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ON THE MOLECULAR STRUCTURE OF STRONG ACIDS

Wayne E. Gargrave
(M. S. Thesis)

December 1967

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ON THE MOLECULAR STRUCTURE OF STRONG ACIDS

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Abstract

The molecular structure of strong electrolytes has been considerably elucidated in the last quarter of a century by the examination of Raman spectra, infrared spectra, and nuclear magnetic resonance. Quite a few questions are unanswered. The present work contributes some tools for the investigation of several strong acids.

The activities of perchloric acid and water have been derived from available vapor pressure data. Various checks of the involved calculation have been devised and used. Activities give information about the molecular structure and are indispensable in the interpretation of other data.

Measurements of the rate of the reaction

$$H_2SO_4 + H_2O_2 = H_2SO_5 + H_2O$$

confirm the undissociated molecule H_2SO_4 as an intermediate. Thus rate determinations, in addition to Raman intensities and nuclear magnetic resonance, furnish a third method of exploring the molecular constitution of strong acids. Partial substitution of H by D did not change the rate.

1. Introduction

The molecular structure of the strong electrolytes has been a problem since 1887, when Arrhenius proposed his theory of dissociation. The theories of ionic interaction by Debye and Hückel and others made it probable that many salts are practically completely dissociated. Some strong acids, however, are certainly practically undissociated in the anhydrous state. The very low values of the electrical conductivity of anhydrous nitric, perchloric and sulfuric acids indicate low concentrations of ions.

The first quantitative determination of the dissociation of a strong electrolyte was based on the intensities of Raman lines[1]. The value 21 for the dissociation constant of nitric acid was confirmed by the precise Raman measurements of T. F. Young and his coworkers[2], and by determinations of nuclear magnetic resonance (NMR)[3,4,5]. The dissociation of perchloric acid presented serious problems[3,4,6,7].

Other acids, in particular sulfuric acid, have been investigated by Young and other authors using the same methods.

For the determination of the thermodynamic dissociation constants the knowledge of the activities is required. They are well known for moderately dilute solutions, namely, for nitric acid from precise freezing point measurements, and for perchloric acid from isopiestic determinations. For high concentrations the computation of activities depends on vapor pressures, which have been redetermined in recent years. Such computations have been discussed[8] a short time ago. In this report some details on perchloric acid are presented.

For sulfuric acid, the measurements of Young and Walrafen[9] furnish

data on the first dissociation at very high concentrations. A kinetic investigation[10] of the reaction between sulfuric acid and hydrogen peroxide indicated an opportunity to obtain information for much lower concentrations. The earlier results are checked and expanded in the present report. In addition, several measurements with H-D mixtures contribute to the kinetic interpretation of the reaction studied.

2. Perchloric Acid

The principal objective of this discussion is the determination of the activity in the whole concentration range.

21. Total Pressure

The calculations were based on Mascherpa's[11] measurements of total pressure. Isopiestic determinations of the water vapor pressure below the azeotrope by Robinson and Baker[12] and Haase and coworkers[13] provided information needed for extrapolation to infinite dilution.

The data are represented in Figure 1. Robinson and Baker's data have been omitted because of their good agreement with Haase's data.

After the calculations had been completed, Chemical Abstracts reported new measurements by Lilich and Shalygin[14]. As Figure 2 shows, their data are considerably below those of Mascherpa. There is no specific reason to question either of the investigations. The discrepancy is too great for compromising on an average value. Since Mascherpa worked in the laboratory of Potier, who had presented excellent vapor pressures of nitric acid, his results were retained as the basis of the calculation.

22. Calculation of Partial Pressures

The derivation of activities from total pressures has been discussed for a simple case[15] by Rosanoff in 1914 and since by numerous

authors. Even if the vapor, as in the present problem, can be assumed to be a perfect gas mixture, the calculation is involved. For liquid solutions that do not deviate very much from the perfect solution the most efficient method is probably the selection of an appropriate function for the excess free energy; the parameters of such a function are then, as a rule, easily derived from the observed pressures.

For strong electrolytes a suitable function in general cannot be found. The peculiar shape of the vapor pressure curve (Figure 1) indicates extreme difficulties in any algebraic representation. A few attempts were entirely unsuccessful and soon discontinued.

The most direct, though somewhat circumstantial method is the integration of the differential equation[16] between the total pressure P and the mole fractions x_2 and y_2 of the second component in the liquid and vapor

$$d \ln P/dy_2 = (y_2-x_2)/[y_2(1-y_2)] \ . \qquad (22.1)$$

The automatic computer is very useful in this calculation. There are four distinct intervals in the whole concentration range: (a) from $x_2 = 0$ (mole fraction of perchloric acid) to the azeotrope ($x_2 = 0.32$ at 25°C); (b) from the azeotrope to the lower solubility limit of $HClO_4 \cdot H_2O$ ($x_2 = 0.417$ at 25°C); (c) from there to the upper solubility limit ($x_2 = 0.71$ at 25°C); (d) from there to the anhydrous acid.

Both end points of the first interval are singular. In order to introduce the boundary condition one starts the integration at $x_2 = 0$ with arbitrarily selected values of

$$L = \lim_{x_2=0} dP/dy_2 \ . \qquad (22.2)$$

Figure 2 shows log P against x_2 as curve A. The curves B and C are the integral curves for log P against y_2 for two different values of L. From a family of such curves one selects the one that is tangent to curve A in the azeotrope (C in Figure 2).

One proceeds in a similar way for the higher concentrations. For this purpose, one completes the vapor pressure curve preliminarily through the three-phase region.

For the final results various adjustments are made. The calculation of the activity a_2 of $HClO_4$ below the azeotrope must be in reasonable agreement with the results of Robinson and Baker, and Haase.

A computation according to Gibbs and Duhem furnishes the activity a_2 of perchloric acid for concentrations below the azeotrope. Similarly, the water activity is obtained above the azeotrope, with due consideration being given to the constancy of the product a_1a_2 of the activities in the presence of the solid hydrate. An additional criterion is based on the activity coefficients γ_1 and γ_2: the curve of log (γ_1/γ_2) against x_2 must be smooth.

Moreover, total pressures recalculated from the activities must agree with the observed values within experimental errors of about 0.05 mm. The computation must also satisfy[8] the slope condition for the function

$$Q_p = x_1 \log a_1 + x_2 \log a_2 , \qquad (22.3)$$

namely,

$$dQ_p/dx_2 = \log (a_2/a_1) . \qquad (22.4)$$

An example of the latter test (concentration near the azeotrope for 30°C) is shown in Figure 3.

Results of the computation are given in Tables 1 and 2. The activity

Table 1. 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	$\log \gamma_2$	$\log a_1$
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 2. Activity b_2 of Perchloric Acid.

(above $x_2 = 0.710$; $b_2 = p_2/p_2^o$)

x_2	$-\log b_2$ 0°C	25°C
0.71		0.278
0.72		0.271
0.74		0.257
0.76		0.241
0.78		0.222
0.80		0.202
0.82		0.180
0.835	0.223	-----
0.84	0.217	0.157
0.86	0.189	0.139
0.88	0.164	0.119
0.90	0.139	0.102
0.92	0.117	0.084
0.94	0.095	0.066
0.96	0.074	0.049
0.98	0.044	0.024

coefficients in Table 1 are defined for the range below the appearance of the solid hydrate in the usual way. But for the high concentrations the definition $b_2 = p_2/p_2^o$ for the activity of perchloric acid is preferable. For any concentration $\log(b_2/a_2)$ equals 9.00.

The compliance with all these obviously necessary conditions is not easily accomplished with perchloric acid. Experimental errors are greatly exaggerated in the involved calculations. Only repeated adjustment leads to reasonably consistent results.

23. Vapor Pressure and Molecular Structure

Raman investigations[6] and NMR[3] supported the idea that small amounts of water dissolved in anhydrous perchloric acid are completely dissociated according to

$$HClO_4 + H_2O = H_3O^+ + ClO_4^- \quad . \qquad (23.1)$$

Mascherpa showed that the activity of perchloric acid in the limit of high concentrations confirms the complete dissociation. The straight line in Figure 4 indicates the activity of the solvent in a perfect solution in which each molecule of the solute produces two ions. This straight line is very closely approached by the observed values of a_2.

Recent determinations[17] of NMR in the system $HClO_4$-$DClO_4$-water furnished evidence that the hydrogen ion in these solutions is solvated. Apparently one or more molecules of $HClO_4$ are hydrogen-bonded to the hydronium ion. Such a solvation has no appreciable influence on the vapor pressure or the activity in the concentration range considered.

3. Sulfuric Acid

The interesting point in the kinetic investigation of the reaction between sulfuric acid and hydrogen peroxide is the opportunity to find information on the undissociated molecules.

31. The Reaction with Hydrogen Peroxide

An earlier investigation[10] of the reaction rate of sulfuric acid with hydrogen peroxide

$$H_2SO_4 + H_2O_2 = H_2SO_5 + H_2O \qquad (31.1)$$

led to surprising and at first confusing results. At a constant concentration of hydrogen peroxide (1.0 moles per liter) the initial reaction rate increased roughly by a factor of 10^5 when the concentration of sulfuric acid was increased from 5.0 to 12.0 moles per liter. But within each single run the rate followed the classical relation for bimolecular reactions.

The explanation was found in the assumption that hydrogen peroxide reacts reasonably fast with undissociated molecules of the acid but not at all with HSO_4^-. The reaction is therefore an example of the typical case of a sequence of an instantaneous reaction (formation of H_2SO_4 from the ions) and a moderately fast reaction. There is no anomalous drop of the rate during a single run because the hydrogen ion concentration is maintained by the monoperoxysulfuric acid formed; the concentration of the molecule is therefore proportional to the first order of the stoichiometric concentration of sulfuric acid.

A check and expansion of the earlier investigation was desirable for several reasons. The kinetic study appears to be a third method for the determination of the dissociation of a strong electrolyte, in

addition to Raman intensities and NMR. Contrary to an often stated opinion, the nature of the intermediate in the sequence of a fast and a slow reaction can indeed be found. It appeared interesting to see whether the initial reaction rate approaches more closely the activity of sulfuric acid or Hammett's acidity function. Finally, a preliminary study of the influence of deuterium substitution was considered to be desirable.

32. Experimental Technique

The reacting solutions were contained in glass vessels of about 100 ml. The vessels were constructed so that a portion of the reaction liquor could be forced into a pipet by a stream of dry nitrogen. Dry nitrogen blown reversely through the discharge tube agitated the mixture during the initial stages of the reactions. Ungreased ground glass joints were used. The pipets were recalibrated after glass joints were fused on. Temperature was controlled within 0.01°C.

The reaction liquid was prepared by mixing solutions of the acid in redistilled water with cold aqueous hydrogen peroxide (30%). The initial concentration of the peroxide was about 1.0 moles per liter and that of the acids ranged from about 6.5 to 12.5 moles per liter. Heavy water was used as a diluent of D_2SO_4 for a series of runs.

The initial total volume in the experiments with the light acid was about 50 ml. Only 15 to 20 ml of the mixtures containing deuterium were prepared.

Light sulfuric acid, heavy water and hydrogen peroxide were purchased from commercial sources. The peroxide solution contained no decomposition inhibitors. The deuterium sulfate was prepared by R. W. Duerst[17] by

distillation of Sulfan (stabilized sulfur trioxide) into a receiver containing ice-cold heavy water.

Samples of approximately one or two ml were removed from the reaction vessels at predetermined intervals. The reaction was stopped by at least 50-fold dilution with ice-cold dilute sulfuric acid. Analysis followed immediately.

Hydrogen peroxide and peroxyacid contents of the samples were determined by one of the methods of Rius and Zulueta[18], namely, titration of hydrogen peroxide by permanganate and subsequent determination of peroxyacid in the same sample by addition of excess potassium iodide and titration with sodium sulfite to the starch-iodine end point.

The sodium sulfite solution (0.045 to 0.055 equivalents / liter) was stored in a large glass bottle fitted with an aspirator. Every day the solution was vigorously mixed and then standardized against 0.1 N KIO_3.

The potassium permanganate solution (0.1 equivalents/liter) was boiled for 30 minutes before being filtered into a glass storage bottle. It was aged for several months before use and shielded from direct light. Frequent standardization (against freshly standardized Na_2SO_3) indicated negligible change in concentration with time.

The 10% KI solution used in all iodine titrationswas prepared in small batches and stored in the dark.

The acid concentration of the reaction liquors was determined by titration of separate samples with NaOH. The NaOH concentration had been determined by distilled hydrochloric acid standardized as silver chloride.

33. A Second Order Reaction

As stated earlier in this report, the reaction between sulfuric acid and hydrogen peroxide can be well represented by the classical bimolecular rate law; an equilibrium is reached long before completion of the reaction. The common rate equation for unequal initial concentrations of the two reactants can be expressed in terms of the specific rate k_1, the equilibrium constant K (expressed in concentrations), the peroxyacid concentration x at time t (x = 0 for t = 0), the initial concentrations of the i th component c_i'. The subscripts 1 to 4 are used for: H_2SO_4, H_2O_2, H_2SO_5 and H_2O. Introducing the abbreviations

$$A = K - 1, \tag{33.1}$$

$$B = K\cdot(c_1'+c_2') + c_4' , \tag{33.2}$$

$$C = K\, c_1' c_2' , \tag{33.3}$$

$$q = B^2 - 4AC \tag{33.4}$$

we obtain

$$Y = k_1 t = (K/q)\, ln\, \frac{(2Ax-B-q)(-B+q)}{(2Ax-B+q)(-B-q)} . \tag{33.5}$$

Plotting an experimental set of values of Y against t should yield a straight line with slope k_1.

A problem in an experimental investigation of a reversible reaction is the accurate extrapolation to infinite time. One starts from a first approximation value of the extrapolated concentration x of the peroxyacid. Small variations of this value furnish a family of curves of Y against t. The family contains a straight line which defines the correct equilibrium value of x.

A typical example of the determination of the equilibrium concentrations from this study is shown in Figure 5. The upper and lower sets of points represent values for a variation of two percent in the

extrapolated sodium sulfite titration value. This is about five times the reasonable uncertainty of the extrapolated value. The straight line, accepted as a representation of the data, is well defined by the first three points of Figure 5.

The deviation of the representative straight line in Figure 5 from the origin is explained by a slightly higher rate due to the heat of mixing, unavoidable because of the fairly high concentrations of sulfuric acid.

The decomposition of hydrogen peroxide, checked by the sum of the permanganate and sodium sulfite titrations, was proportionally divided between peroxide and peroxyacid. It never exceeded the amount of normal analytical errors.

34. Reaction Rate, Activity and Acidity Function

The dependence of the initial rate on the concentration of sulfuric acid is extremely high (Table 3 and Figure 6). The results of Monger and Redlich[10] are well confirmed. The reaction rate is not perceptibly changed by a deuterium substitution for 86% of the hydrogen present.

The activity of sulfuric acid at 25°C is very well established by the concordant compilations of Harned and Owen[19], Gmitro and Vermeulen[20,21], and by the work of Giauque and coworkers[22]. Reliable values of the acidity function of sulfuric acid are given by Paul and Long[23] and Jorgenson and Hartter[24].

The logarithms of the initial rates are represented as a function of the concentration by the points marked in Figure 6. Their slope is in fair agreement with the slope 0.71 of the logarithm of the activity of sulfuric acid. The rate data can be represented slightly better with a slope value 0.64; the difference is a little outside the experimental errors.

Table 3. Rate Coefficients and Initial Rates

C_{acid} moles/ℓ	r D/(H+D)	k_1 ℓ/mole·min	initial rate mole/ℓ·min
5.00*	----	1.8×10^{-6}	9.12×10^{-7}
6.71	0.87	6.64×10^{-6}	4.57×10^{-5}
6.78	----	3.88×10^{-6}	2.55×10^{-5}
7.33	----	5.60×10^{-6}	5.06×10^{-5}
8.39	0.86	2.59×10^{-5}	2.28×10^{-4}
8.73	----	4.88×10^{-5}	4.28×10^{-4}
9.46	0.85	1.46×10^{-4}	1.46×10^{-3}
9.65*	----	1.22×10^{-3}	9.23×10^{-4}
11.61	----	2.54×10^{-3}	2.82×10^{-2}
12.00*	----	8.70×10^{-3}	1.05×10^{-1}
12.21	----	6.86×10^{-3}	7.93×10^{-2}
12.49	----	7.48×10^{-3}	8.75×10^{-2}

* Monger and Redlich.

The acidity function is well represented with a slope 0.52 in the concentration range under consideration. It is obviously less suitable for the representation of the rate data. The later data of Jorgenson and Hartter cover only the range above c = 9.15 moles/lit; their slope between c = 9 and c = 12.5 is 0.58.

The kinetic results are in better accord with the activity. The agreement corroborates the earlier interpretation that the reacting intermediate is the undissociated molecule H_2SO_4. This simple, direct and unbiased interpretation says much more than the classification of the rate increase as a "solvent effect." Such a classification and also the introduction of the acidity function have been useful enough in many cases, where a strightforward explanation has not been achieved. In the present case there is no need for auxiliary terms which by necessity are not very precisely defined.

The interpretation of H_2SO_4 as an intermediate reactant and of its concentration as a rate controlling factor does not require strict proportionality of activity and rate. It is well known that the true activity coefficient of the molecule HNO_3 varies considerably with the concentration of the acid. A similar increase of the activity coefficient ("salting out") should be expected for the molecule H_2SO_4.

4. Conclusions

The activities of nitric acid in aqueous solutions are well established over the whole concentration range at 25°C but for other temperatures the experimental basis is not sufficient. The new values are in sufficient accord with data used previously in the interpretation of measurements of Raman intensities and nuclear magnetic resonance (NMR). The older determinations of the dissociation are thus confirmed.

The vapor pressure data for perchloric acid of Mascherpa and of Lilich and Shalygin differ considerably. No explanation of the discrepancy can be given. Activities have been calculated from Mascherpa's results for the total pressure (0 - 30°C). The activities for the highly concentrated solutions of perchloric acid definitely corroborate the earlier model of complete dissociation of water in nearly anhydrous acid. The extension of the activities over the entire concentration range furnishes an opportunity to discuss Raman and NMR data more completely and reliably.

The rate of the reaction of sulfuric acid and hydrogen peroxide is not changed by deuterium substitution for 86% H. The interpretation of the reaction as a sequence of an instantaneous reaction ($H^+ + HSO_4^- = H_2SO_4$) and a rate controlling reaction is confirmed. It is a misunderstanding to assume that in such a case the nature of the intermediate cannot be determined kinetically.

Rate measurements may become a third method for the determination of the dissociation of a strong electrolyte.

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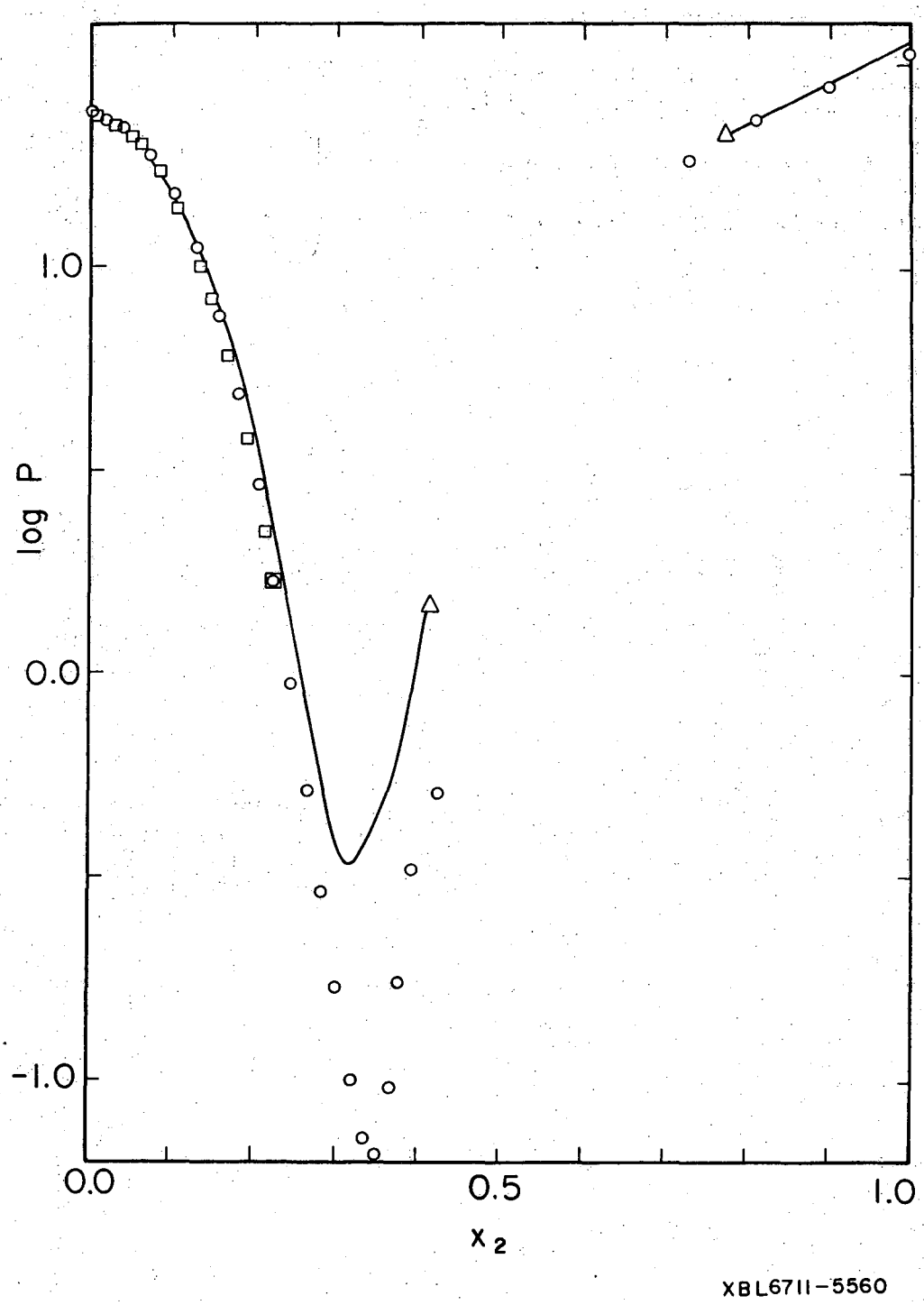

Fig. 1 Vapor pressure of aqueous perchloric acid at 25°C (P vapor pressure in mm Hg; x_2 mole fraction of perchloric acid; -- Mascherpa; □ Haase; ○ Lilich and Shalygin; △ solubility limits measured by Mascherpa).

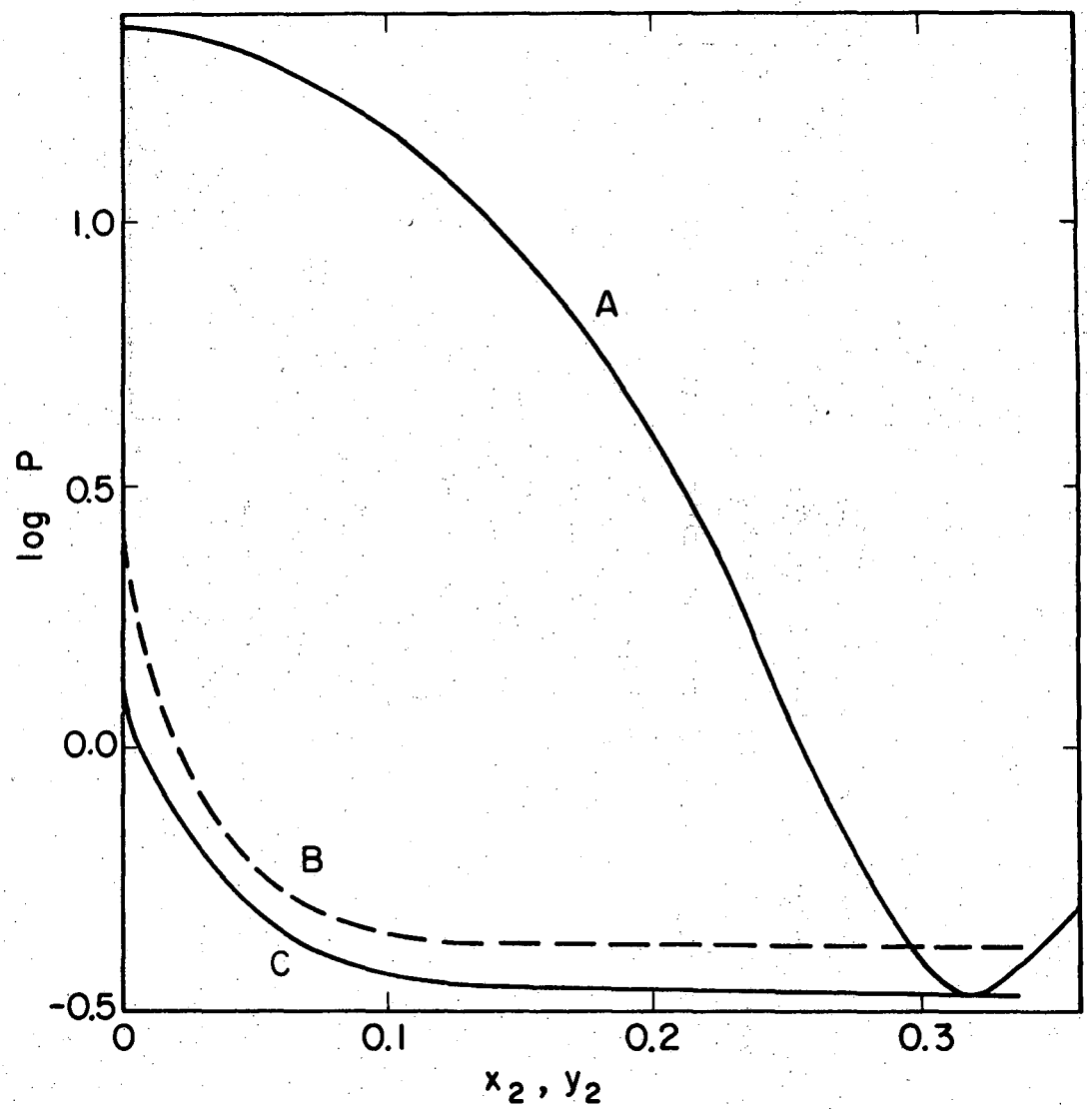

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Fig. 2 Logarithm of the vapor pressure of perchloric acid in mm Hg (A as a function of the mole fraction x_2 in the liquid, B and C as functions of the mole fraction y_2 in the vapor).

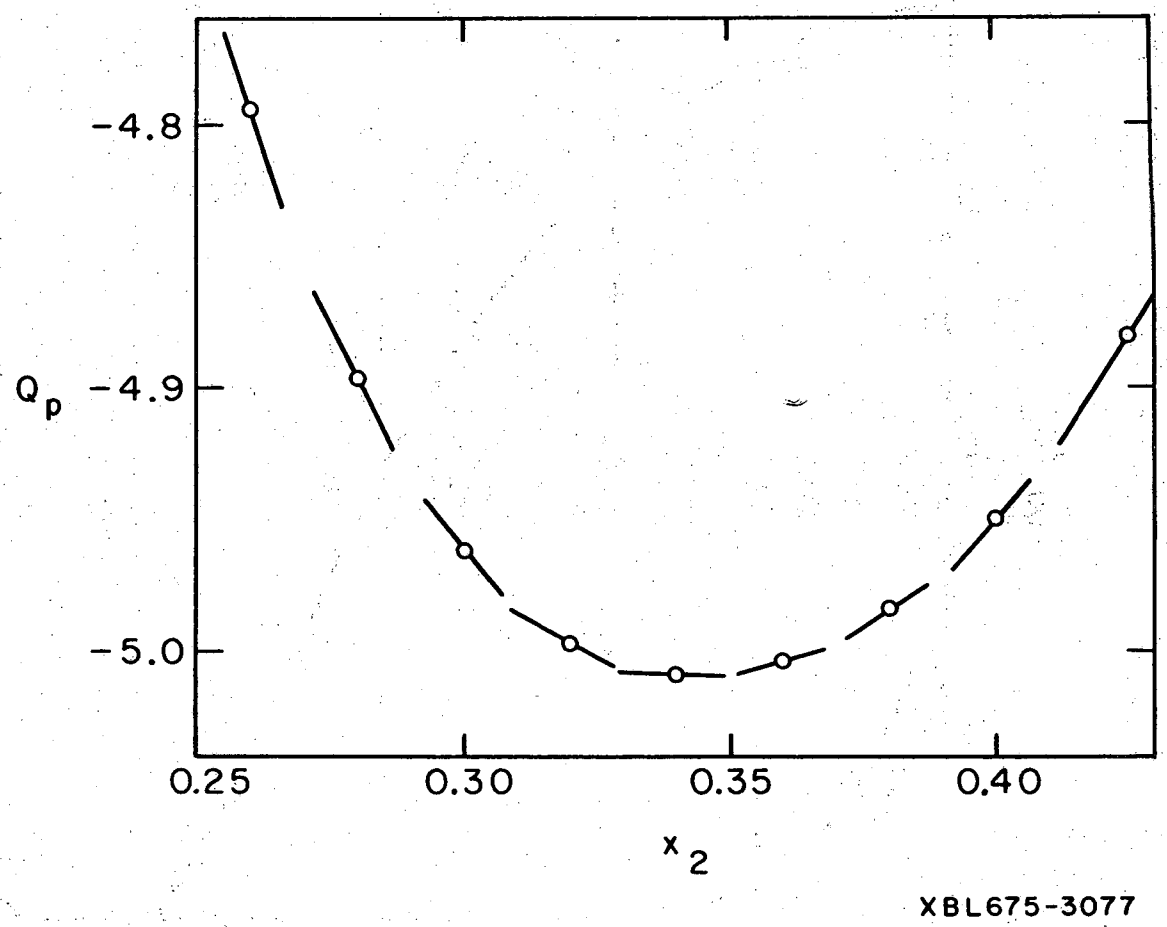

Fig. 3 Consistency of the results for perchloric acid at 30°C (Q_p is given by Eq. (22.3), the slope by Eq. 22.4)).

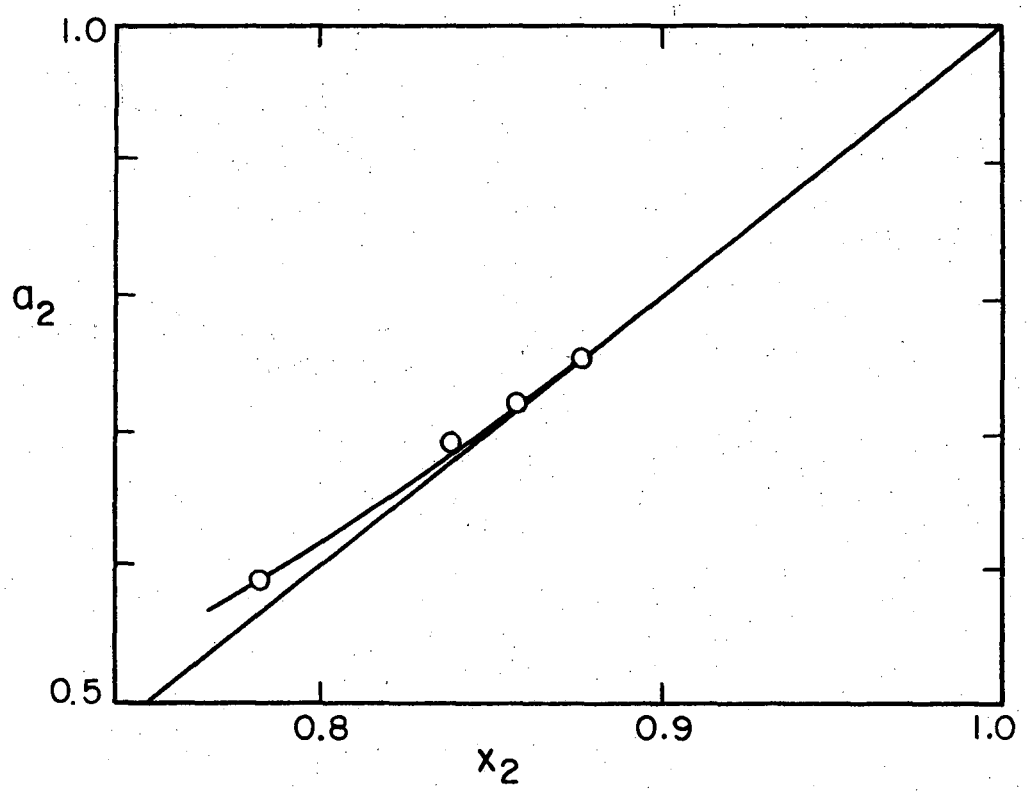

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Fig. 4 Activity $a_2 = p_2/p_2^o$ (Mascherpa, 25°C) at high concentrations.

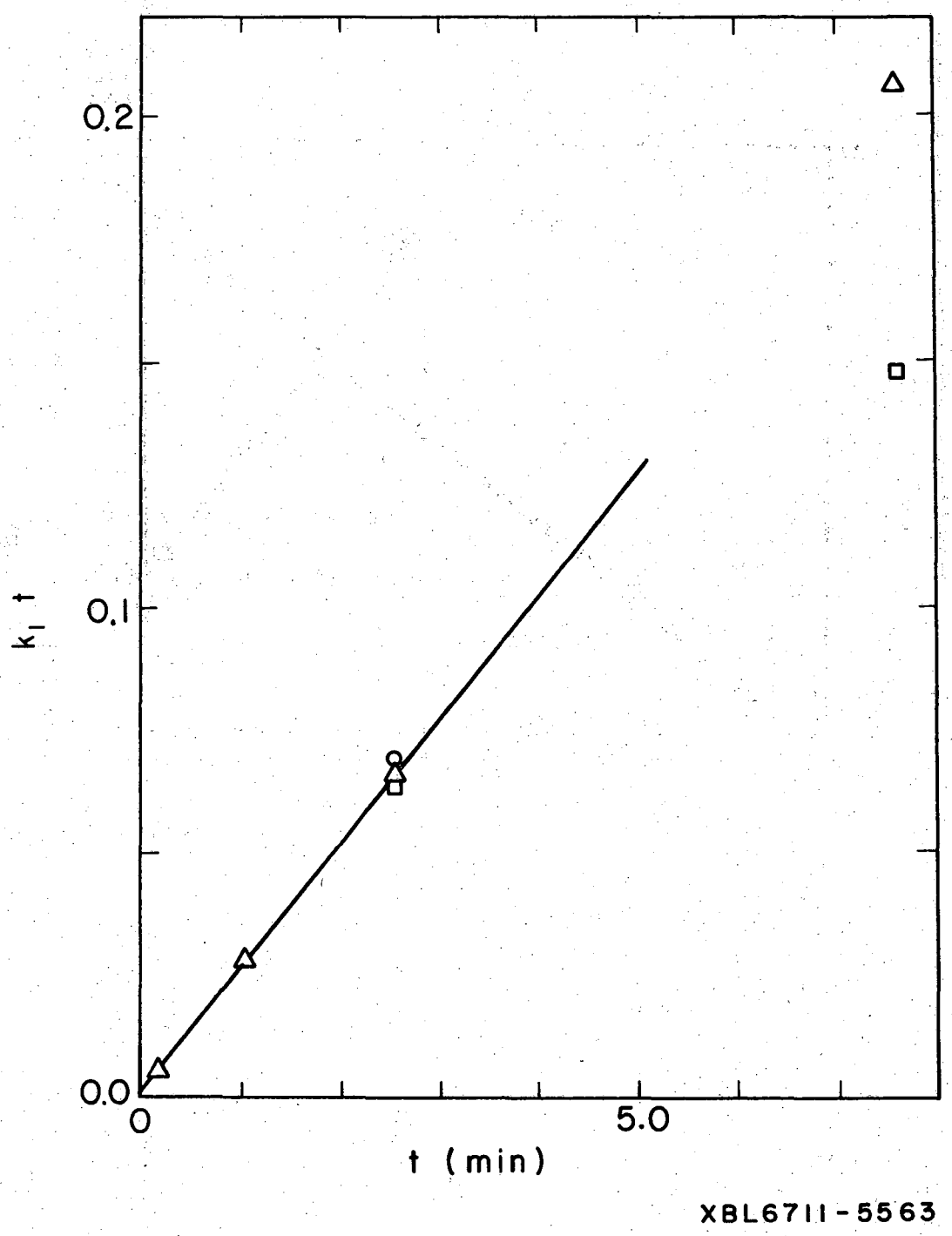

Fig. 5 The function $Y = k_1 t$ [acid concentration 11.61 moles/ℓ; equilibrium concentrations of the peroxyacid: △ 0.382 (titrated), ○ 0. 375 and □ 0.390 (assumed)].

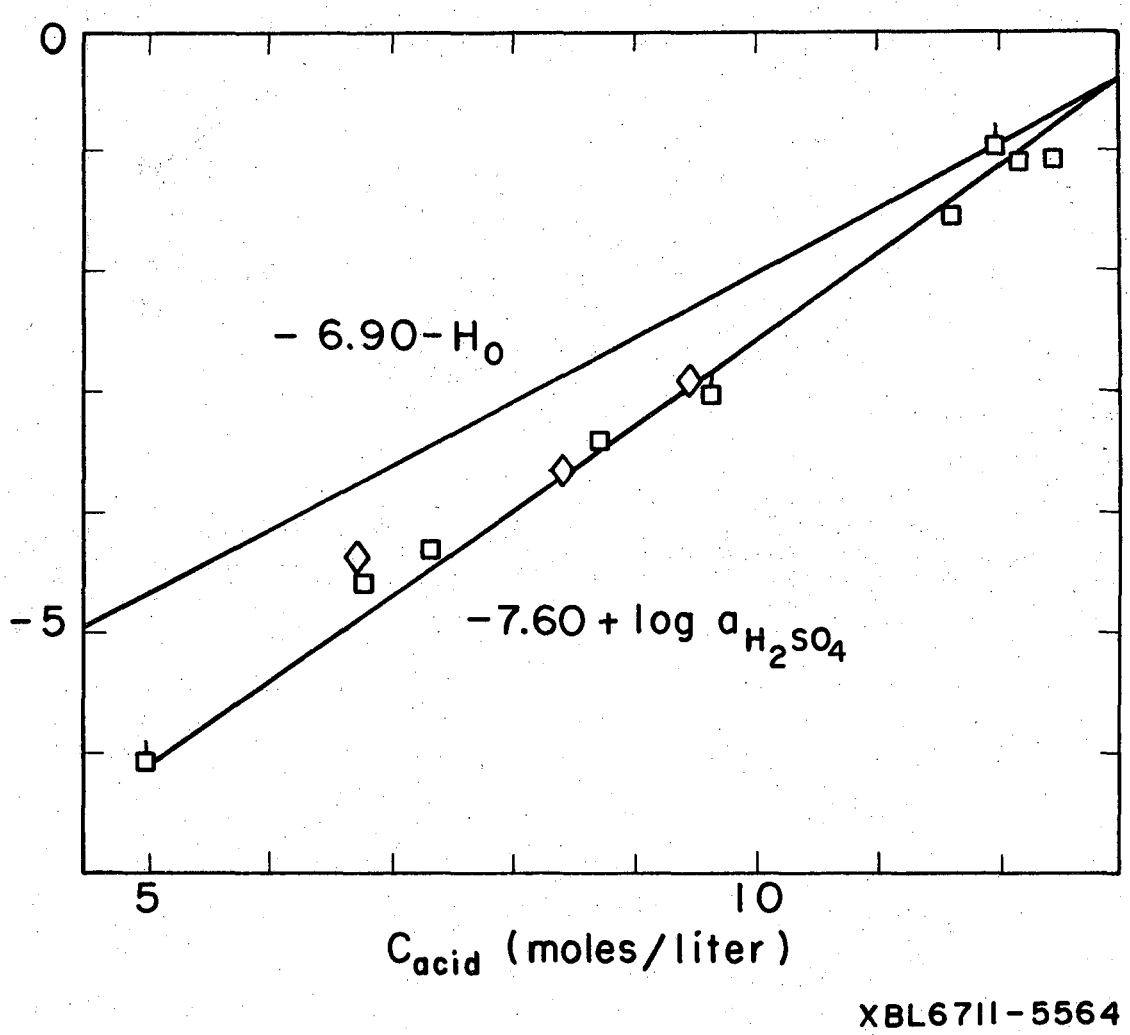

Fig. 6 Acidity function H_o and logarithms of the activity $a_{H_2SO_4}$ and the initial reaction rate (⊥□ H_2SO_4 Monger and Redlich; □ H_2SO_4 and ◇ D_2SO_4 present work).

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