UCRL-17694

cy. 2

University of California

Ernest O. Lawrence Radiation Laboratory

THERMODYNAMICS OF SOLUTIONS XII.
CONSISTENCY OF SPARSE DATA.
ACTIVITIES OF NITRIC AND PERCHLORIC ACIDS.

O. Redlich, W. E. Gargrave and W. D. Krostek

July 1967

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

UCRL-17694 cy. 2

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.

THERMODYNAMICS OF SOLUTIONS XII. CONSISTENCY OF SPARSE DATA. ACTIVITIES OF NITRIC AND PERCHLORIC ACIDS.

O. Redlich, W. E. Gargrave and W. D. Krostek

Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

July, 1967

Abstract

Usual consistency checks for activities can be applied only to fairly extensive sets of data. A new variant is proposed that can be used even if data are available only for three concentrations.

The activities of nitric and perchloric acids are computed in the whole concentration range from total vapor pressure and partly from other data.

Introduction

The application of the relation of Gibbs and Duhem to tests of the consistency of data for solutions has been frequently discussed in the last twenty years. If measurements are available only for a small number of solutions, the usual methods of testing fail. Such a check, however, was desired for a few determinations of the partial pressures of nitric acid solutions, differing from other information. A method useful in such cases was therefore developed for a revision of the activities of nitric and perchloric acids, needed in an investigation of their molecular structures.

The Differential Test for Sparse Data

For a binary mixture we define

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 \tag{1}$$

and find[1], according to the relation of Gibbs and Duhem,

$$dQ/dx_2 = \log (\gamma_2/\gamma_1) \ . \tag{2}$$

An analogous relation holds for the activities a_1 and a_2 and the function

$$Q_p = x_1 \log a_1 + x_2 \log a_2 \ , \tag{3}$$

namely,

$$dQ_p/dx_2 = \log (a_2/a_1) \ . \tag{4}$$

The activities may also be replaced by partial vapor pressures if the vapor is perfect.

Davis and de Bruin[2] reported partial vapor pressures p_1(water) and p_2(acid) for solutions of nitric acid at three concentrations. Their measurements, including results for p_2 at other concentrations, deviate considerably from the results of Potier[3]. This author's data, by the way,

are in sufficient agreement with an older compilation[4]. From the partial pressures of Davis and de Bruin for three concentrations we derive Q_p and separately dQ_p/dx_2 (Equation (4)). The data for Q_p are indicated in Figure 1 by the circles, the slopes by the short straight lines through the experimental points.

The differential test is now carried out by drawing the best line representing the points as well as the indicated slopes. The example of Figure 1 shows that no smooth curve satisfying the prescribed slopes can be drawn through the experimental points (In addition, the discrepancies between the data of Davis and de Bruin and other authors are appreciable).

The magnitude of the inconsistency of the original data can be estimated by drawing the "best" smooth curve in a diagram similar to Figure 1 but drawn on a sufficiently large scale. Then the points at the experimental concentrations and the tangents are marked. The values of Q_p and dQ_p/dx_2 are read off the diagram. Now Equations (3) and (4) are solved for a_1 and a_2 (or p_1 and p_2, or γ_1 and γ_2).

These graphical operations can be easily performed with sufficient precision. In the very unlikely case that the required scale did turn out to be inconvenient, one would design a suitable deviation function. In actual use this application of a differential equation to a few given points has been found to be very efficient.

Nitric Acid

The activity coefficients of nitric acid are to be based on determinations of the freezing points[4,5,6], partial pressures[2,7,8] and total pressures[3,4].

Freezing points unquestionably give the best information below $x_2 = 0.06$. Results for the whole range at 25°C are shown in Figure 2. The abscissa $x_2^{0.5}$ has been chosen because here the theory of Debye and Hückel prescribes a finite limiting slope.

The definition of the activity coefficient γ_2 chosen in the present work is different from the usual convention. The activity is expressed by

$$a_2 = (x_2\gamma_2)^2 \quad ; \quad \lim_{x_2=0} a_2 = x_2^2 \, . \tag{5}$$

The conventional definition by the molality

$$a_2' = (m\gamma_2')^2 \quad ; \quad \lim_{m=0} a_2' = m^2 \tag{6}$$

leads to the relation

$$\gamma_2 = (1 + 0.018016\ m)\ \gamma_2' \, . \tag{7}$$

Haase's data[8] are based on a long extrapolation to $x_2 = 0$. They can be tied quite well to the freezing point results[4] by addition of 0.009 to his values of log γ_2. The comparison of Potier's results[3] (extrapolated from 0 and 20° to 25°C) with the other data gives a difference of 0.957 in the standard state values of log γ_2. In other words, log γ_2 for pure HNO_3 based on (5) is 0.957 and log a_2 of HNO_3 is 1.914, while it is normed at unity by Potier.

A compilation of the best values of log γ_2 and log a_1 (obtained from freezing point data and by straightforward application of the equation of Gibbs and Duhem is shown in Table 1.

Perchloric Acid

The isopiestic measurements of Robinson and Baker[9] and of Haase and coworkers[8] below $x_2 = 0.22$ are in good agreement. Information over

Table 1. Activity Coefficients of Nitric Acid at 25°C.

$(a_2 = (x_2\gamma_2)^2 \; ; \; \lim_{x_2=0} a_2 = x_2^2 \; ; \; \lim_{x_2=0} a_1 = 1)$

x_2	$\log \gamma_2$	$-\log a_1$
1.80×10^{-5}	-0.01518	1.544×10^{-5}
9.00×10^{-5}	-0.03248	7.635×10^{-5}
3.60×10^{-4}	-0.06146	3.016×10^{-4}
1.799×10^{-3}	-0.1044	1.469×10^{-3}
8.930×10^{-3}	-0.1420	7.400×10^{-3}
1.770×10^{-2}	-0.1350	1.533×10^{-2}
0.02	-0.131	1.750×10^{-2}
0.04	-0.076	0.0388
0.06	-0.006	0.0645
0.08	0.058	0.0928
0.10	0.126	0.125
0.16	0.314	0.241
0.22	0.459	0.373
0.28	0.579	0.523
0.34	0.683	0.692
0.40	0.772	0.879
0.46	0.838	1.070
0.52	0.886	1.264
0.58	0.921	1.46
0.64	0.945	1.68
0.70	0.965	1.91
0.74	0.974	2.08
0.78	0.979	2.26
0.82	0.981	2.45
0.86	0.980	2.66
0.90	0.977	2.90
0.94	0.972	3.22
0.98	0.963	
1.00	0.957	

the rest of the range has been based on Mascherpa's total pressures[10].

In addition to the definition (5) we also define activities b_1 and b_2 based on the pure acid as reference state by

$$\lim_{x_2=1} (b_1/x_1^2) = 1 \; ; \; \lim_{x_2=1} b_2 = 1 \; . \tag{8}$$

The vapor may be considered to be a perfect gaseous mixture. Denoting the total pressure and partial pressures by P, p_1 and p_2, and the vapor pressures of the pure components by p_1^o and p_2^o, we have for the azeotropic solution

$$a_1 = p_1/p_1^o = x_1 P/p_1^o \tag{9}$$

and

$$b_2 = p_2/p_2^o = x_2 P/p_2^o \tag{10}$$

(The definitions of a_1 and b_2 are conventional for non-electrolytes, those for a_2' and γ_2' for binary electrolytes).

In the range $0.417 < x_2 < 0.710$ perchloric acid solutions at 25°C ($0.393 < x_2 < 0.835$ at 0°) are in equilibrium[10] with the solid hydrate $HClO_4 \cdot H_2O$. Therefore the product $a_1 a_2$ (or the product $b_1 b_2$) has the same value in the entire interval.

The derivation of activities from total pressures has often been discussed. The peculiar form of the pressure curve of perchloric acid caused considerable difficulties. Finally the differential equation of Lewis and Murphree[11] was integrated with increasing x_2 beginning from $x_2 = 0$ for an arbitrary set of values of $\lim_{x_2=0} dy_2/dx_2$, and with decreasing x_2 beginning from $x_2 = 1$ for a set $\lim_{x_2=1} dy_2/dx_2$. The criteria for the selection of the final curve from the family of integral curves were:

(a) Correct results for the azeotropic a_1 and b_2.

(b) The computation according to Gibbs and Duhem furnished the activity a_2 of perchloric acid for concentrations below the azeotrope. Similarly the water activity was obtained above the azeotrope, with due consideration being given to the constancy of the product $b_1 b_2$ in the presence of the solid hydrate. A criterion is the smoothness of the curve of $\log (\gamma_1/\gamma_2)$.

(c) Recalculated total pressures must check within experimental errors of about 0.05 mm.

(d) The computation must satisfy Equations (3) and (4).

In principle these conditions are trivial, but actually they are not easily satisfied due to the influence of experimental and small computational errors.

The results are shown in Figures 3 and 4 and Tables 3 and 4. The activity coefficients in Figure 3 are defined as

$$\gamma_2 = b_2^{0.5}/x_2 \ . \tag{11}$$

The limiting value of $\log \gamma_2 = -4.50$ for $x_2 = 0$ shows that the difference of the standards for $\log a_2$ and $\log b_2$ is -9.00.

The fact that $\log (b_1/x_2^2)$ has a finite limit at $x_2 = 1$ (normed to zero) expresses the complete dissociation of water in nearly anhydrous perchloric acid.

Recent measurements of perchloric acid pressures by Lilich and Shalygin[12] are not in good agreement with Mascherpa's data. An appreciably higher value is given for the azeotropic composition (see Table 2). We have not been able to find any reason for the discrepancies.

Table 2. Azeotrope of Perchloric Acid.

Temp. °C	x_2	P, total pressure	log a_1	log b_2
0 (Mascherpa)	0.3155	0.082	-1.900	-2.652
25 (Mascherpa)	0.3195	0.34	-2.009	-2.523
25 (Lilich)	0.344	0.064	-2.752	-3.166

Table 3. Activity Coefficients of Perchloric Acid

(below $x_2 = 0.417$; $a_2 = (x_2\gamma_2)^2$; $\lim_{x_2=0} a_2 = x_2^2$; $\lim_{x_2=0} a_1 = 1$)

x_2	log γ_2	log a_1
0.0004	-0.051	
0.0016	-0.089	
0.0036	-0.110	
0.0064	-0.119	
0.0100	-0.113	
0.0144	-0.101	
0.02	-0.075	-0.017
0.04	+0.071	-0.044
0.08	0.476	-0.135
0.12	1.004	-0.278
0.16	1.602	-0.492
0.20	2.150	-0.786
0.24	2.756	-1.175
0.28	3.334	-1.617
0.32	3.723	-2.013
0.36	3.959	-2.286
0.40	4.139	-2.539

Table 4. Activities b_1 and b_2 of Perchoric Acid Solutions.

(above $x_2 = 0.710$; $\lim_{x_2=1} b_1 = 1$; $\lim_{x_2=1} b_1 = x_1^2$)

	$-\log b_2$		$\log (b_1/x_1^2)$	
x_2	0°C	25°C	0°C	25°C
0.71		0.278		-0.146
0.72		0.271		-0.132
0.74		0.257		-0.105
0.76		0.241		-0.086
0.78		0.222		-0.073
0.80		0.202		-0.068
0.82		0.180		-0.068
0.835	0.223	-----	0.377	-----
0.84	0.217	0.157	0.368	-0.067
0.86	0.189	0.139	0.329	-0.065
0.88	0.164	0.119	0.292	-0.061
0.90	0.139	0.102	0.251	-0.055
0.92	0.117	0.084	0.207	-0.044
0.94	0.095	0.066	0.158	-0.034
0.96	0.074	0.049	0.106	-0.020
0.98	0.044	0.024	0.055	-0.009

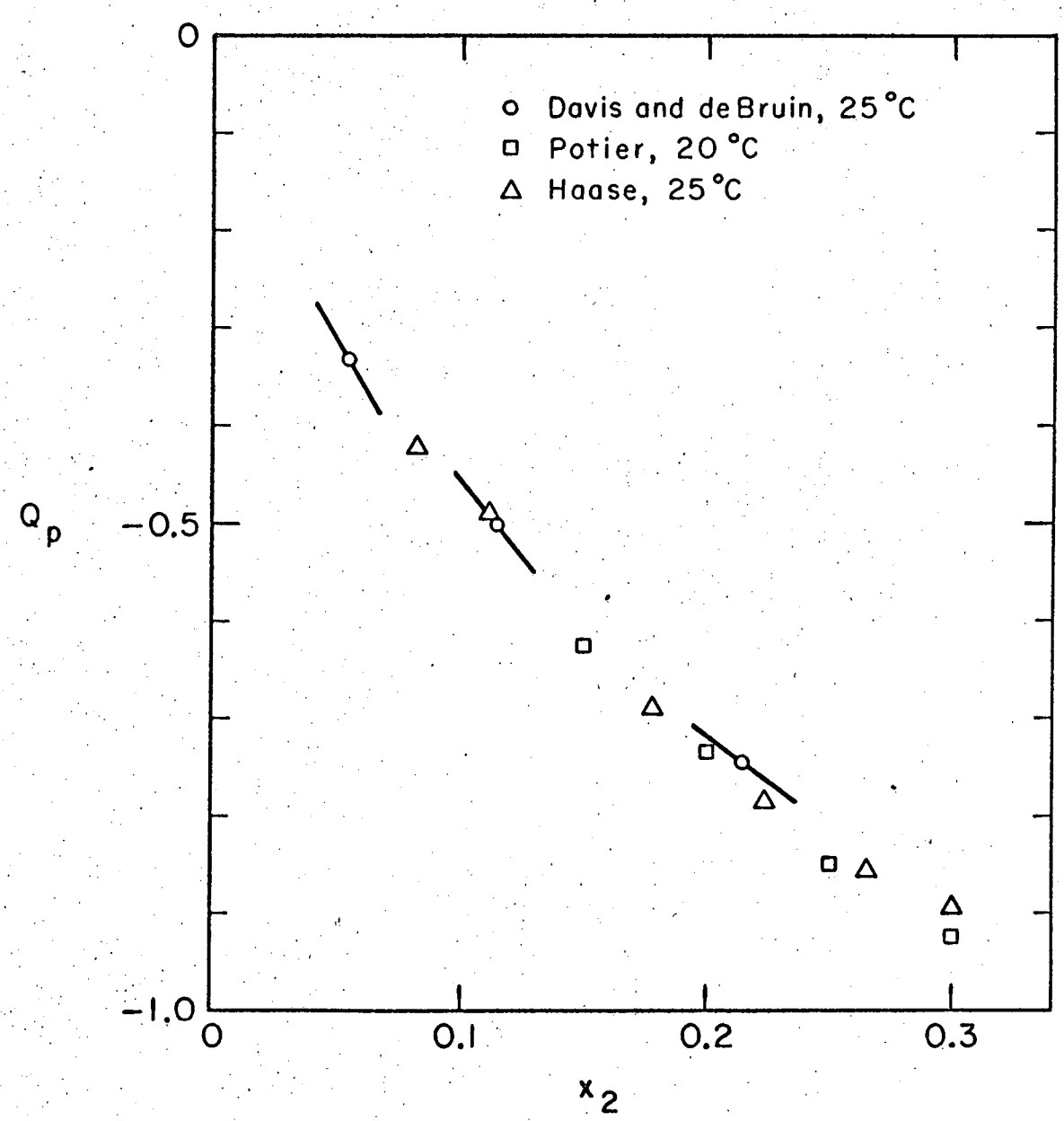
The preceding eleven communications of the series "Thermodynamics of Solutions" are listed as references 13 to 20.

Acknowledgement

This work was performed under the auspices of the United States Atomic Energy Commission at the Lawrence Radiation Laboratory of the University of California.

Bibliography

1. O. Redlich and A. T. Kister, Ind. Eng. Chem 40, 345 (1948).
2. W. Davis, Jr. and A. J. de Bruin, J. Inorg. Nucl. Chem. 26, 1069 (1964).
3. A. Potier, Ann. fac. sci. univ. Toulouse 20, 1-98 (1956).
4. Landolt-Börnstein Tabellen (Suppl. III), p.2145 (1935).
5. E. Abel, O. Redlich and B. v. Lengyel, Z. physik. Chem. 132, 189 (1928).
6. F. Hartmann and P. Rosenfeld, Z. physik. Chem. (A) 164, 377 (1933). See also ref. 4.
7. M. R. Vandoni and M. Laudy, J. Chem. Phys. 49, 99 (1952).
8. R. Haase, K.-H. Dücker and H. A. Küppers, Ber. Bunsen-Gesellschaft 69, 97 (1965).
9. R. A. Robinson and O. J. Baker, Proc. Roy. Soc., New Zealand, 76, 260 (1946).
10. G. Mascherpa, Revue de Chimie Minérale 2, 379 (1965).
11. W. K. Lewis and E. V. Murphree, J. Amer. Chem. Soc. 46, 1 (1924).
12. L. S. Lilich and V. M. Shalygin. Vestn. Leningrad Univ. 21 (22), Ser. Fiz. Chim. No. 4, 104-10 (1966).
13. I to IV. O. Redlich and A. T. Kister, Ind. Eng. Chem. 40, 341, 345 (1948). J. Chem. Phys. 15, 849 (1947). J. Amer. Chem. Soc. 71, 505 (1949).
14. V. O. Redlich and J. N. S. Kwong, Chem. Revs. 44, 233 (1949).
15. VI. O. Redlich, A. T. Kister and C. E. Turnquist, Chem. Eng. Progress, Symposium Ser. 48, No.2, 49 (1952).
16. VII. O. Redlich and A. T. Kister, J. Chem. Phys. 36, 2002 (1962).
17. VIII. O. Redlich and A. K. Dunlop, Chem. Eng. Progress, Symposium Ser. 59, No.44, 95 (1963).
18. IX. F. J. Ackerman and O. Redlich, J. Chem. Phys. 38, 2740 (1963).
19. X. G. W. Lundberg, J. Chem. Eng. Data, 9, 193 (1964).
20. XI. O. Redlich, F. J. Ackerman, R. D. Gunn, Max Jacobson, and S. Lau, Ind. Eng. Chem. Fundamentals, 4, 396 (1965).



XBL 675-3214

Fig. 1 Function Q_p for nitric acid (x_2 = mole fraction HNO_3).

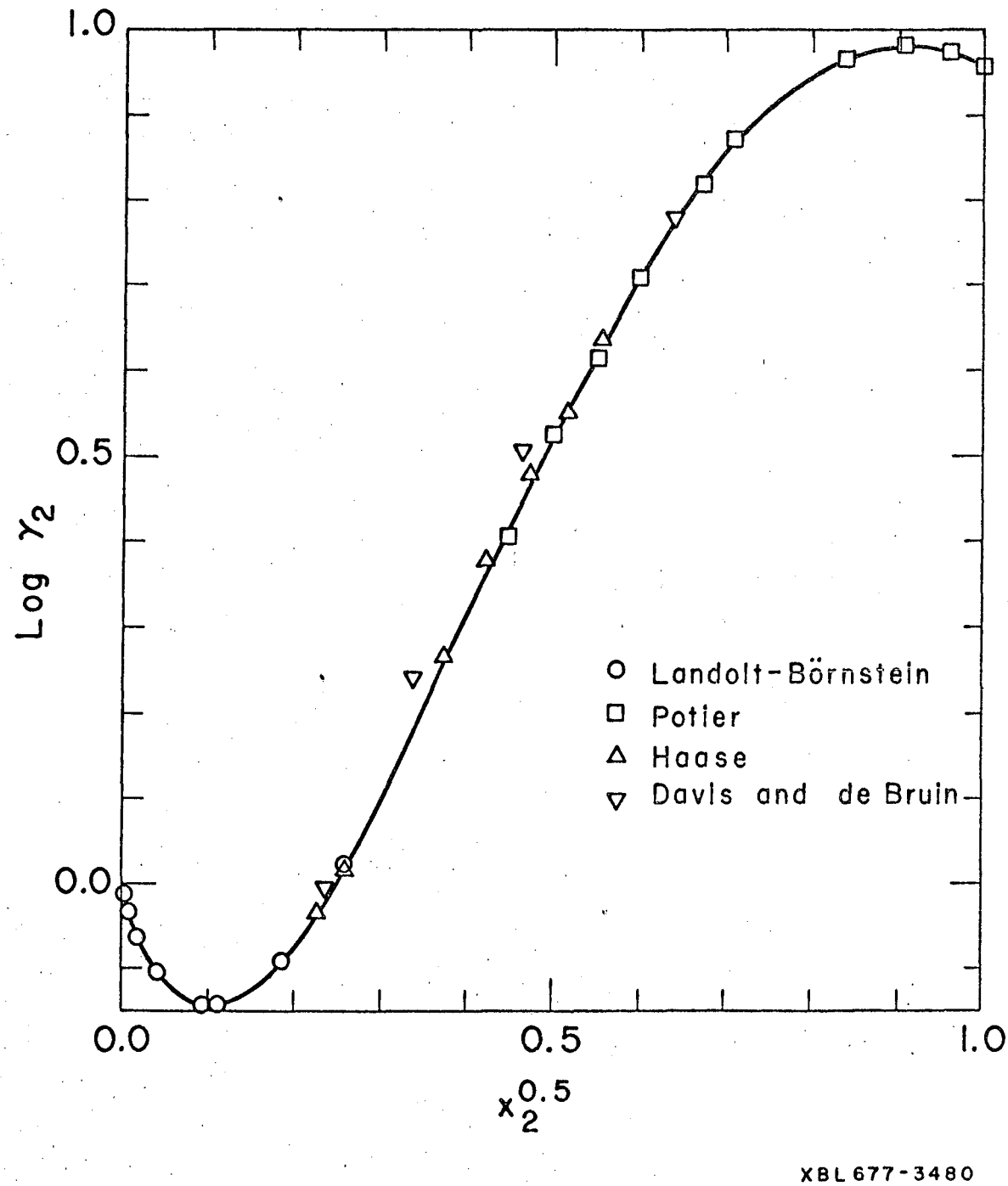


Fig. 2 Activity coefficient of nitric acid

Fig 2

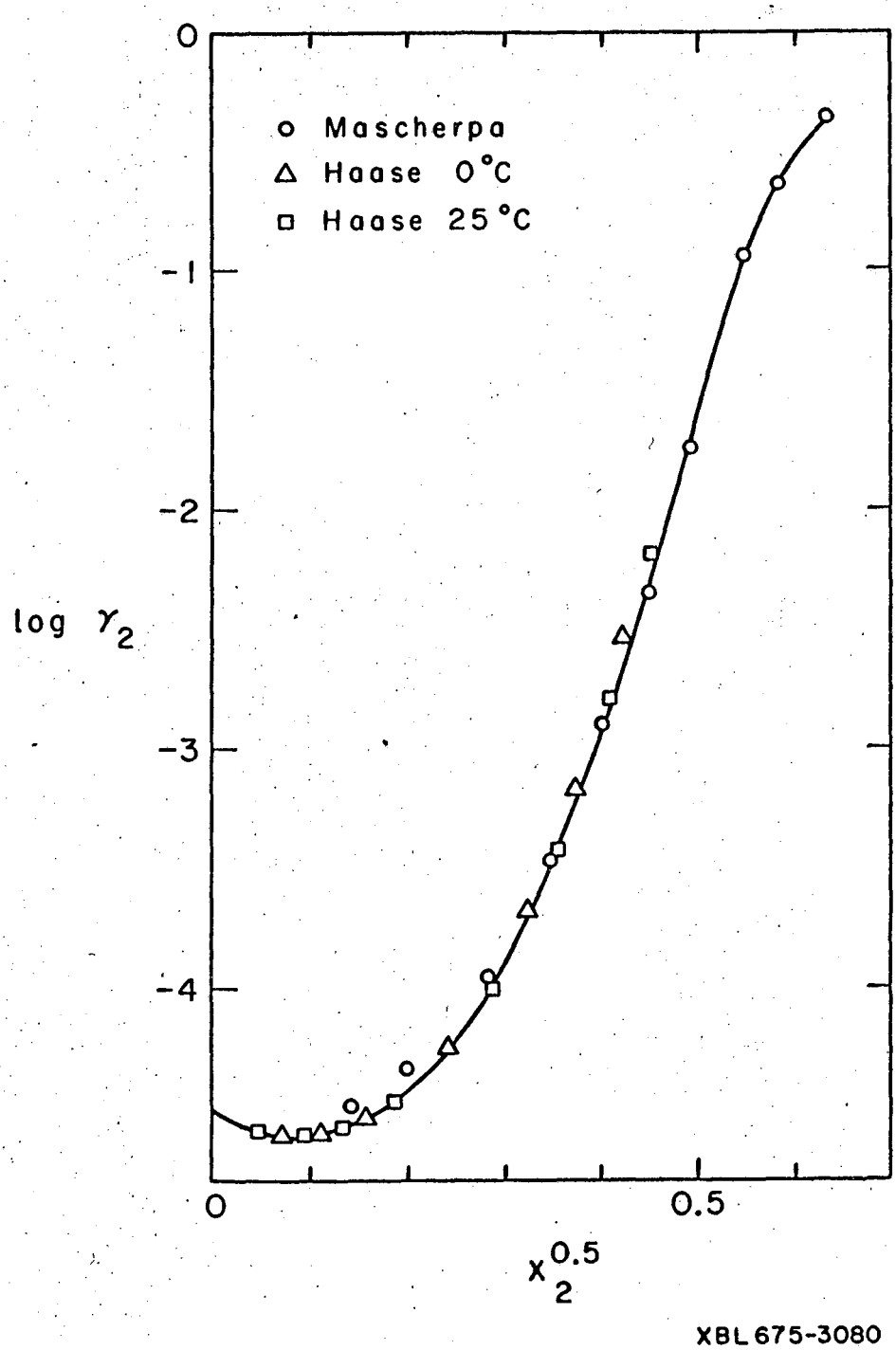


Fig. 3 Activity coefficient of perchloric acid (lim γ_2 = 1)
x_2 = 1

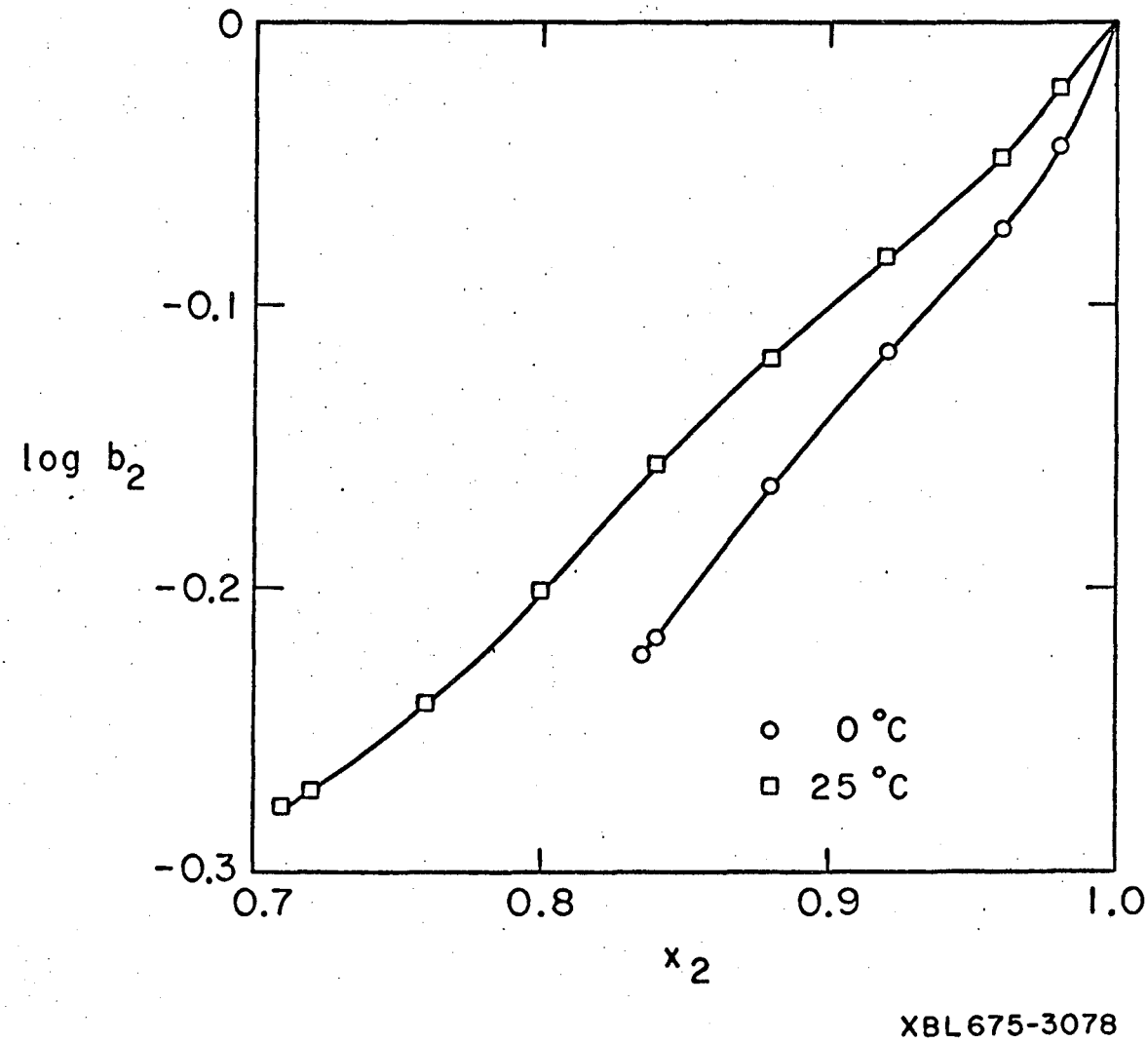


Fig. 4 Activity b_2 of perchloric acid ($\lim_{x_2 = 1} b_2 = 1$)