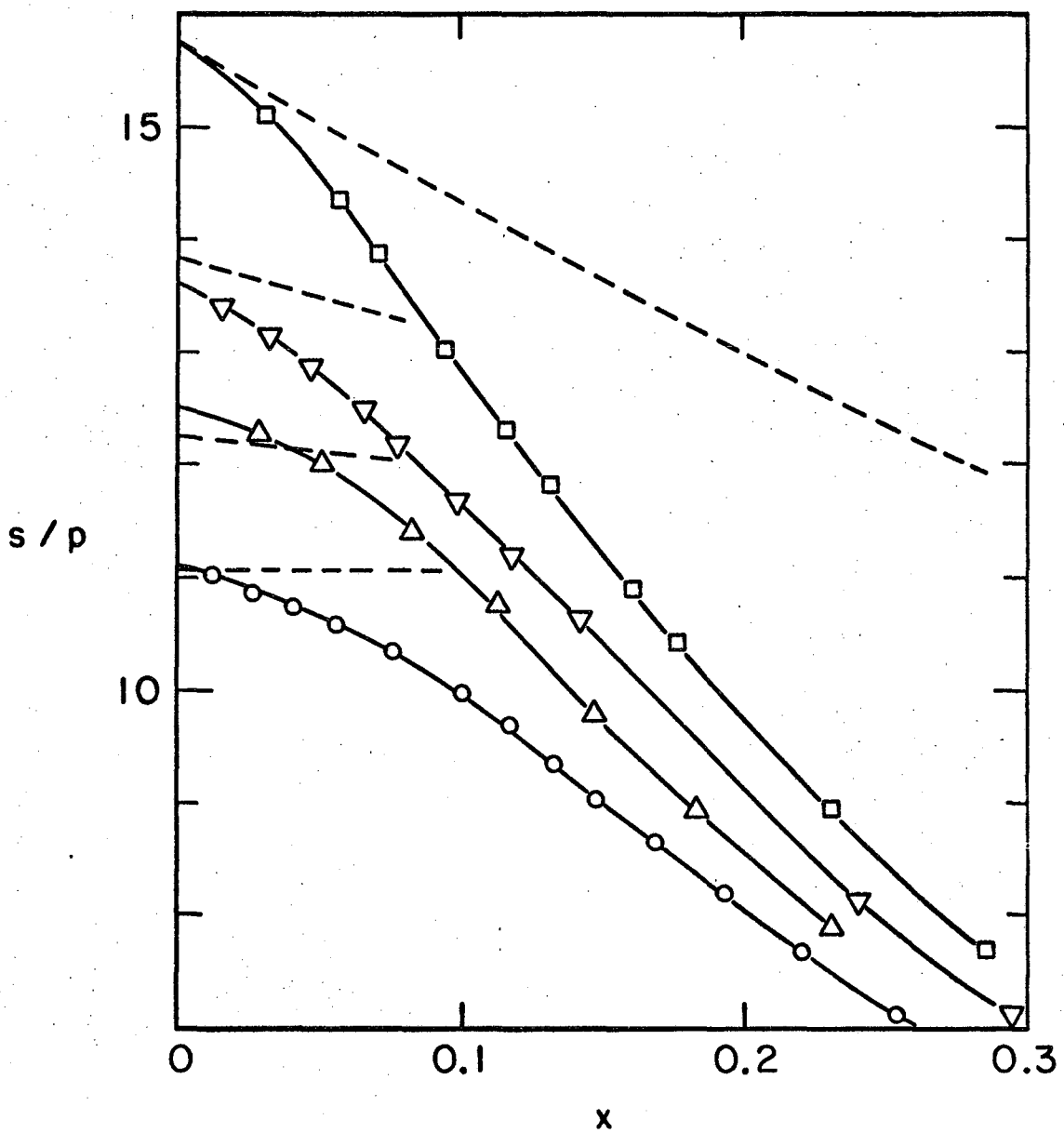

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Fig. 2 Nitric acid, the same as Fig. 1, but for 25°C, q = 4.55.

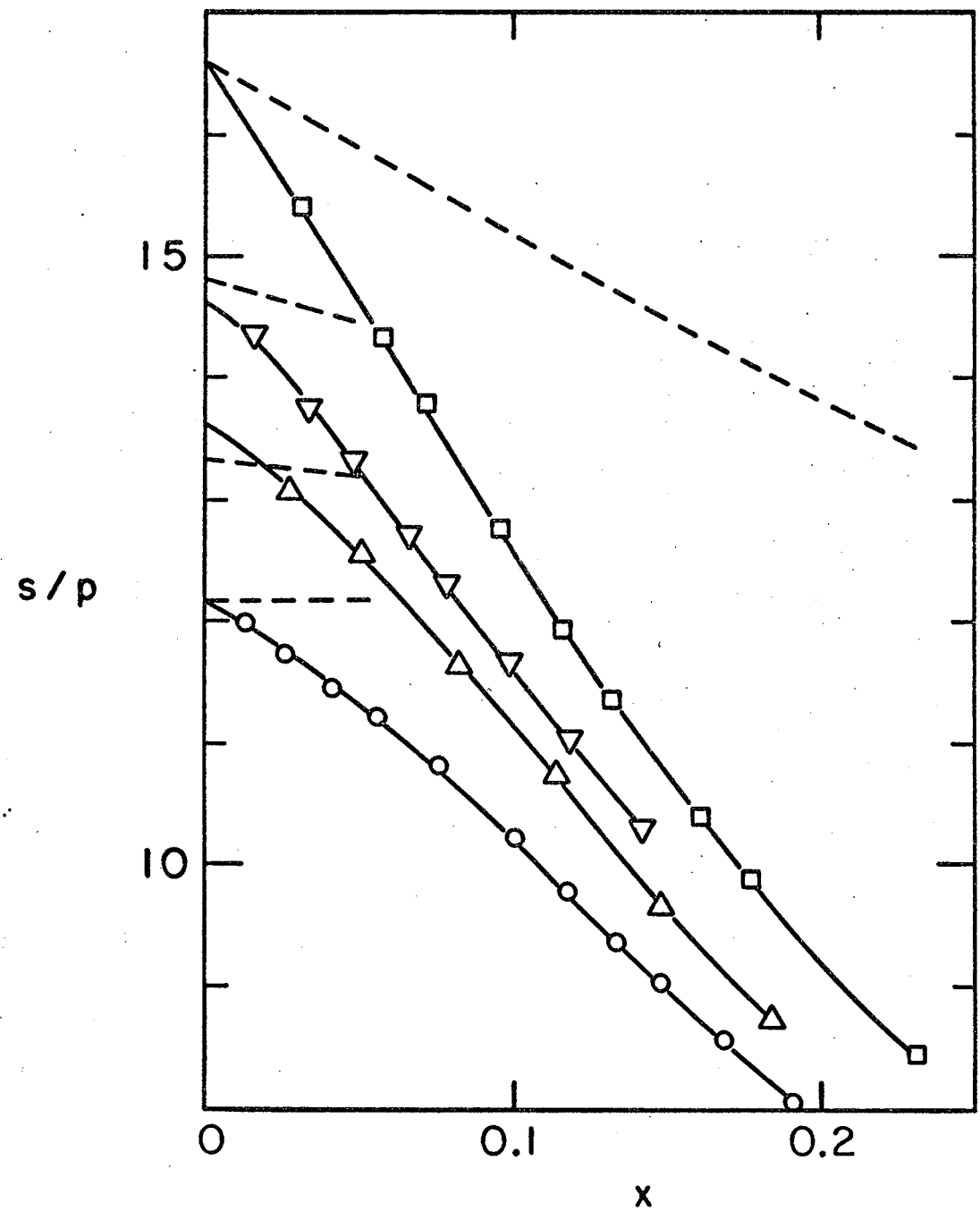

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Fig. 3 Nitric acid, the same as Fig. 1, but for 65°C, q = 4.95.

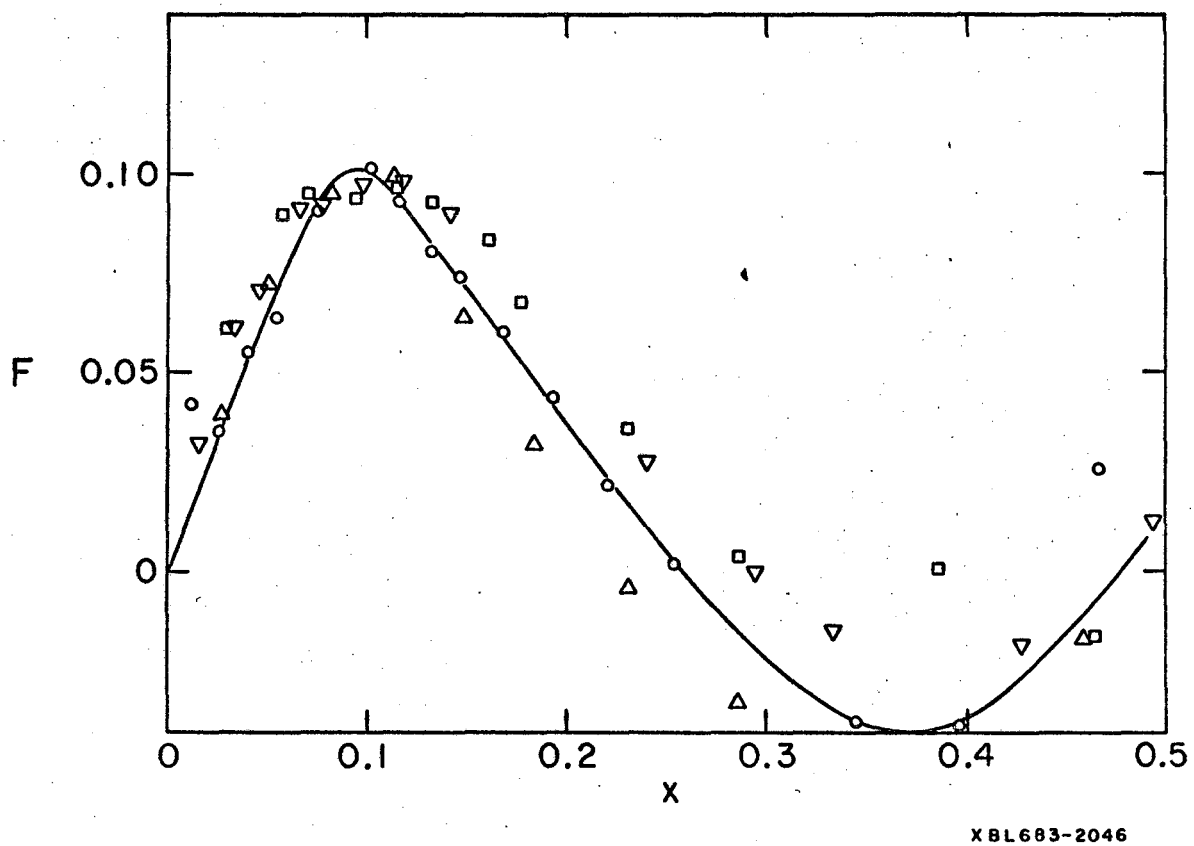

Fig. 4 Nitric acid, deviation function $F = 1-\alpha+2x$, 0°C.

○ r = 0
△ r = 0.32
▽ r = 0.67
□ r = 1

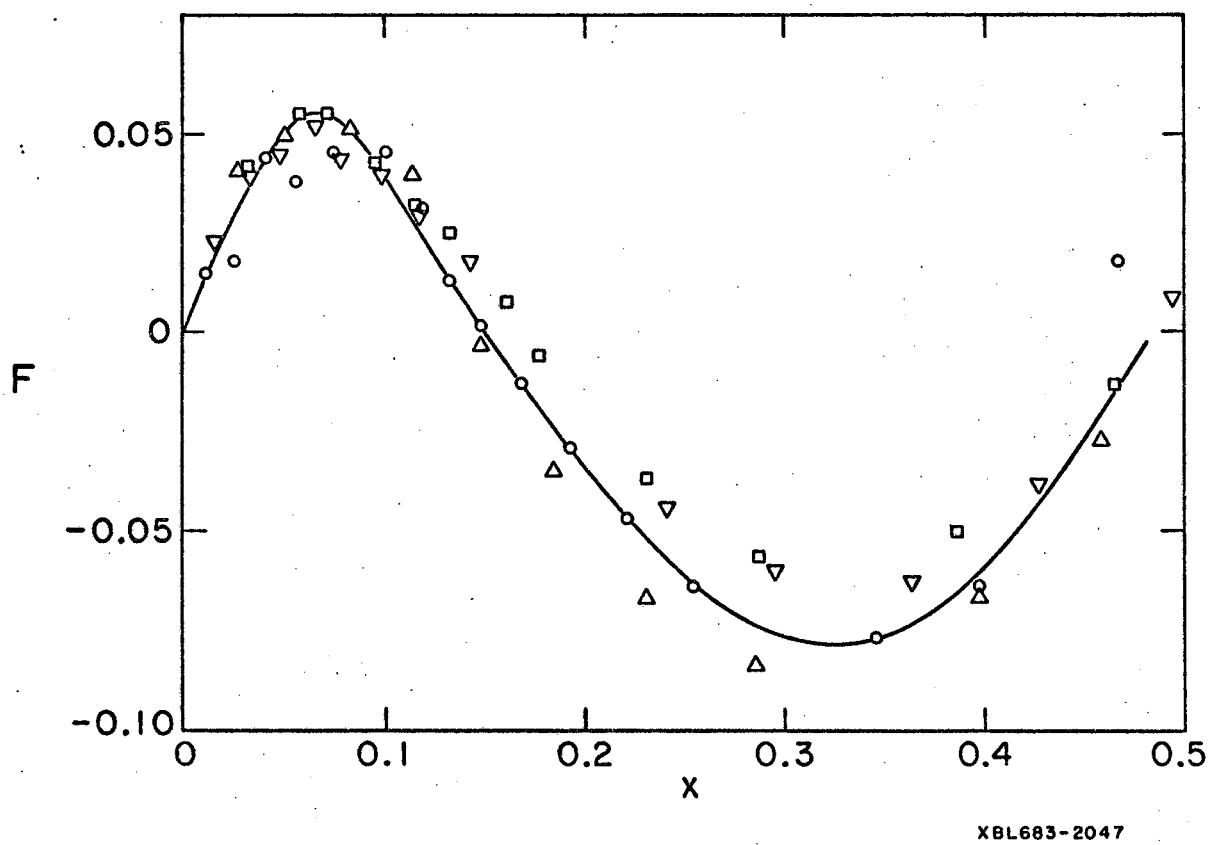

Fig. 5 Nitric acid, F for 25°C.

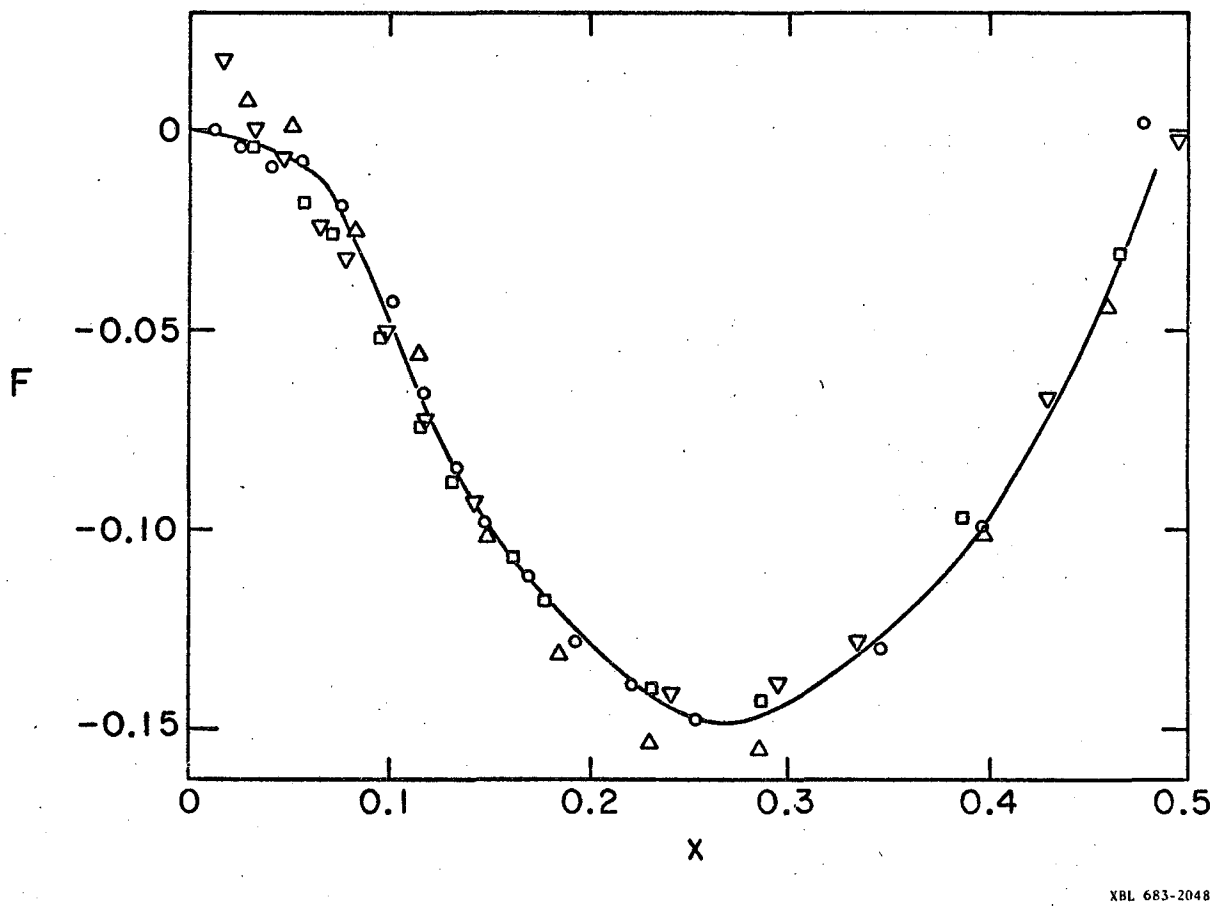

Fig. 6 Nitric acid, F for 65°C.

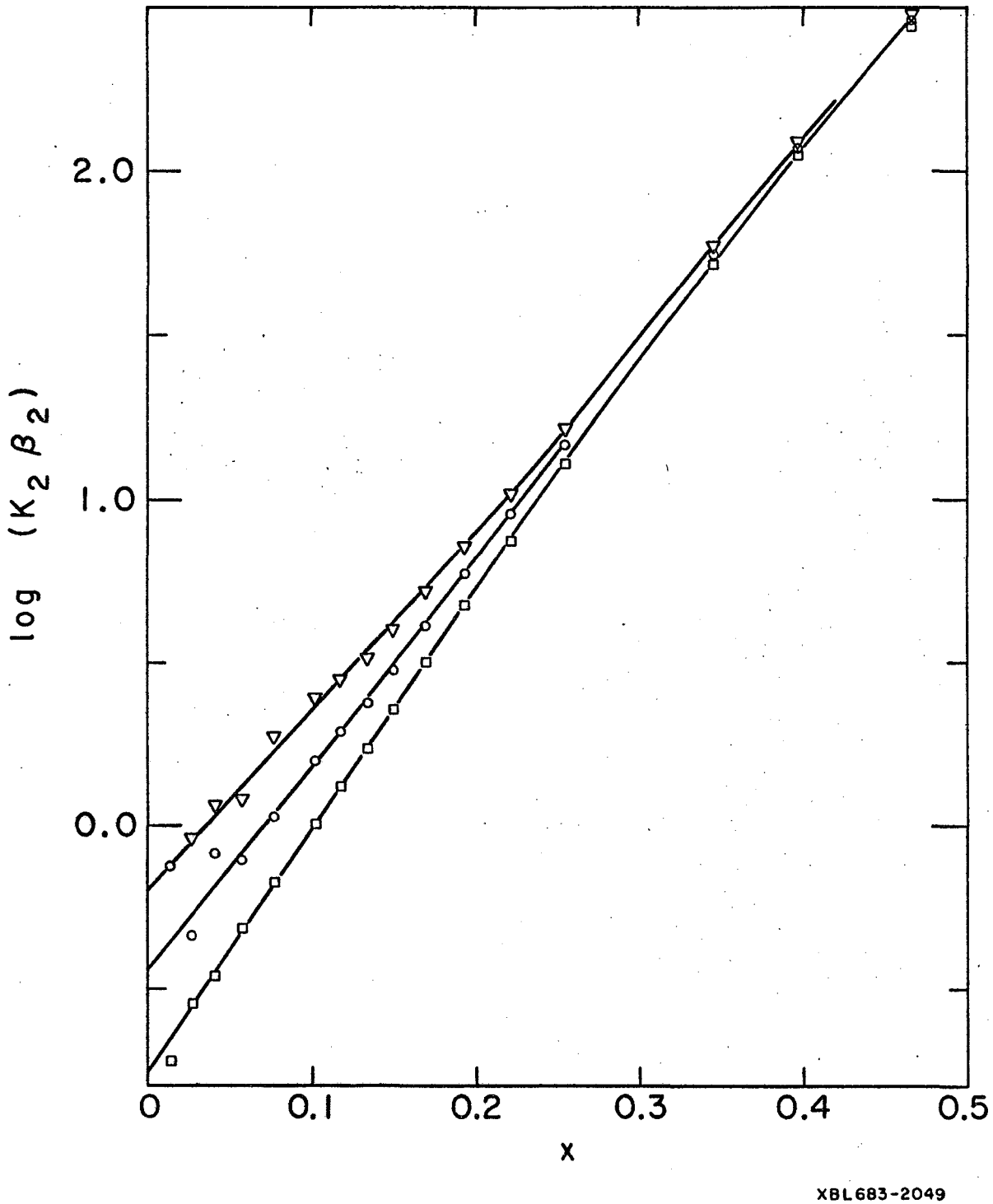

Fig. 7 Dissociation constant K_2 of HNO_3.

▽0°C
○25°
□65°

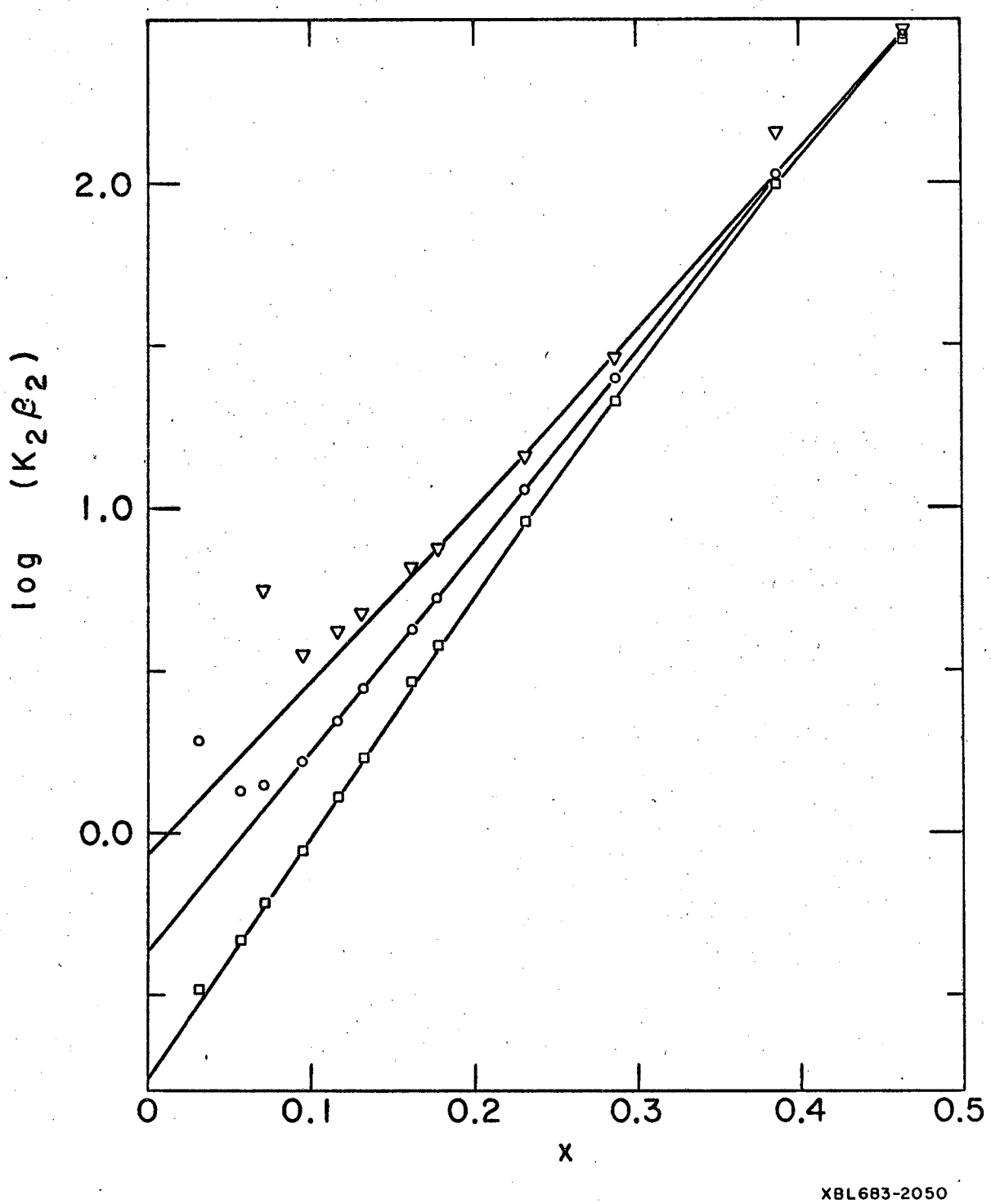

Fig. 8 Dissociation constant K_2 of DNO_3

▽ 0°C
○ 25°C
□ 65°C

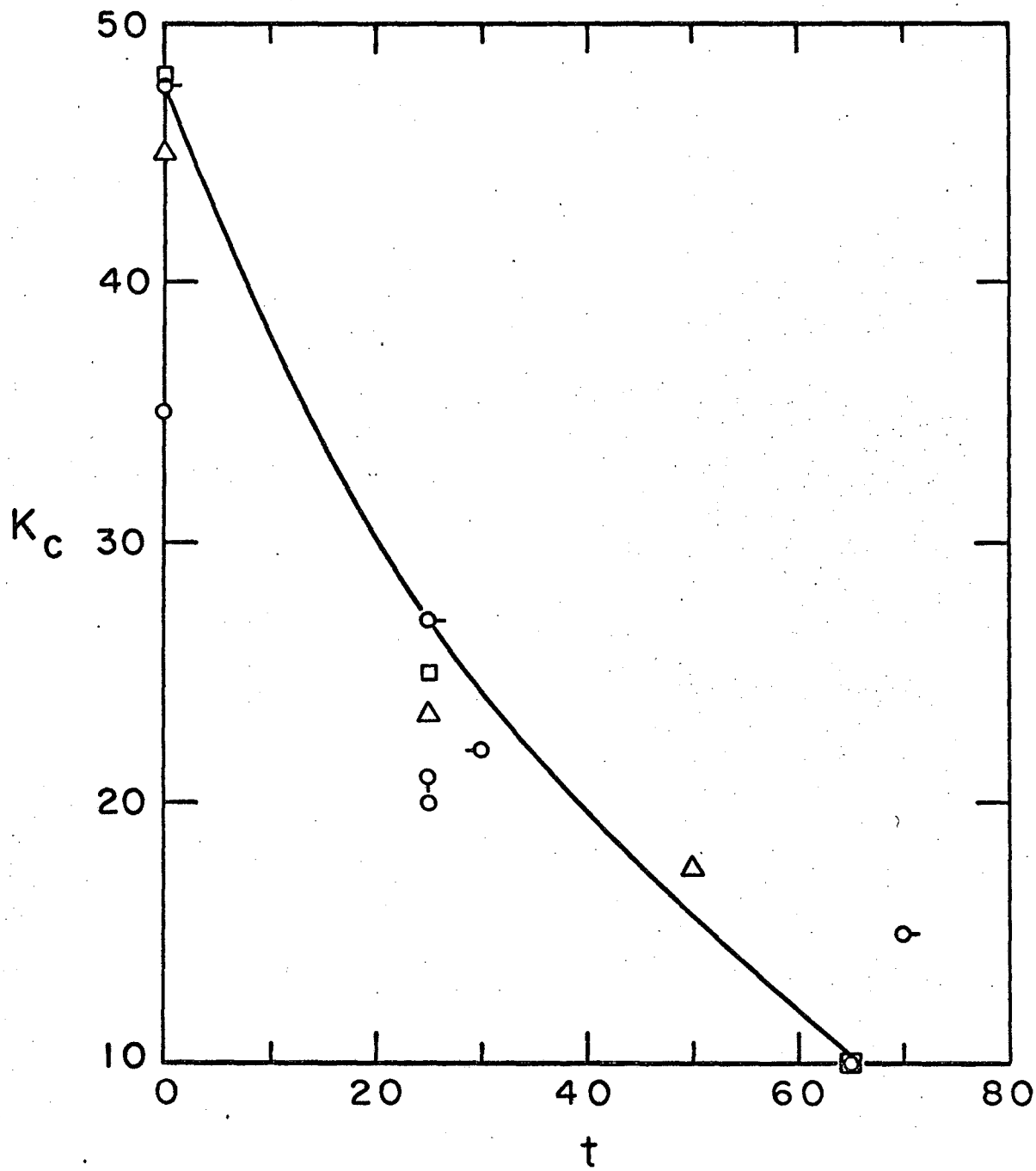

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Fig. 9 Dissociation constants K_c of nitric acid

Redlich and Bigeleisen[1]; Hood, Redlich, Reilly[3]; △ Young and Krawetz[12,14]; Hood and Reilly[8]; ○ Present work; □ Present work (DNO_3)

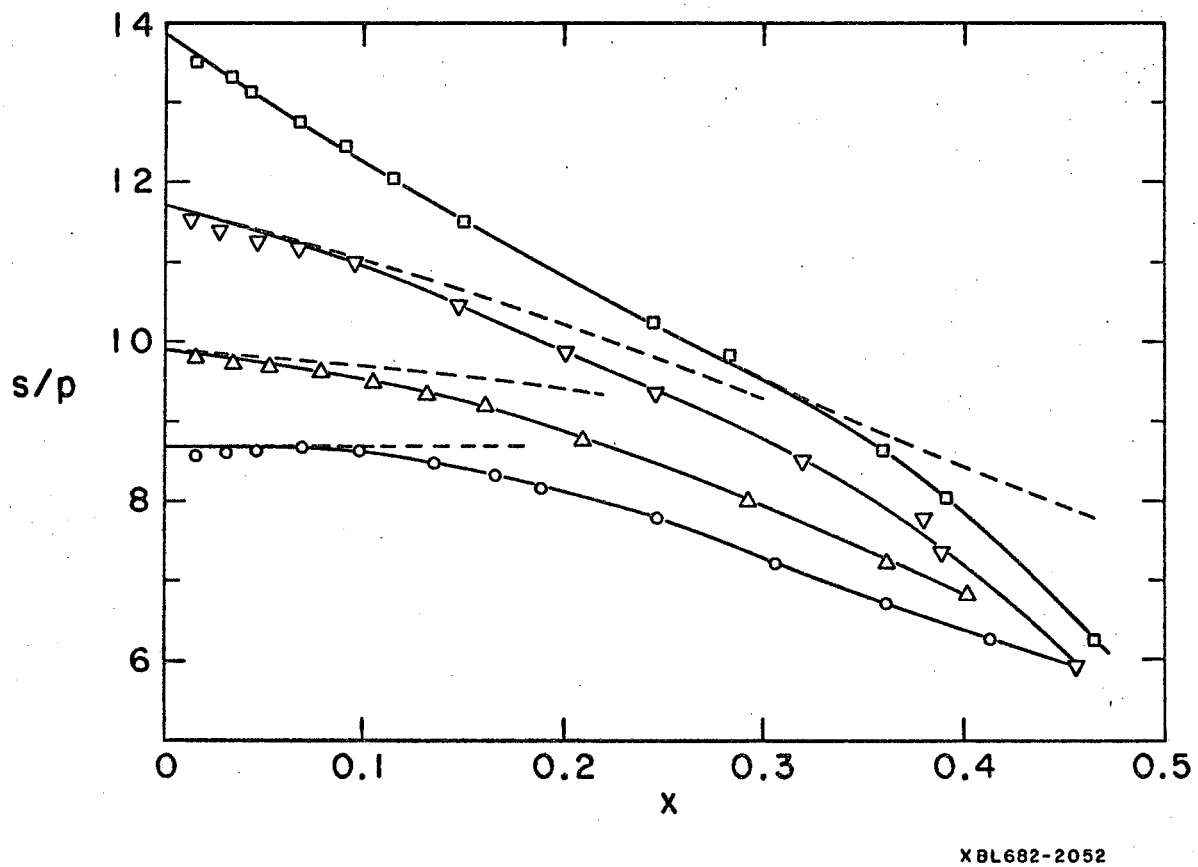

Fig. 10 Perchloric acid, s/p at 0°C, q = 4.3

○ r = 0
△ r = 0.32
▽ r = 0.67
□ r = 1

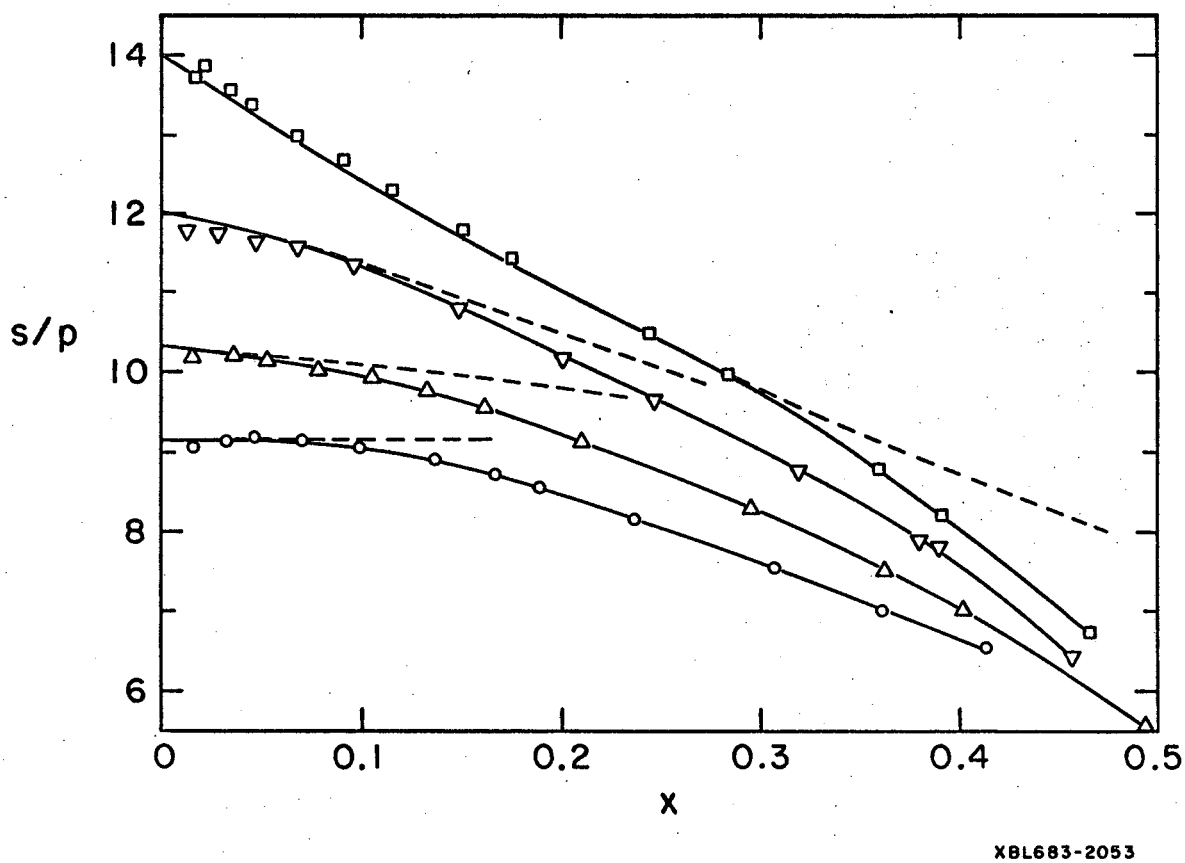

Fig. 11 Perchloric acid, s/p at 25°C, q = 4.55.

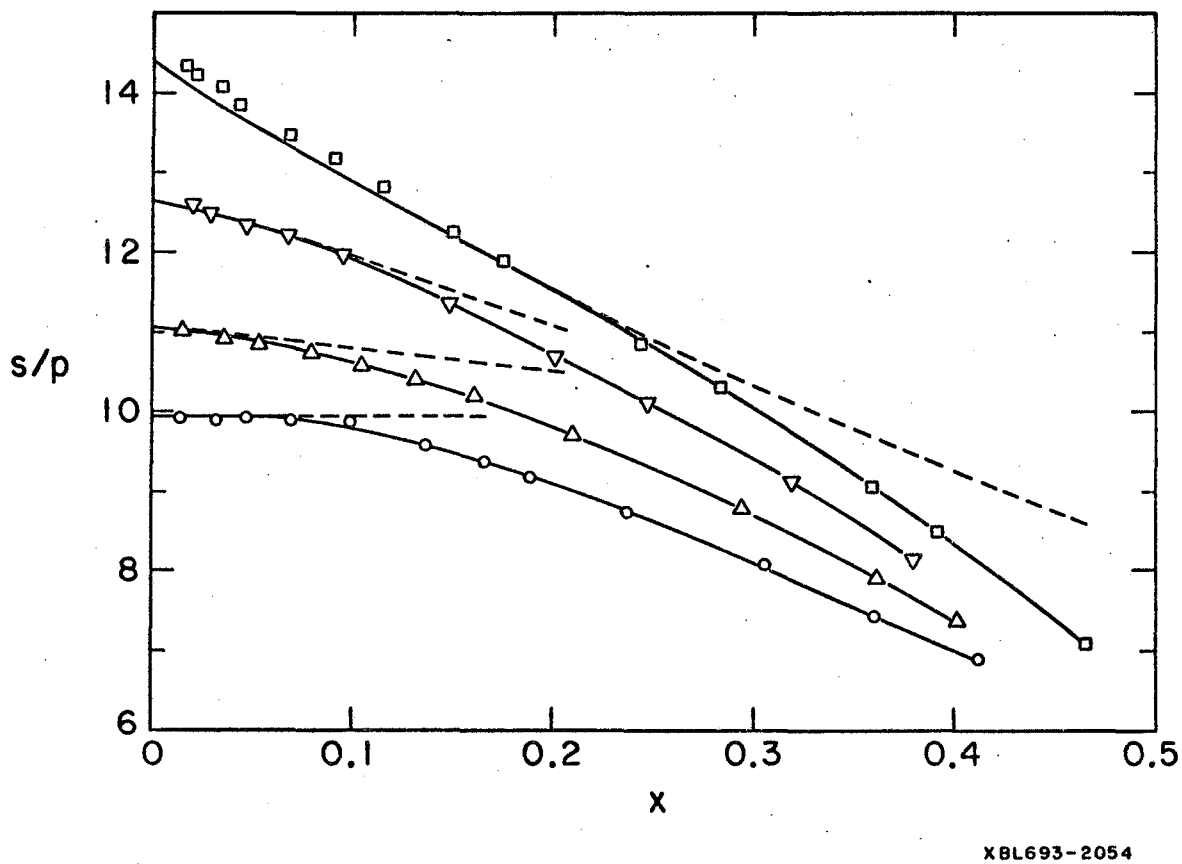

Fig. 12 Perchloric acid, s/p at 65°C, q = 4.95.

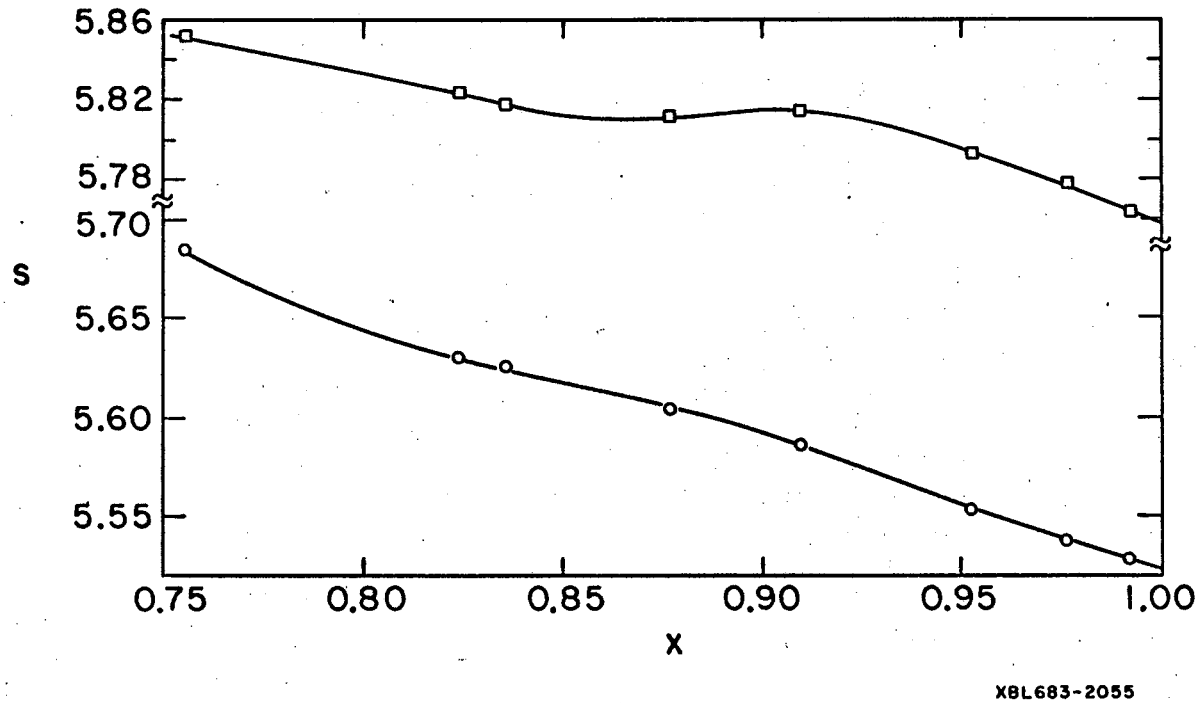

Fig. 13 Shifts of perchloric acid at high concentrations

○ 25°C

□ 65°C

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