

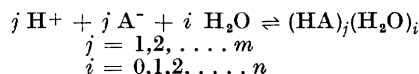
The Complex Formation between Water and Strong Acids

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A simple and consistent picture of the equilibria between strong acids and water can be obtained if the following two assumptions are made: (1) Raman and nuclear magnetic resonance measurements as used so far have not made any distinction between acid molecules and complexes between acid molecules and water. Such measurements give the sum of all these species. (2) Each species behaves ideally in the concentration range, where it exists in appreciable amounts.

Consider the following equilibria:



Application of the law of mass action to these equilibria gives

$$\log [(\text{HA})_j(\text{H}_2\text{O})_i] = \log K_{j,i} + j \log \{\text{H}^+\} \{\text{A}^-\} + i \log \{\text{H}_2\text{O}\}$$

where $[\]$ denote concentration and $\{\ \}$ activity. $K_{j,i}$ is the thermodynamic equilibrium constant of the reaction given above.

The results for the three strong acids HNO_3 , HClO_4 and H_2SO_4 can be summarized in the following way.

System	Complex	$\log K_{j,i}$	Concentration range
$\text{HNO}_3 - \text{H}_2\text{O}$	$\text{HNO}_3(\text{H}_2\text{O})_3$	-1.44 ± 0.05	2-24 M HNO_3
	$\text{HNO}_3(\text{H}_2\text{O})_1$	-2.09 ± 0.01	
	HNO_3	-3.78 ± 0.01	
$\text{HClO}_4 - \text{H}_2\text{O}$	$\text{HClO}_4(\text{H}_2\text{O})_7$	-2.12	3-10 M HClO_4
	$\text{HClO}_4(\text{H}_2\text{O})_3$	-4.08	
$\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$	$\text{H}_2\text{SO}_4(\text{H}_2\text{O})_1$	-4.93	15-18.6 M H_2SO_4
	H_2SO_4	-8.30	

From Raman and nuclear magnetic resonance (NMR) measurements, the degree of dissociation (α) for strong acids has been determined by several investigators. With knowledge of α the product $K_{\text{HA}y_{\text{HA}}}$ for the strong acid HA has been evaluated from

$$K_{\text{HA}y_{\text{HA}}} = \{\text{H}^+\} \{\text{A}^-\} / C(1-\alpha)$$

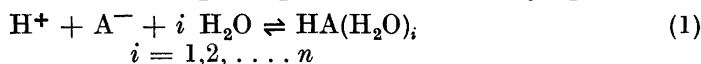
where $\{\text{H}^+\} \{\text{A}^-\}$ is the activity product of H^+ and A^- , which can be evaluated from activity coefficient data in the literature. The stoichiometric molarity of

the acid HA is denoted by C . K_{HA} is the thermodynamic dissociation constant of HA and y_{HA} the activity coefficient of undissociated HA. One finds now that the product $K_{\text{HA}}y_{\text{HA}}$ varies about 2.5 powers of ten for HNO_3 in the range 2–24 M HNO_3 and about 6 powers of ten for HClO_4 in the range 3–10 M HClO_4 . For H_2SO_4 , molecules of H_2SO_4 appear only in the most concentrated solutions and in the range 15–18.6 M H_2SO_4 $K_{\text{H}_2\text{SO}_4} y_{\text{H}_2\text{SO}_4}$ varies about one power of ten. The large variation of these activity coefficients indicates that the acid molecules must interact strongly with each other or with the water.

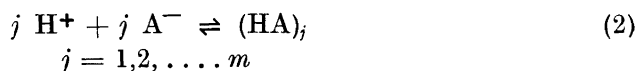
In a thorough but semiquantitative discussion of the system $\text{HNO}_3\text{—H}_2\text{O}$ Chedin¹ suggested that nitric acid in aqueous solution might form the two compounds $\text{HNO}_3(\text{H}_2\text{O})_3$ and $\text{HNO}_3(\text{H}_2\text{O})_1$, both of which are known to exist in the solid state, *cf.* Ref.¹ Recently, a simple method to evaluate approximate hydration numbers was applied to strong acids² as well as to the systems $\text{LiCl—H}_2\text{O}$ and $\text{LiBr—H}_2\text{O}$.³ In the previous investigations the attention was focussed on ionic hydration. In this paper we want to consider the molecules of undissociated acid and the suggestion by Chedin that they may form complexes with water in solution. Using the assumption that Raman and NMR measurements as used so far have not made any distinction between acid molecules and complexes between water and acid molecules but give the sum of all such species and the assumption that these species all behave ideally in the concentration range where they exist in appreciable amounts a simple and consistent picture can be obtained for the equilibria between strong acids and water.

THE METHOD OF EVALUATING THE COMPOSITION OF THE COMPLEXES

Consider the acid HA which can participate in the following equilibria



and



Application of the law of mass action to (1) and (2) gives

$$\{\text{HA}(\text{H}_2\text{O})_i\} = K_{1,i} \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\}^i \quad (3)$$

and

$$\{(\text{HA})_j\} = K_{j,0} \{\text{H}^+\}^j \{\text{A}^-\}^j \quad (4)$$

where $\{\text{HA}\}$ is the activity of HA *etc.* and $K_{1,i}$ and $K_{j,0}$ the thermodynamic equilibrium constants of reactions (1) and (2). Introducing the simplifying assumption that the activity coefficients of the various species $\text{HA}(\text{H}_2\text{O})_i$ and $(\text{HA})_j$ are all equal to unity we find for the total amount of undissociated HA, $C(1-\alpha)$

$$C(1-\alpha) = \sum K_{1,i} \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\}^i + \sum j K_{j,0} \{\text{H}^+\}^j \{\text{A}^-\}^j \quad (5)$$

or

$$C(1-\alpha)/\{\text{H}^+\} \{\text{A}^-\} = \sum K_{1,i} \{\text{H}_2\text{O}\}^i + \sum j K_{j,0} \{\text{H}^+\}^{j-1} [\text{A}^-]^{j-1} \quad (6)$$

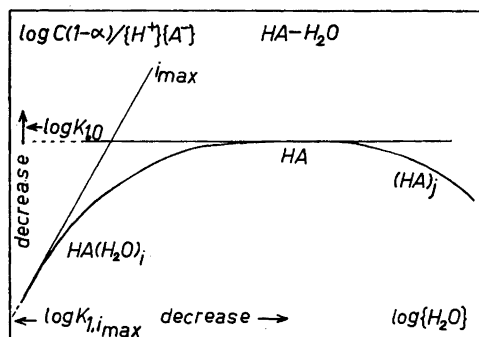


Fig. 1. $\log(C(1-\alpha)/\{H^+\}\{A^-\})$ plotted against $\log\{H_2O\}$ for a hypothetical system $HA-H_2O$ where HA forms complexes with H_2O as well as aggregates $(HA)_2, (HA)_3$ etc.

Consider a range where one (i) of the equilibria defined in eqn. (1) is predominating. From (6) we find

$$\log(C(1-\alpha)/\{H^+\}\{A^-\}) = \log K_{1,i} + i \log \{H_2O\} \quad (7)$$

A plot of $\log(C(1-\alpha)/\{H^+\}\{A^-\})$ against $\log \{H_2O\}$ will give a straight line with a slope equal to i . Quite generally it can be shown that in the range where reaction (2) is negligible

$$\frac{d \log(C(1-\alpha)/\{H^+\}\{A^-\})}{d \log\{H_2O\}} = \bar{n} = \frac{\sum i K_{1,i}\{H_2O\}^i}{\sum K_{1,i}\{H_2O\}^i} \quad (8)$$

where \bar{n} is the average number of water molecules per complex.

A plot of $\log(C(1-\alpha)/\{H^+\}\{A^-\})$ against $\log \{H_2O\}$ will thus give information about the range over which i can vary. In the range where HA predominates the curve will approach a horizontal straight line and if associated species of HA are formed the curve will turn back as indicated in Fig. 1 where $\log(C(1-\alpha)/\{H^+\}\{A^-\})$ is plotted against $\log\{H_2O\}$ for a hypothetical system with reactions of both type (1) and (2). In Fig. 1 the limiting slope when app-

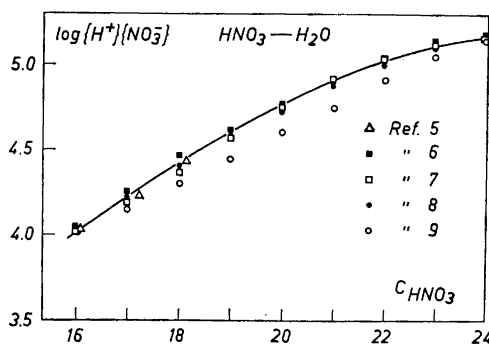


Fig. 2. $\log\{H^+\}\{NO_3^-\}$ for the system HNO_3-H_2O plotted against the stoichiometric molarity of nitric acid, C_{HNO_3} , according to five different sources in the literature. Δ Ref. 5; \blacksquare Ref. 6; \square Ref. 7; \bullet Ref. 8; \circ Ref. 9.

roaching pure water is indicated. This will give the highest value i in eqn. (1) can take. The horizontal line in the range where HA predominates will give the value of $\log K_{1,0}$.

We want now to apply the method outlined above to the three systems $\text{HNO}_3\text{--H}_2\text{O}$, $\text{HClO}_4\text{--H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$. For these acids reasonably good α -values are available.

The system $\text{HNO}_3\text{--H}_2\text{O}$

With the aid of extraction data for nitric acid into benzene a set of fairly consistent water and nitric acid activities in the range 1–14 M HNO_3 was recently evaluated using data from five different sources in the literature.⁴ In order to get a set of consistent activities from 14 M up to pure nitric acid, $\log\{\text{H}^+\}\{\text{NO}_3^-\}$ from five sources in the literature⁵⁻⁹ is plotted against the stoichiometric molarity of nitric acid, C_{HNO_3} , in Fig. 2. In fig. 3 this is done for $\log\{\text{H}_2\text{O}\}$. A smooth curve has been drawn through the experimental points. In Table 1 the values for $\log\{\text{H}^+\}\{\text{NO}_3^-\}$ and $\log\{\text{H}_2\text{O}\}$ obtained from these curves are listed together with

$$\sum X_i \Delta \log\{ \}_i = \bar{X}_{\text{HNO}_3} \Delta \log\{\text{H}^+\}\{\text{NO}_3^-\} + \bar{X}_{\text{H}_2\text{O}} \Delta \log\{\text{H}_2\text{O}\} \quad (9)$$

where \bar{X}_{HNO_3} is the average of two consecutive values for X_{HNO_3} in Table 1 and $\Delta \log\{\text{H}^+\}\{\text{NO}_3^-\}$ the difference of the two corresponding values for $\log\{\text{H}^+\}\{\text{NO}_3^-\}$ etc. According to the Gibbs-Duhem equation

$$X_{\text{HNO}_3} d \log\{\text{H}^+\}\{\text{NO}_3^-\} + X_{\text{H}_2\text{O}} d \log\{\text{H}_2\text{O}\} = 0 \quad (10)$$

From Table 1 it can be seen that the sum (9) differs from zero at most by 0.02, which is well within the uncertainty in $\log\{\text{H}^+\}\{\text{NO}_3^-\}$ and $\log\{\text{H}_2\text{O}\}$ as can be seen from Figs. 2 and 3. To within that accuracy the water and nitric acid activities in Table 1 are consistent with each other according to the requirements of the Gibbs-Duhem equation.

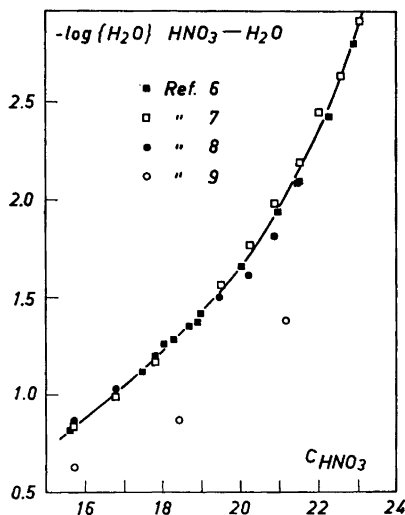


Fig. 3. $-\log\{\text{H}_2\text{O}\}$ for the system $\text{HNO}_3\text{--H}_2\text{O}$ plotted against the stoichiometric molarity of nitric acid, C_{HNO_3} , according to four different sources in the literature. ■ Ref. 6; □ Ref. 7; ● Ref. 8; ○ Ref. 9.

Table 1. Thermodynamic consistency test for the system HNO₃-H₂O.

C_{HNO_3}	X_{HNO_3}	$\log\{H_2O\}$	$\log\{H^+\}\{NO_3^-\}$	$\bar{X}_{\text{HNO}_3} \Delta \log\{H^+\}\{NO_3^-\}$	$\bar{X}_{H_2O} \Delta \log\{H_2O\}$	$\Sigma \bar{X}_i \Delta \log\{i\}$
14	0.338	-0.67	3.62	+0.0680	-0.0770	-0.0090
15	0.373	-0.79	3.81	0.0826	-0.0667	+0.0159
16	0.414	-0.90	4.02	0.0873	-0.0789	+0.0084
17	0.459	-1.04	4.22	0.0921	-0.0876	+0.0045
18	0.510	-1.21	4.41	0.0971	-0.0921	+0.0050
19	0.569	-1.41	4.59	0.0962	-0.0956	+0.0006
20	0.634	-1.65	4.75	0.0941	-0.1017	-0.0076
21	0.710	-1.96	4.89	0.0979	-0.0914	+0.0065
22	0.796	-2.33	5.02	0.0760	-0.0827	-0.0067
23	0.892	-2.86	5.11	0.0568	-0.0616	-0.0048
24	1.00	(-4.00)	5.17			

The value for the water activity in 24 M HNO₃ is put within parenthesis because this value is only a rough extrapolation.

Using the water and nitric acid activities given in Table 1 and those of Table 9 in Ref.⁴ together with the Raman measurements by Krawetz¹⁰ the quantity $C(1-\alpha)/\{H^+\}\{NO_3^-\}$ has been evaluated. The quantity $C(1-\alpha)$ was obtained by interpolation on a graph over the concentrations of the species present in HNO₃-H₂O kindly sent to me by Dr. H. A. C. McKay, Harwell, who has access to the measurements of Krawetz. In Fig. 4 $\log(C(1-\alpha)/\{H^+\}\{NO_3^-\})$ is plotted against $\log\{H_2O\}$ over the concentration range 2-24 M HNO₃. From Fig. 4 we find that when approaching pure water an asymptote with a slope of 3 can be fitted to the curve. This indicates that HNO₃(H₂O)₃ is the complex between water and nitric acid that is predominating in dilute solutions in agreement with the suggestion by Chedin. Moreover, the extrapolation to pure water gives

$$\log K_{1,3} = -1.40 \tag{11}$$

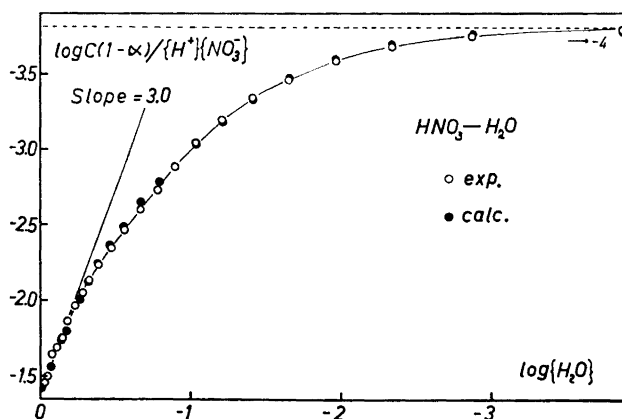


Fig. 4. $\log(C(1-\alpha)/\{H^+\}\{NO_3^-\})$ plotted against $\log\{H_2O\}$ for the system HNO₃-H₂O. Two asymptotes, one with a slope of 3 and one with a slope of zero are also indicated. ● exptl. points; ○ points calculated from the constants given in (19).

When approaching pure nitric acid the slope tends towards zero and the horizontal asymptote indicates

$$\log K_{1,0} = -3.78 \quad (12)$$

From eqns. (3) and (4) we get with the constants given by (11) and (12)

$$\log[\text{HNO}_3(\text{H}_2\text{O})_3] = -1.40 + \log\{\text{H}^+\}\{\text{NO}_3^-\} + 3 \log\{\text{H}_2\text{O}\} \quad (13)$$

and

$$\log [\text{HNO}_3] = -3.78 + \log\{\text{H}^+\}\{\text{NO}_3^-\} \quad (14)$$

From (13) and (14) the amounts of $\text{HNO}_3(\text{H}_2\text{O})_3$ and HNO_3 have been computed over the range 2–24 M HNO_3 . Then their sum was subtracted from the total amount of undissociated nitric acid present. If we denote this amount by $[\text{HNO}_3]_{\text{diff}}$ we have

$$C(1-\alpha) - [\text{HNO}_3(\text{H}_2\text{O})_3] - [\text{HNO}_3] = [\text{HNO}_3]_{\text{diff}} \quad (15)$$

It was found that

$$\log[\text{HNO}_3]_{\text{diff}} - \log\{\text{H}^+\}\{\text{NO}_3^-\} - \log\{\text{H}_2\text{O}\}$$

was practically constant in the range 10–23 M HNO_3 . This implies a 1:1 complex and the following value for the equilibrium constant was obtained

$$\log K_{1,1} = -2.09 \pm 0.05 \quad (16)$$

The amount of $\text{HNO}_3(\text{H}_2\text{O})_1$ could now be computed from

$$\log[\text{HNO}_3(\text{H}_2\text{O})_1] = -2.09 + \log\{\text{H}^+\}\{\text{NO}_3^-\} + \log\{\text{H}_2\text{O}\} \quad (17)$$

We can thus conclude that in the range 0–24 M HNO_3 undissociated nitric acid exists mainly as $\text{HNO}_3(\text{H}_2\text{O})_3$, $\text{HNO}_3(\text{H}_2\text{O})_1$ and HNO_3 as suggested by Chedin. Using eqns. (13), (14), and (17) the sum

$$[\text{HNO}_3(\text{H}_2\text{O})_3] + [\text{HNO}_3(\text{H}_2\text{O})_1] + [\text{HNO}_3] = (\text{HNO}_3)_{\text{tot}} \quad (18)$$

was evaluated. In Fig. 4 the function $\log\{(\text{HNO}_3)_{\text{tot}}/\{\text{H}^+\}\{\text{NO}_3^-\}\}$ evaluated from (18) and the activity data discussed above is given as black dots and is compared with the points obtained from Krawetz Raman data. The agreement between computation and experiment is satisfactory.

In Fig. 5 a comparison is made between $C(1-\alpha)$ according to Krawetz and $(\text{HNO}_3)_{\text{tot}}$ evaluated from (18). The amount of each specie assumed to be present is also indicated. From Fig. 5 it can be seen that the total amount according to (18) scatters somewhat but follows the experimental curve fairly well in view of the simplifying assumption of ideal behavior of the three species as well as the experimental uncertainty in the activities of water and nitric acid as seen in Figs. 2 and 3. Moreover $C(1-\alpha)$ was obtained by interpolation on a rather small graph. For these reasons a more refined treatment must await better experimental data.

It is known that nitric acid is associated in concentrated solutions, probably to dimers¹¹. From Fig. 4 it is seen that the thermodynamic data do not indicate any extensive association of HNO_3 . According to the infrared measurements by Dalmon and Freymann¹¹ the associated component becomes negligible at about 19 M HNO_3 . In the range 19–24 M HNO_3 the nitric acid activity varies by only a factor of 3. It seems that this is too small a range of variation

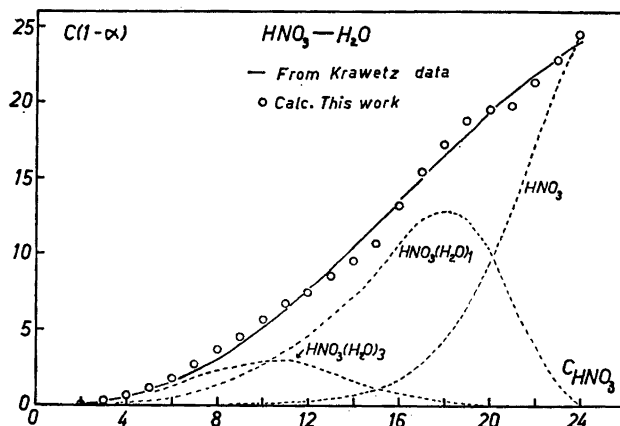


Fig. 5. $C(1-\alpha)$ plotted against the stoichiometric molarity of nitric acid, C_{HNO_3} , for the system $\text{HNO}_3-\text{H}_2\text{O}$. — curve, obtained from Krawetz Raman measurements; \circ points, calculated from the constants given in (19); ----- curves, indicating the amounts of the three species assumed to be present.

in nitric acid activity to find the association indicated by the infrared measurements; however, better Raman and activity data are needed in order to finally settle the question.

In order to check the equilibrium constants given by (11), (12), and (16) a least square refinement according to the method "Letagropvid" worked out by Sillén and Ingri¹² and programmed in the Mercury Autocode for the Mercury Ferranti Computer was carried out for the nitric acid data. The data were run on the Mercury Ferranti Computer belonging to AB Atomenergi and placed at the Royal Institute of Technology. Three alternatives were used: (1) the complexes are $\text{HNO}_3(\text{H}_2\text{O})_3$, $\text{HNO}_3(\text{H}_2\text{O})_1$, and HNO_3 , (2) the complexes are $\text{HNO}_3(\text{H}_2\text{O})_3$, $\text{HNO}_3(\text{H}_2\text{O})_2$, $\text{HNO}_3(\text{H}_2\text{O})_1$ and HNO_3 , (3) the complexes are $\text{HNO}_3(\text{H}_2\text{O})_3$, $\text{HNO}_3(\text{H}_2\text{O})_1$, HNO_3 and $(\text{HNO}_3)_2$. For the first alternative the following constants were obtained:

$$\begin{aligned} \log K_{1,3} &= -1.44 \pm 0.05 \\ \log K_{1,1} &= -2.09 \pm 0.01 \\ \log K_{1,0} &= -3.78 \pm 0.01 \end{aligned} \quad (19)$$

The constants given in (19) agree well with those given by (11), (12), and (16).

The second alternative gave a slightly better fit, but the difference was immaterial and the assumption of a complex $\text{HNO}_3(\text{H}_2\text{O})_2$ does not seem justified. The third alternative made the equilibrium constant for the formation of $(\text{HNO}_3)_2$ practically zero and no improvement of the fit to the experimental data could be obtained in that way.

The system $\text{HClO}_4-\text{H}_2\text{O}$

The experimental material for this system is not as extensive as that of nitric acid. In order to see if the treatment outlined for nitric acid applies

also to perchloric acid this acid has been investigated in an analogous manner. In Fig. 6 $\log(C(1-\alpha)/\{H^+\}\{ClO_4^-\})$ is plotted against $\log\{H_2O\}$. The NMR data by Redlich *et al.*¹³ have been used in the evaluation of $C(1-\alpha)$ and the activity measurements of Robinson and Baker¹⁴ for the evaluation of $\{H^+\}\{ClO_4^-\}$. From Fig. 6 it is found that two asymptotes with the slopes 7 and 3 can be fitted to the curve. This suggests at least two complexes of the composition $HClO_4(H_2O)_7$ and $HClO_4(H_2O)_3$ in the range 3–10 M $HClO_4$. We assume the following two reactions:



and



The intercepts of the asymptotes with the vertical axis at unit water activity give

$$\log K_{1,7} = -2.12 \quad (22)$$

and

$$\log K_{1,3} = -4.08 \quad (23)$$

We assume again that the two complexes behave ideally and find, by applying the law of mass action to (20) and (21)

$$\log [HClO_4(H_2O)_7] = -2.12 + \log\{H^+\}\{ClO_4^-\} + 7 \log\{H_2O\} \quad (24)$$

$$\log [HClO_4(H_2O)_3] = -4.08 + \log\{H^+\}\{ClO_4^-\} + 3 \log\{H_2O\} \quad (25)$$

Using equations (24) and (25) the sum

$$[HClO_4(H_2O)_7] + [HClO_4(H_2O)_3] = [HClO_4]_{tot} \quad (26)$$

has been evaluated. In Fig. 6 $\log([HClO_4]_{tot}/\{H^+\}\{ClO_4^-\})$ given as the black dots is compared with the experimental points. From Fig. 6 it is seen that the agreement between computation and experiment is satisfactory.

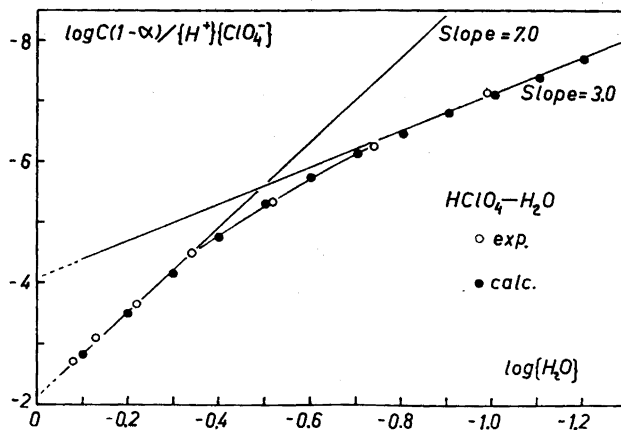


Fig. 6. $\log(C(1-\alpha)/\{H^+\}\{ClO_4^-\})$ plotted against $\log\{H_2O\}$ for the system $HClO_4-H_2O$. Two asymptotes, one with a slope of 7 and one with a slope of 3 are also indicated. \circ exptl. points; \bullet points computed from eqns. (24)–(26).

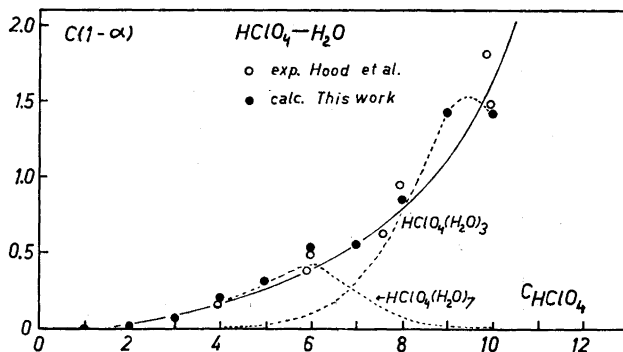


Fig. 7. $C(1-\alpha)$ plotted against the stoichiometric molarity of perchloric acid, C_{HClO_4} , for the system $\text{HClO}_4-\text{H}_2\text{O}$. \circ exptl. points; \bullet points, calculated from eqns. (24)–(26); ----- curves, indicating the amounts of the two species assumed to be present.

In Fig. 7 $C(1-\alpha)$ as found by Redlich *et al.* is compared with $[\text{HClO}_4]_{\text{tot}}$. The amount of each species assumed to be present is also indicated. Also in this plot the calculated values agree with the experiments within the limits of experimental error.

This picture outlined for the system $\text{HClO}_4-\text{H}_2\text{O}$ must be tentative in view of the experimental material available. Much more numerous and accurate data are needed in order to get a more refined picture.

The system $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$

For this system the activity data discussed in Ref.² together with the Raman measurements of Young *et al.*¹⁵ have been used in the evaluation of $C(1-\alpha_1)/\{\text{H}^+\}^2\{\text{SO}_4^{2-}\}$ and in Fig. 8 $\log\{C(1-\alpha_1)/\{\text{H}^+\}^2\{\text{SO}_4^{2-}\}\}$ is plotted against $\log\{\text{H}_2\text{O}\}$ for this system. α_1 stands for the degree of dissociation of H_2SO_4 as distinguished from HSO_4^- . The shape of the curve indicates at least one complex between H_2SO_4 and H_2O as well as free H_2SO_4 . There is no indication of further association, which may exist but not being extensive enough to show up in this plot.

From the horizontal asymptote we find

$$\log K_{1,0} = -8.30 \quad (27)$$

In order to evaluate the complex between water and sulfuric acid the amount of H_2SO_4 was first computed from:

$$\log[\text{H}_2\text{SO}_4] = -8.30 + \log\{\text{H}^+\}^2\{\text{SO}_4^{2-}\} \quad (28)$$

The amount computed from (28) was then subtracted from the total amount giving

$$[\text{H}_2\text{SO}_4]_{\text{diff}} = C(1-\alpha_1) - [\text{H}_2\text{SO}_4] \quad (29)$$

It was found that the expression

$$\log[\text{H}_2\text{SO}_4]_{\text{diff}} - \log\{\text{H}^+\}^2\{\text{SO}_4^{2-}\} - \log\{\text{H}_2\text{O}\} = \log K_{1,1} \quad (30)$$

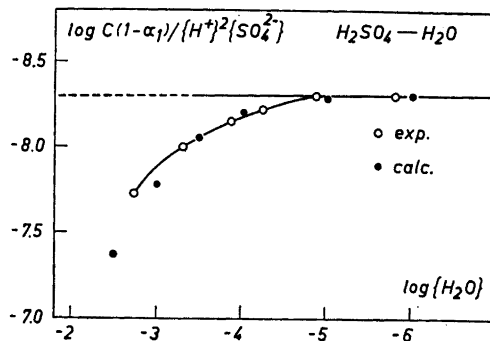


Fig. 8. $\log(C(1-\alpha_1)/\{H^+\}^2\{SO_4^{2-}\})$ plotted against $\log\{H_2O\}$ for the system $H_2SO_4-H_2O$. One asymptote with a slope of zero is indicated. \circ expl. points; \bullet points computed from eqns. (28), (32), and (33).

did not show any systematic variations. The average value was

$$\log K_{1,1} = -4.93 \pm 0.20 \quad (31)$$

Using this value the amount of $H_2SO_4(H_2O)_1$ was computed from

$$\log[H_2SO_4(H_2O)_1] = -4.93 + \log\{H^+\}^2\{SO_4^{2-}\} + \log\{H_2O\} \quad (32)$$

From eqns. (28) and (32) the sum

$$[H_2SO_4]_{tot} = [H_2SO_4] + [H_2SO_4(H_2O)_1] \quad (33)$$

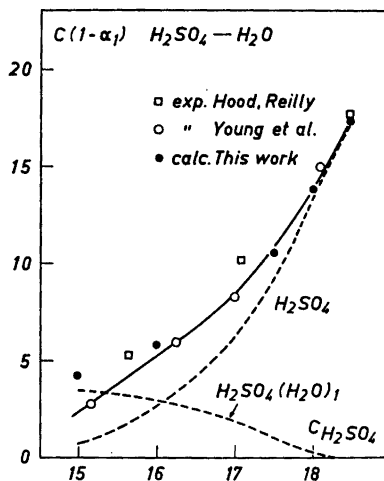
has been evaluated. In Fig. 8 the function $\log([H_2SO_4]_{tot}/\{H^+\}^2\{SO_4^{2-}\})$ given by the black dots is compared with the experimental values. Within the limits of experimental error the agreement is satisfactory. In Fig. 9 $[H_2SO_4]_{tot}$ is compared with $C(1-\alpha_1)$ according to the Raman measurements by Young *et al.* as well as the NMR data by Hood and Reilly¹⁶. Also the amounts of the two species assumed to be present are marked out. The agreement between the computed amount and the measurements is satisfactory, but more and better experimental data are needed in order to get a more refined picture.

It is worth emphasizing, however, that formation of complexes with water seems to account for most of the variation of the activity coefficients of the undissociated parts of the acids in mixtures of strong acids with water. It is hardly conceivable that these large variations are due to salting out effects¹⁷. Any theory for salting out effects in other than dilute solutions is unfortunately not available¹⁷.

THE THERMODYNAMIC EQUILIBRIUM CONSTANTS

It has been common practice to extrapolate the quantity $\{H^+\}\{A^-\}/C(1-\alpha)$ to pure water in order to obtain a value for the thermodynamic dissociation constant, K_{HA} , of the acid in question. This value, however, will be the inverse of the equilibrium constant for the complex containing most water according

Fig. 9. $C(1-\alpha_1)$ plotted against the stoichiometric molarity of sulfuric acid, $C_{H_2SO_4}$, for the system $H_2SO_4-H_2O$. \square exptl. points, Hood and Reilly; \circ exptl. points, Young *et al.*; \bullet points computed from eqns. (28), (32), and (33); --- curves indicating the amounts of the two species assumed to be present.



to the picture outlined in this paper. From (12), (23), and (27) we find the following values for K_{HA} (Table 2).

Table 2. Dissociation constants for strong acids at 25°C.

Acid	$\log K_{HA}$
HNO_3	3.78
$HClO_4$	> 4
H_2SO_4	8.30

For $HClO_4$ we can only give a lower limit because the thermodynamic data do not extend to high enough concentrations for finding any appreciable amounts of $HClO_4$ -molecules. The values in Table 2 certainly indicate that the strong acids are really strong, although there is a considerable difference between HNO_3 and H_2SO_4 , which seems reasonable in view of the fact that HNO_3 acts like a base towards H_2SO_4 .

According to the picture outlined in this paper, extrapolations of stoichiometric equilibrium constants to pure water have to be done with caution. Equilibrium constants found at high ionic strengths and thermodynamic constants obtained by extrapolation may not refer to the same species.

CONCLUDING REMARKS

The very simple picture of the equilibria between water and strong acids given in this paper gives a surprisingly good quantitative description and it seems to be the main part of the answer to the behavior of such mixtures. A complete and refined description requires much more numerous and accurate data and has to be left to the future.

A simple argument in favor of the model outlined above is that dissociation constants of 23.5 and 38 for HNO_3 and HClO_4 are incompatible with the fact that an indicator like 2,4-dichloro-6-nitroaniline with $\text{p}K = -3.30$ acts like a base towards these acids. According to the values given above for the dissociation constants of the two acids they should behave like bases towards this indicator instead of the reverse. Many examples like that can be found.

Concerning $\text{p}K$ -values for indicators like that given above, the Hammett stepwise comparison method does not give the thermodynamic dissociation constant at infinite dilution but rather the constant referring to the degree of hydration the indicator has in the H_o -range where it is used.

One also finds a simple explanation of the fact that the stronger perchloric acid has a measurable degree of dissociation in rather dilute solutions as contrary to sulfuric acid. The latter acid has little tendency to form complexes with water while perchloric acid does. This complex formation extends the range of existence for undissociated perchloric acid over a broader concentration range than if no complex formation were to occur.

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