

Relations between the Hammett Acidity Function, H_0 , and Ion Activities in Mixtures of strong Acids and Water

ERIK HÖGFELDT

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

By combining of the Hammett acidity function, H_0 , with activity data in mixtures of strong acids with water, functions $\varphi^\nu \cdot a_{X^\nu}$ can be constructed. ν is the ionic charge of species X and $\varphi = y_B / y_{BH^+}$ *i.e.* the activity coefficient ratio of the basic and acid forms of the indicators used for the determination of H_0 . The properties of these functions are investigated. It is found that the plot of $\log \varphi \cdot a_{H_3O^+}$ versus H_0 is the same for the acids, HCl, HBr, HNO₃, HClO₄ and H₂SO₄.

The functions $\varphi^{-1} \cdot a_{A^-}$ (A^- = anion of the acid HA) show a more individualistic behavior. The plots of $\log \varphi^{-1} \cdot a_{ClO_4^-}$ and $\log \varphi^{-1} \cdot a_{HSO_4^-}$ versus H_0 practically coincide in the range of overlap, those for Br⁻ and Cl⁻ form a different set of almost parallel curves but the curve for NO₃⁻ differs from all of the others.

From a plot of $\log \varphi^\nu \cdot a_{X^\nu}$ versus H_0 for several species assumed to be present in H₂SO₄-H₂O mixtures, it is found that, from 10 M H₂SO₄ up to pure H₂SO₄, the curve for H₃O⁺ runs parallel with that of HSO₄⁻, that for SO₄²⁻ with $\log a_{H_2O}$ and the curve for H₂SO₄⁺ with that of HS₂O₇⁻. This behavior is found to be the result of the almost complete constancy of the activity coefficient expression $\varphi^2 \cdot y_{H_3O^+} / y_{HSO_4^-}$. Also, the following relation holds in the same concentration range:

$$-2 H_0 - \log a_{H^+} \cdot a_{SO_4^{2-}} + \log a_{H_2O} = 3.95 \pm 0.03$$

A function closely related to the average degree of hydration of the various ions present is introduced. In concentrated solutions of H₂SO₄, this function tends towards unity for H⁺ and towards zero for HSO₄⁻ implying the existence of H⁺ as H₃O⁺ in these concentrated solutions and that HSO₄⁻ is practically unhydrated.

From the slope of curves $\log \varphi^\nu \cdot y_{X^\nu}$ versus H_0 where y symbolizes a kind of a stoichiometric activity coefficient, it is found that protons seem to be hydrated to the same extent in all strong acids when compared at the same water activity. The anions, ClO₄⁻ and HSO₄⁻, seem to be hydrated to approximately the same extent up to about 7 M and much more so than NO₃⁻, the slopes indicating a difference of 3 in hydration number.

In a preceding paper¹, activities and activity coefficients of hydrated ions were derived and their properties investigated. In addition a function closely related to the average degree of hydration of the ions was constructed and its bearing on the existence of maxima in ionic concentration demonstrated. Since individual ionic activities cannot be measured separately, the approximate hydration numbers evaluated referred to various combinations of positive and negative ions. In the following it will be shown, however, that for solutions of strong acids in water, combination of acidity function data with water and acid activities will give functions that depend mainly upon the activity of one of the ions.

LIST OF SYMBOLS

a_{X^v}	Activity on the molarity scale of constituent X^v
a_n	Activity of $H^+(H_2O)_n$
C	Stoichiometric molarity of acid
C_{X^v}	Concentration of X^v on the molarity scale
D	Spacing between the curves $\log \varphi \cdot a_{H_3O^+}$ and $\log \varphi^{-1} \cdot a_{HSO_4^-}$
d_0	Density of pure water
f_{X^v}	Activity coefficient on the mole fraction scale of X^v
K_1, K_n etc	Thermodynamic equilibrium constants
m	Stoichiometric molality of acid
M	Molar = moles · liter ⁻¹
\bar{n}	Average hydration number
\bar{n}', \bar{n}''	Functions closely related to \bar{n} , defined by eqns (38) and (40)
pK	$-\log K$
S	$S = \sum K_n a_{H_2O}^n$
X_{X^v}	Mole fraction of X^v
y_{X^v}	Stoichiometric activity coefficient on the molarity scale of X^v
$y = [y_{H^+} \cdot y_{A^-}]^{\frac{1}{2}}$	» mean activity coefficient of H^+ , A^-
y_+, y_-	''True'' activity coefficients on the molarity scale
$\varphi = y_B/y_{BH^+}$	Ratio of the activity coefficients on the molarity scale of the acid and base forms of the indicator B
α	Degree of dissociation of the strong acid HA
$\gamma = [\gamma_{H^+} \cdot \gamma_{A^-}]^{\frac{1}{2}}$	Stoichiometric mean activity coefficient of H^+ , A^- on the molality scale
ν	Ionic charge.

THE IONIC ACTIVITY FUNCTIONS

For the acid-base equilibrium of an uncharged weak base indicator B, we can write:



The thermodynamic equilibrium constant of this reaction is defined by

$$K_{\text{BH}^+} = a_{\text{H}^+} \cdot a_{\text{B}} \cdot a_{\text{BH}^+}^{-1} \quad (2)$$

H^+ and a_{H^+} in (1) and (2) refer formally to the bare, unhydrated proton. a_{H^+} is so defined that it approaches C_{H^+} upon dilution.

By taking the logarithm of (2) and rearranging, we get:

$$\text{p}K_{\text{BH}^+} - \log(C_{\text{BH}^+} / C_{\text{B}}) = -\log a_{\text{H}^+} - \log(y_{\text{B}} / y_{\text{BH}^+}) \equiv H_0 \quad (3)$$

Eqn. (3) defines H_0 . The left hand side indicates how it can be determined experimentally, *e.g.* by spectrophotometric measurements of the ratio $C_{\text{BH}^+} / C_{\text{B}}$. The right hand side shows the relation of H_0 to the activity of free protons. Activities and concentrations are expressed on the molarity scale. When not otherwise stated this scale is used throughout the paper.

The quotient

$$\varphi = y_{\text{B}} / y_{\text{BH}^+} \quad (4)$$

is unknown although it has been suggested² that this term becomes nearly independent of electrolyte content over a wide range of concentration, *e.g.* for H_2SO_4 above 4–5 M. It is generally accepted that, at any given concentration of strong acid, φ is independent of indicator used as long as it belongs to the same charge type³.

With the aid of (4), eqn. (3) rearranges to:

$$\log \varphi \cdot a_{\text{H}^+} = -H_0 \quad (5)$$

As stated by Guggenheim⁴, single activities like a_{H^+} and activity coefficient ratios like $y_{\text{B}} / y_{\text{BH}^+}$ can be neither experimentally determined nor satisfactorily defined within the framework of thermodynamics. Only by using some extra-thermodynamic assumption can ion activities be defined — as exemplified⁵ by the definition of pH . As seen from (5), however, the quantity $y_{\text{B}} \cdot y_{\text{BH}^+}^{-1} \cdot a_{\text{H}^+}$ is experimentally available. It is obvious that H_0 is closely related to the activity of free protons although this activity cannot, of course, be evaluated because of the unknown function φ .

Since free protons do not exist in measurable amounts in water solutions but are known to be hydrated, it may be of interest now to consider the thermodynamic functions of these constituents.

For the reaction:



the law of mass action yields:

$$K_n = \frac{a_n}{a_{\text{H}^+} \cdot a_{\text{H}_2\text{O}}^n} \quad (7)$$

where a_n is a convenient notation for the activity of $\text{H}^+(\text{H}_2\text{O})_n$. The activity scale of the hydrated proton is conveniently fixed to that of H^+ by putting $K_n = 1$ as was done by Brönsted^{6,7} for $n = 1$.

a_n is thus defined by:

$$a_n = a_{\text{H}^+} \cdot a_{\text{H}_2\text{O}}^n \quad (8)$$

By combining (5) and (8) we get

$$\log \varphi \cdot a_n = -H_o + n \log a_{H_2O} \quad (9)$$

In the following, we shall limit the discussion to H_3O^+ , *i.e.* $n = 1$ in (9).

In order to derive the analogous function for A^- (anion of the strong acid HA), we make use of the reaction:



with the thermodynamic equilibrium constant, K , defined by:

$$K = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{H_2O} \cdot a_{HA}} \quad (11)$$

From (9) and (11):

$$\log \varphi^{-1} \cdot a_{A^-} = H_o + \log K \cdot a_{HA} \quad (12)$$

The quantity $K \cdot a_{HA}$ can be obtained from:

$$K \cdot a_{HA} = a_{H^+} \cdot a_{A^-} = (d^\circ \cdot \gamma \cdot m)^2 \quad (13)$$

Since our activities are given on the molarity scale, it is necessary to transform the activity on the molality scale to that on the molarity scale — this is done using d° , the density of pure water. The stoichiometric mean molality activity coefficient, γ , is frequently tabulated in the literature together with a_{H_2O} or the osmotic coefficient. The ion activity functions (9) and (13) can thus be computed from such data, and often over considerable concentration ranges.

EXPERIMENTAL DATA SELECTED

In the following, a short survey of the experimental data employed in this investigation will be given. With the exception of HBr, they are more thoroughly discussed in Ref.¹

a) *HCl*. Densities of HCl solutions at 25°C have been computed from formulas given by Åkerlöf and Teare⁸. Hydrochloric acid activities have been taken from Harned and Owen⁹ for dilute solutions and from Robinson and Stokes for concentrated solutions^{10a}. Water activities were computed from osmotic coefficients compiled by Robinson and Stokes.^{10b}

b) *HBr*. Densities of HBr solutions at 20°C were taken from Landolt-Börnstein^{11a}. Water and hydrobromic acid activities are also from the same source^{11b} where Redlich has made a compilation of available freezing point, vapor pressure and emf data from several different investigations.

c) *HNO₃*. Densities of HNO₃ solutions at 20°C have been taken from Landolt-Börnstein^{11a}. Water and nitric acid activities at the same temperature have been computed from vapor pressure measurements by Potier¹². The concentrations of dissociated and undissociated acid have been taken from NMR measurements reported by Redlich et al¹³.

d) *HClO₄*. Densities of HClO₄ solutions at 25°C have been taken from Markham¹⁴ and water and perchloric acids activities from the isopiestic measurements of Robinson and Baker¹⁵. The concentrations of dissociated respectively undissociated acid are from Ref 13.

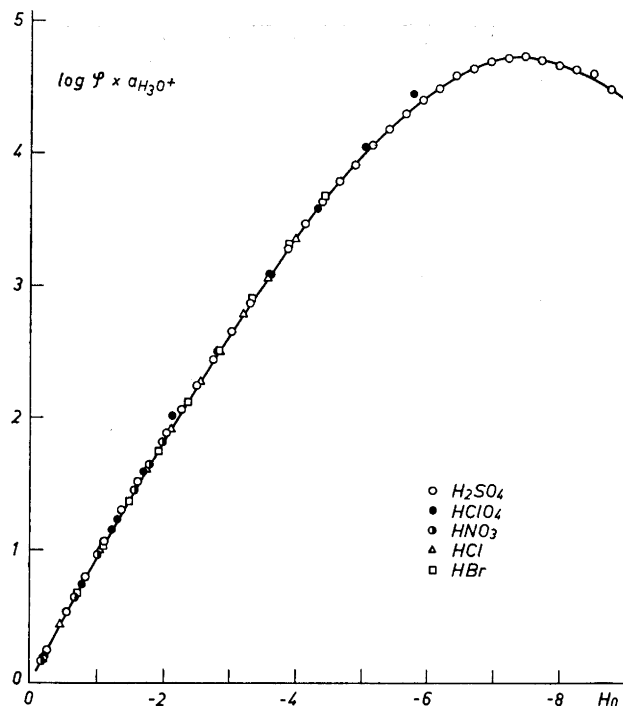


Fig. 1. The function $\log \varphi \cdot a_{\text{H}_3\text{O}^+}$ versus H_0 for various strong acids: \circ H_2SO_4 ; \bullet HClO_4 ; \ominus HNO_3 ; \triangle HCl ; \square HBr .

e) H_2SO_4 . Densities of H_2SO_4 solutions at 25°C have been taken from International Critical Tables¹⁶. Water and sulfuric acid activities are the recent isopiestic measurements by Glueckauf and Kitt¹⁷ which extended up to about 16 M. Above that concentration, water activities given by Deno and Taft¹⁸ from an empirical relation between H_0 and $a_{\text{H}_2\text{O}}$ were used and the corresponding water activities computed with the aid of the Gibbs—Duhem equation by the present writer. As discussed in Ref.1, the activities thus computed agree quite well with the vapor and freezing point measurements recently reported by Giauque *et al*¹⁹. Concentrations of species present have been taken from the Raman measurements reported by Young *et al*.^{20a}.

f) H_0 -data. The H_0 -data for dilute HCl solutions and H_2SO_4 solutions up to 12 M were taken from the author's own measurements²¹ and in other cases from the review by Paul and Long³. Where the measurements of the present writer overlap those in the compilation of Paul and Long, the agreement was found to be good.

COMPARISON OF ION ACTIVITY FUNCTIONS IN SOME DIFFERENT ACIDS

Using the experimental data selected above, the ion activity functions $\varphi \cdot a_{\text{H}_3\text{O}^+}$ and $\varphi^{-1} \cdot a_{\text{A}^-}$ have been computed for the five acids in question.

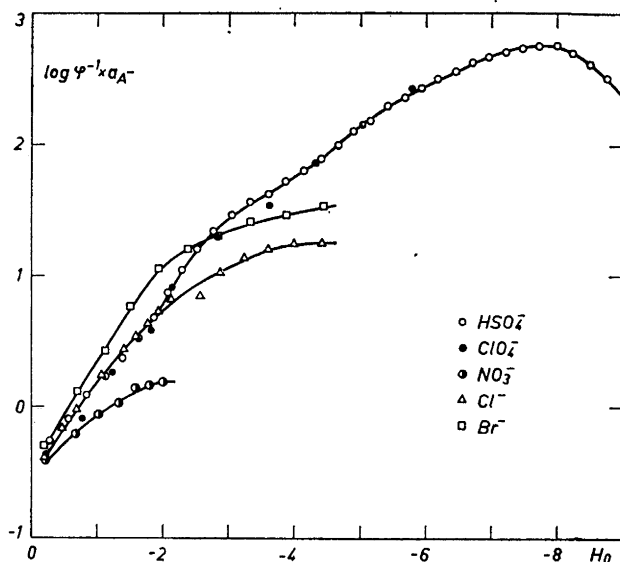


Fig. 2. The function $\log \varphi^{-1} \cdot a_{A^-}$ versus H_0 for various anions: \circ HSO_4^- ; \bullet ClO_4^- ; \ominus NO_3^- ; \triangle Cl^- ; \square Br^- .

In Fig. 1, $\log \varphi \cdot a_{\text{H}_3\text{O}^+}$ is plotted *versus* H_0 and it can be noted that, within the limits of experimental error and within the range of overlap, they all fall on a single curve. This is equivalent to a finding by Wyatt²² that, when H_0 was plotted against $a_{\text{H}_3\text{O}^+}$ for several acids, all data fell on a single curve. From eqn. (9) it is seen that, if the curve H_0 vs $a_{\text{H}_3\text{O}^+}$ is the same for all acids, $\varphi \cdot a_{\text{H}_3\text{O}^+}$ vs H_0 must also be the same. This behavior can be imagined to be due to the fact that the hydration equilibria:

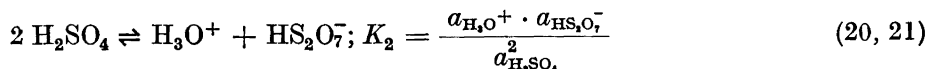
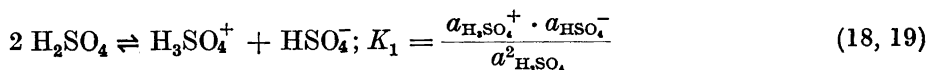
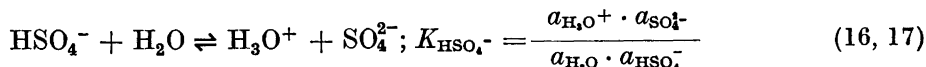


as well as the φ -values are the same in all acids when the comparison is made at the same water activity.

In Fig. 2, $\log \varphi^{-1} \cdot a_{A^-}$ is plotted *versus* H_0 for the five anions: Cl^- , Br^- , NO_3^- , ClO_4^- , HSO_4^- . The anions behave more individually than the common cation, and no coinciding curves are obtained with the exception of the curves for the structurally similar ions HSO_4^- and ClO_4^- which lie quite close to each other. The curves for Br^- and Cl^- are nearly parallel and distinctly different from those for ClO_4^- and HSO_4^- and even more so from the curve for NO_3^- since the latter deviates markedly from all of the other anions already in dilute solutions. The significance of these differences is difficult to grasp with our present knowledge of concentrated electrolytes. That structural similarities should enter into the explanation seems plausible from the way into which the curves divide themselves into different groups with structurally similar ions.

THE PLOT $\log \varphi^{\nu} \cdot a_{\pm}^{\nu}$ FOR $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$

The only acid where H_0 and activity data are available over the whole concentration range from pure water up to pure acid is sulfuric acid. Since this acid is a dibasic acid, there are several species present and the relations between H_0 and the ionic activities take a slightly different form as compared with the monobasic acids. Consider the reactions:



For H_3O^+ we have eqn. (9) and for the other ions we find from (9), (15), (17), (19), (21) and (22)

$$\left. \begin{aligned} \log \varphi \cdot a_{\text{H}_3\text{SO}_4^+} &= -H_0 + \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} + 2 \text{p}K_{\text{H}_2\text{SO}_4} + \\ &+ \text{p}K_{\text{HSO}_4^-} - \text{p}K_1 \\ \log \varphi^{-1} \cdot a_{\text{HSO}_4^-} &= H_0 + \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} + \text{p}K_{\text{HSO}_4^-} \\ \log \varphi^{-2} \cdot a_{\text{SO}_4^{2-}} &= 2 H_0 + \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} \\ \log \varphi^{-1} \cdot a_{\text{HS}_2\text{O}_7^-} &= H_0 + 2 \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} - \log a_{\text{H}_2\text{O}} + \\ &+ 2 \text{p}K_{\text{H}_2\text{SO}_4} + 2 \text{p}K_{\text{HSO}_4^-} - \text{p}K_2 \end{aligned} \right\} (23 \text{ a-d})$$

All of the constants except $K_{\text{H}_2\text{SO}_4}$ are known with some certainty. For $K_{\text{HSO}_4^-}$, the recent value 1.00×10^{-2} given by Hamer^{20a} from considerations of available literature data has been accepted. For K_1 and K_2 , Kirkbride and Wyatt²³ report $K_1 = 3.45 \times 10^{-4}$ (moles per kg H_2SO_4)² and $K_2 = 1.8 \times 10^{-4}$ (moles per kg H_2SO_4)² in pure H_2SO_4 . These values are fairly consistent with those reported by Gillespie and co-workers²⁴⁻²⁶. K_1 and K_2 are given with concentrations in moles per kg H_2SO_4 and with pure sulfuric acid as standard state for $a_{\text{H}_2\text{SO}_4}$. All other activities are referred to pure water and therefore K_2 and K_4 have to be transformed to the molarity scale and the standard state of H_2SO_4 changed to that in water. Using the density of pure sulfuric acid, 1.83, and the value¹ $\log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} = 9.55$ in pure H_2SO_4 , this transformation was performed with the aid of (22) giving:

$$\text{p}K_1 = 26.04 - 2 \text{p}K_{\text{H}_2\text{SO}_4} \quad (24 \text{ a,b})$$

$$\text{p}K_2 = 26.31 - 2 \text{p}K_{\text{H}_2\text{SO}_4}$$

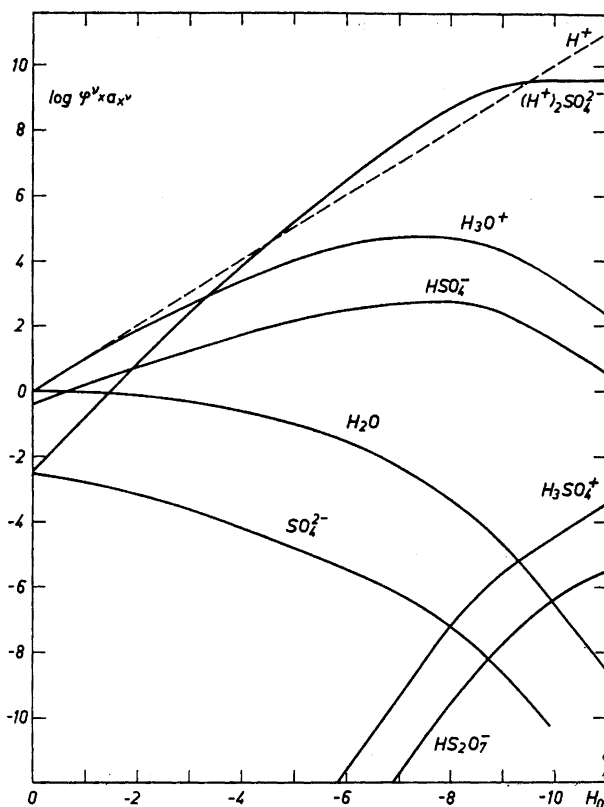


Fig. 3. The functions $\log \varphi^\nu \cdot a_{x^\nu}$ versus H_0 for several species assumed to be present in mixtures of water and sulfuric acid.

Inserting the value for $pK_{\text{HSO}_4^-}$ and the expression for pK_1 and pK_2 from (24) into (23), we get:

$$\begin{aligned} \log \varphi \cdot a_{\text{H}_3\text{SO}_4^+} &= -H_0 + \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} - 24.04 \\ \log \varphi^{-1} \cdot a_{\text{HSO}_4^-} &= H_0 + \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} + 2.00 \\ \log \varphi^{-1} \cdot a_{\text{HS}_2\text{O}_7^-} &= H_0 + 2 \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} - \log a_{\text{H}_2\text{O}} - 22.31 \end{aligned} \quad (25 \text{ a,b,c})$$

In Fig. 3 the functions $\log \varphi^\nu \cdot a_{x^\nu}$ for H^+ , H_3O^+ , H_3SO_4^+ , H_2O , $(\text{H}^+)_2\text{SO}_4^{2-}$, HSO_4^- , HS_2O_7^- and SO_4^{2-} , are plotted versus H_0 .

For H_2SO_4 eqn. (22) has been used and the quantity $\log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}}$, which differs from $\log a_{\text{H}_2\text{SO}_4}$ by the constant $\log K_{\text{H}_2\text{SO}_4} \cdot K_{\text{HSO}_4^-}$, is plotted in Fig. 3. Since $K_{\text{H}_2\text{SO}_4}$ is unknown, $\log a_{\text{H}_2\text{SO}_4}$ itself cannot be evaluated.

The curve for H^+ , is dashed because measurable amounts of hydrogen ions do not occur, a_{H^+} being only a formal quantity equal to $a_{\text{H}_3\text{O}^+}/a_{\text{H}_2\text{O}}$. It deserves also to be mentioned that there is still some uncertainty about the composition of the main species in concentrated sulfuric acid solutions²⁶.

SOME RELATIONS BETWEEN ACTIVITIES AND ACTIVITY COEFFICIENTS IN CONCENTRATED SOLUTIONS OF SULFURIC ACID

As seen from Fig. 3, all species with the exception of H_2SO_4 give curves that can be divided into three different sets of parallel or nearly parallel curves. The spacing between the curves for H_3O^+ and HSO_4^- will be denoted by $2D$, i.e.

$$\log \varphi \cdot a_{\text{H}_3\text{O}^+} - \log \varphi^{-1} \cdot a_{\text{HSO}_4^-} = 2D$$

which can be rearranged to give the following expression for

$$\varphi = \frac{y_{\text{B}}}{y_{\text{BH}^+}} = 10^D \left(\frac{a_{\text{HSO}_4^-}}{a_{\text{H}_3\text{O}^+}} \right)^{\frac{1}{2}} \quad (26)$$

Above 12 M, where the concentration of SO_4^{2-} can be neglected in comparison to HSO_4^- , $C_{\text{H}_3\text{O}^+} = C_{\text{HSO}_4^-}$ and we obtain from eqn. (26)

$$\varphi^2 \cdot \frac{y_{\text{H}_3\text{O}^+}}{y_{\text{HSO}_4^-}} = 10^{2D} \quad (27)$$

In order to test how constant D is, we make use of the expression

$$-2H_o - \log a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}} + \log a_{\text{H}_3\text{O}^+} = 2D + pK_{\text{HSO}_4^-} = 2(D + 1.00) \quad (28)$$

which can be obtained from (26), (9) and (25b). Since all three quantities, H_o , $a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}}$ and $a_{\text{H}_3\text{O}^+}$ have been measured, we can find the range of validity of a constant D value. In Table 1, values of H_o , $a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}}$ and $a_{\text{H}_3\text{O}^+}$ are listed together with the quantity $2(D + 1.00)$ computed from (28). It is seen that, above about 10 M H_2SO_4 , $2(D + 1.00)$ is practically constant. For most of the data, the deviation from the average is less than ± 0.1 . This is about the accuracy with which H_o can be determined in concentrated sulfuric acid²¹. Since the accuracy of the water and sulfuric acid activities is higher¹⁹, it can be concluded that, within the uncertainty in H_o , the relation (28) with a constant D -value is valid in the concentration range 10 — 18.61 M H_2SO_4 .

Consequently the relation:

$$\varphi^2 \cdot \left(\frac{y_{\text{H}_3\text{O}^+}}{y_{\text{HSO}_4^-}} \right) = 10^{1.95 \pm 0.03} = 89 \pm 6 \quad (29)$$

will hold from 12 to 18.61 M H_2SO_4 .

It is tempting to speculate about the physical significance of (29). In any such discussion must enter, however, a knowledge of the electrostatic interactions between the ions. Our lack of knowledge of the variation of the dielectric constant in these concentrated solutions does not permit a comparison with even very naive models for the ion-ion interactions. Until the necessary data and useful theories for concentrated solutions have been obtained, (29) must stand as a surprisingly simple empirical relation covering a large concentration range. Another consequence of the constant D -value is the parallelism of the three sets of curves: H_3O^+ and HSO_4^- , SO_4^{2-} and H_2O , and H_3SO_4^+ and HS_2O_7^- .

Table 1. Water and sulfuric acid activities and H_0 data for the system $H_2O-H_2SO_4$.

C	$\log a_{H_2O}$	$\log a_{H^+} \cdot a_{SO_4^{2-}}$	H_0	$2(D + 1.00)$ from eqn. (28)
0.10	-0.00	-4.13	+0.83	2.47
0.50	-0.01	-2.74	+0.13	2.47
1.0	-0.02	-2.00	-0.26	2.50
1.5	-0.03	-1.53	-0.56	2.62
2.0	-0.05	-1.07	-0.84	2.70
2.5	-0.06	-0.65	-1.12	2.83
3.0	-0.08	-0.25	-1.38	2.93
3.5	-0.11	+0.14	-1.62	2.99
4.0	-0.14	0.53	-1.85	3.03
4.5	-0.18	0.93	-1.06	3.01
5.0	-0.22	1.32	-2.28	3.02
5.5	-0.27	1.71	-2.51	3.04
6.0	-0.32	2.09	-2.76	3.11
6.5	-0.38	2.49	-3.03	3.19
7.0	-0.45	2.88	-3.32	3.31
7.5	-0.52	3.22	-3.60	3.46
8.0	-0.59	3.59	-3.87	3.56
8.5	-0.67	3.94	-4.14	3.67
9.0	-0.76	4.29	-4.40	3.75
9.5	-0.86	4.64	-4.65	3.80
10.0	-0.97	4.99	-4.89	3.82
10.5	-1.08	5.33	-5.15	3.89
11.0	-1.22	5.70	-5.41	3.91
11.5	-1.36	6.03	-5.67	3.95
12.0	-1.51	6.36	-5.93	3.99
12.5	-1.68	6.68	-6.18	4.00
13.0	-1.84	7.00	-6.44	4.04
13.5	-2.05	7.33	-6.70	4.02
14.0	-2.26	7.63	-6.96	4.03
14.5	-2.49	7.93	-7.22	4.02
15.0	-2.73	8.21	-7.47	4.00
15.5	-3.00	8.48	-7.72	3.95
16.0	-3.31	8.74	-7.98	3.91
16.5	-3.59	8.94	-8.23	3.93
17.0	-3.88	9.11	-8.49	3.99
17.5	-4.26	9.27	-8.75	3.97
18.0	-4.88	9.43	-9.04	3.77
18.1	-5.03	9.46	-9.13	3.77
18.2	-5.20	9.49	-9.22	3.75
18.3	-5.36	9.52	-9.36	3.84
18.4	-5.57	9.53	-9.56	4.02
18.5	-5.82	9.54	-9.89	4.42
18.61	-8.81*	9.55	-11.10	3.84

* From Giaque *et al.*¹⁹Average : 3.95 ± 0.03
in the range 10 - 18.61 M

Eqn. (19) can be used for defining single ion activities in the concentration range where D is found to be practically constant. The simplest choice is perhaps to define

$$y_{\text{H}_2\text{O}^+} = y_{\text{HSO}_4^-} \text{ for } 12 \leq C \leq 18.61 \quad (30)$$

Inserting (30) into (29) gives:

$$\varphi = 9.4 \pm 0.3 \text{ for } 12 \leq C \leq 18.61 \quad (31)$$

Expressions for the activities of the other ions are obtained by inserting the φ -value given in (31) into (9), (23 c) and (25). Especially the expression for the activity of SO_4^{2-} takes a very simple form:

$$\log a_{\text{SO}_4^{2-}} = \log a_{\text{H}_2\text{O}} - 2.00 \quad (32)$$

According to (32), the solubility of sulfates should be proportional to the water activity provided that the activity coefficient of the cation stays practically constant. No simultaneous solubility and water activity measurements seem to exist at present so the exact relation between solubility and water activity cannot be obtained. For the solubility of BaSO_4 in concentrated sulfuric acid solutions, Hammet and Deyrup²⁷ noted that the solubility decreased with increasing water content in qualitative agreement with (32).

Finally it may be mentioned that Brand²⁸ as well as Deno and Taft¹⁸ have found empirical relations between H_o and the concentrations of various species present in concentrated sulfuric acid solutions. Analogous expressions can be derived from (9), (25b) and (23) using the transformation from the molarity to the mole fraction scale. Using the Raman data of Young et al.^{20a} it was found that

$$\log \frac{\varphi^{-1} \cdot f_{\text{HSO}_4^-}}{K_{\text{H}_2\text{SO}_4} \cdot f_{\text{H}_2\text{SO}_4}} \sim 8.51 = H_o - \log \frac{X_{\text{HSO}_4^-}}{X_{\text{H}_2\text{SO}_4}} \quad (33)$$

above 16 M H_2SO_4 (90 % H_2SO_4), in excellent agreement with Brand's empirical constant 8.48 (corrected to the H_o -scale adopted by Paul and Long³).

Analogously, it was found that the same Raman data^{20a} gave

$$\log \frac{f_{\text{H}_2\text{O}}}{\varphi \cdot f_{\text{H}_2\text{O}^+}} - 1.74 \sim 7.06 = H_o - \log \frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_2\text{O}^+}} \quad (34)$$

above 15 M H_2SO_4 .

This differs by about 0.3 from the value 6.78 used by Deno and Taft (corrected to the H_o -scale adopted by Paul and Long³). The range of validity of (34) is the same as that found by Deno and Taft for their empirical relation. The Raman data thus confirm the validity of their equation although there is some uncertainty about the exact value of their empirical constant.

The relations (29), (33) and (34) show that the variations of several activity coefficients must practically cancel each other in concentrated solutions. Deno and Taft suggested that the individual activity coefficients may approach constancy in concentrated sulfuric acid. The ideal behavior of such solutions was suggested to be a result of the high dielectric constant²⁹. The similarity to fused salts which are known to behave as practically ideal solutions³⁰ was also emphasized.

COMPARISON OF ION ACTIVITY COEFFICIENT FUNCTIONS IN SOME DIFFERENT ACIDS

In a preceding paper, stoichiometric activity coefficient products for hydrated ions were investigated¹. With the aid of the functions (9), (12), (23c) and (25), analogous functions for the single ions can be defined. For H_3O^+ we can write:

$$\varphi \cdot y_{H_3O^+} = \frac{\varphi \cdot a_{H_3O^+}}{C_{H^+}} \quad (35)$$

where $\varphi \cdot a_{H_3O^+}$ is given by eqn. (9) with $n = 1$ and C_{H^+} is the total, *i.e.* the equilibrium concentration of solvated protons in the solution. In Fig. 4, $\log \varphi \cdot y_{H_3O^+}$ is plotted versus H_0 for the three acids, HNO_3 , $HClO_4$ and H_2SO_4 , for which Raman and NMR data have made possible a distinction between dissociated and undissociated acid. As seen, the three acids give practically parallel straight lines in the range of overlap. It does not seem unreasonable to suppose that, if no systematic experimental errors were present, all three curves would coincide as do the corresponding activities.

In analogy to (35) the function $\varphi^{-1} \cdot y_{A^-}$ is defined by:

$$\varphi^{-1} \cdot y_{A^-} = \frac{\varphi^{-1} \cdot a_{A^-}}{C_{A^-}} \quad (36)$$

where C_{A^-} is the equilibrium amount of A^- . For a monobasic acid HA, we have:

$$C_{H^+} = C_{A^-} = \alpha \cdot C \quad (37)$$

where α is the degree of dissociation of HA.

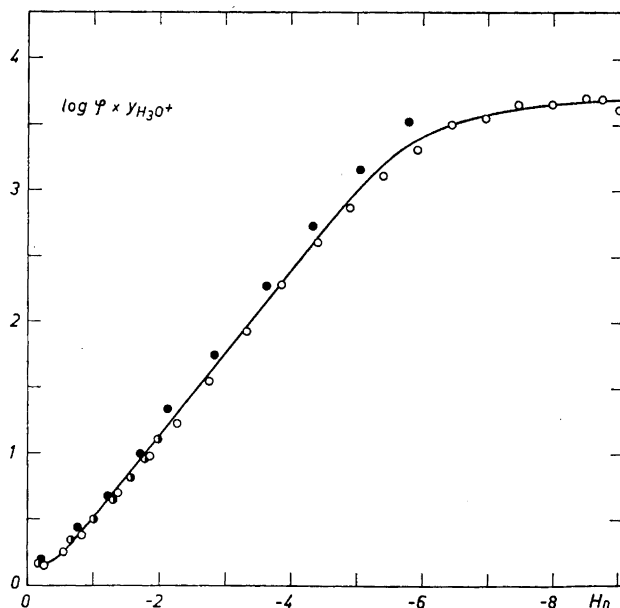


Fig. 4. The function $\log \varphi \cdot y_{H_3O^+}$ versus H_0 for the acids: \circ H_2SO_4 ; \bullet $HClO_4$; \ominus HNO_3

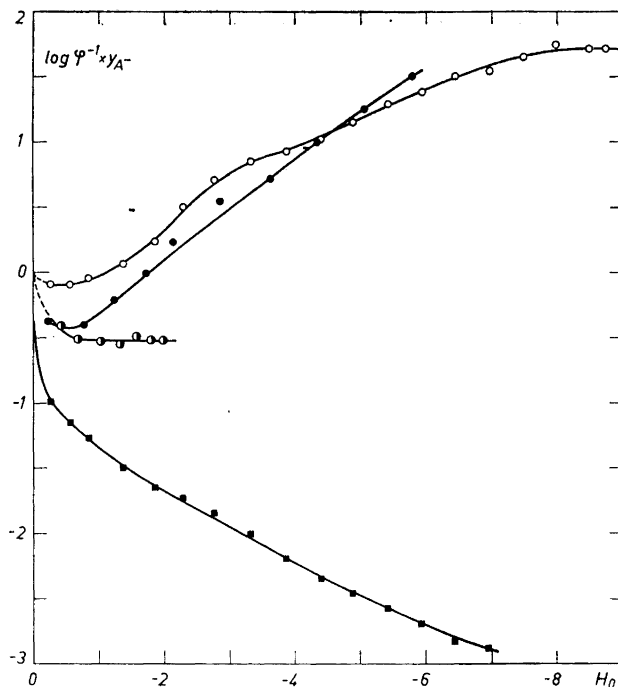


Fig. 5. The function $\log \varphi^{-1} \cdot y_{A^-}$ versus H_0 for various anions: \circ HSO_4^- ; \bullet ClO_4^- ; \ominus NO_3^- ; \blacksquare SO_4^{2-} .

In Fig. 5, $\log \varphi^{-1} \cdot y_{A^-}$ is plotted against H_0 for the anions, NO_3^- , ClO_4^- , HSO_4^- and SO_4^{2-} . As seen, HSO_4^- and ClO_4^- give parallel curves for H_0 down to -3 while the curve for NO_3^- seems to be practically constant and the curve for SO_4^{2-} slopes in the other direction. In the following section, it will be shown how the slopes of the activity coefficient curves are related to the average degree of hydration.

THE AVERAGE DEGREE OF HYDRATION

In a preceding paper¹, it was shown that a function \bar{n}' approximating to the average degree of hydration of the ions H^+ , A^- could be computed from

$$\bar{n}' = -\frac{d \log \left(\frac{y}{a} \right)^2}{d \log a_{\text{H}_2\text{O}}} = -\frac{d \log y_{\text{H}^+} \cdot y_{\text{A}^-}}{d \log a_{\text{H}_2\text{O}}} \quad (38)$$

where \bar{n}' approaches the true hydration number \bar{n} when

$$\frac{d \log y_+ \cdot y_-}{d \log a_{\text{H}_2\text{O}}} \sim 0 \quad (39)$$

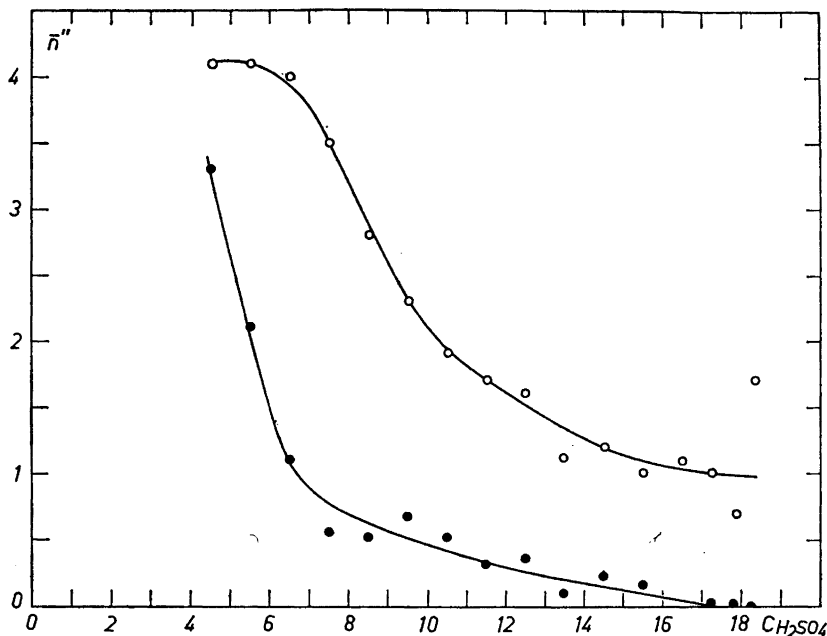


Fig. 6. The function \bar{n}'' for H^+ and HSO_4^- in H_2SO_4 versus the stoichiometric molarity, C , of the acid: $\circ H^+$; $\bullet HSO_4^-$.

y_+ and y_- are the «true» activity coefficients of the various hydrated ions with the simplifying assumption that y_+ is the same for all differently hydrated protons and y_- the same for all differently hydrated anions at each concentration.

From (38) we obtain by introducing the φ -function:

$$\bar{n}''_{H^+} = \frac{-d \log \varphi \cdot y_{H^+}}{d \log a_{H_2O}} \quad \bar{n}''_{A^-} = \frac{-d \log \varphi^{-1} y_{A^-}}{d \log a_{H_2O}} \quad (40 \text{ a,b})$$

Using the definition of H_o (eqn. 3) (40a) can be rearranged to

$$\bar{n}''_{H^+} = \frac{\delta \log C_{H^+} + \delta H_o}{\delta \log a_{H_2O}} \quad (41)$$

\bar{n}''_{H^+} and \bar{n}''_{A^-} approach the true hydration numbers if

$$\frac{d \log \varphi \cdot y_+}{d \log a_{H_2O}} \sim 0, \quad \frac{d \log \varphi^{-1} \cdot y_-}{d \log a_{H_2O}} \sim 0 \quad (42 \text{ a,b})$$

which may happen in concentrated solutions where, as seen in Fig. 3, a_{H_2O} decreases rapidly while the activity coefficients may approach constant values as indicated in Figs. 4 and 5 by the behavior of the stoichiometric coefficients. In Fig. 6, \bar{n}''_{H^+} and $\bar{n}''_{HSO_4^-}$ are plotted versus C from 4 M to pure H_2SO_4 . In this concentration range, \bar{n}''_{H^+} decreases from about 4 in dilute solutions

to 1 in concentrated solutions while $\bar{n}''_{\text{HSO}_4^-}$ decreases from about 3 to 0. That $\text{H}^+(\text{H}_2\text{O})_n$ tends towards H_3O^+ , and $\text{HSO}_4^-(\text{H}_2\text{O})_n$ towards HSO_4^- is quite reasonable. It thus seems that the conditions (42) may be valid in concentrated solutions and \bar{n}'' close to the real hydration number. Since the curve H_0 versus $a_{\text{H}_2\text{O}}$ is the same for all strong acids, it is seen from eqn. (40) that the slopes of the curves $\log \varphi'' \cdot y_{\text{X}}''$ versus H_0 are proportional to \bar{n}'' and thus closely related to \bar{n} . In Fig. 4 the parallelism of the curves $\log \varphi \cdot y_{\text{H}_3\text{O}^+}$ for different acids implies that when compared at the same water activity (or H_0 -value) the protons seem to be hydrated to the same extent in all strong acids.

In Fig. 5 it is seen that, in dilute and moderately concentrated solutions, ClO_4^- and HSO_4^- seem to be hydrated to the same extent. In more concentrated solutions, ClO_4^- seems to be more strongly hydrated than HSO_4^- as indicated by the steeper slope. On the other hand, the practically constant value for $\log \varphi^{-1} \cdot y_{\text{NO}_3^-}$ implies a much smaller and nearly constant degree of hydration for NO_3^- as compared with ClO_4^- and HSO_4^- in the range of overlap. By adding $3 \cdot \log a_{\text{H}_2\text{O}}$ to $\log \varphi^{-1} \cdot y_{\text{NO}_3^-}$, a curve parallel to those for ClO_4^- and HSO_4^- is obtained. This implies a difference of 3 in hydration number in moderately concentrated solutions between NO_3^- on the one hand and ClO_4^- and HSO_4^- on the other.

For SO_4^{2-} , the slope of the curve $\log \varphi^{-2} y_{\text{SO}_4^{2-}}$ is in the other direction compared with those for ClO_4^- and HSO_4^- . No explanation of this behavior has been found. Solvation by H_2SO_4 instead of H_2O might explain the different slope although it is difficult to see how this might occur in solutions where SO_4^{2-} exists in measurable amounts only up to 12 M while measurable amount of H_2SO_4 do not seem to appear below 14 M.

Note added in proof. Recently, Young²⁶ and Wyatt [*Trans. Faraday Soc.* **56** (1960) 490] have suggested the existence of $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{SO}_4$ in concentrated solutions of sulfuric acid. That $\bar{n}''_{\text{H}_3\text{O}^+}$ nevertheless tends towards unity suggests that to a first approximation the interaction between H_3O^+ and H_2SO_4 can be neglected compared to the strong interaction between H^+ and H_2O .

Acknowledgements. The author wishes to express his sincere thanks to Professor Charles D. Coryell for stimulating discussions and encouraging interest when this work was in its infancy. Much helpful advice from Professor Lars Gunnar Sillén concerning the presentation of the material in this paper is gratefully acknowledged. Professor T. F. Young is thanked for comments on equilibria in concentrated solutions of sulfuric acid and Professor W. F. Giaque for giving access to thermodynamic data unpublished at that time for the system H_2SO_4 — H_2O . Mr Don Gillam corrected the English text. Dr Åke Olin is also thanked for some helpful comments. Thanks are due to the *Swedish Atomic Energy Committee* and the *Swedish Natural Science Research Council* for financial support.

REFERENCES

1. Högfeltdt, E. *Acta Chem. Scand.*, **14** (1960) 1597.
2. Coryell, C. D. and Fix, R. *J. Inorg. Nuclear Chem.* **1** (1955) 119.
3. Paul, M. A. and Long, F. A. *Chem. Revs.* **57** (1957) 1.
4. Guggenheim, E. A. *J. Phys. Chem.* **33** (1929) 842.
5. Bates, R. G. *Electrometric pH Determinations, Theory and Practice*, John Wiley, New York 1954.

6. Brönsted, J. N. *Rec. trav. chim.* **42** (1923) 718.
7. Brönsted, J. N. *Z. physik. Chem.* **169A** (1934) 52.
8. Åkerlöf, G. and Teare, J. J. *Am. Chem. Soc.* **60** (1938) 1226.
9. Harned, H. S. and Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd Ed, Reinhold, N.Y. 1958, p. 716.
10. Robinson, R. A. and Stokes, R. H. *Electrolytic Solutions*, Butterworth, London 1955; a) p. 489, b) p. 468.
11. Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Julius Springer Berlin, a) Eg II a, 1931, p. 254, b) Eg II b, 1936, p. 1118.
12. Potier, A. *Ann. fac. sci., univ. Toulouse* **20** (1956) 1.
13. Hood, G. C., Redlich, O. and Reilly, C. A. *J. Chem. Phys.* **22** (1954) 2067.
14. Markham, A. E. *J. Am. Chem. Soc.* **63** (1941) 874.
15. Robinson, R. A. and Baker, O. J. *Trans. Proc. Roy. Soc. New Zealand*, **76** (1946) 250 as reported in *Chem. Abstr.* **41** (1947) 5000 d.
16. *International Critical Tables*, Vol 3, McGraw Hill, New York 1928, p. 56—57.
17. Glueckauf, E. and Kitt, G. P. *Trans. Faraday Soc.* **52** (1956) 1074.
18. Deno, N. C. and Taft, R. W. Jr. *J. Am. Chem. Soc.* **76** (1954) 244.
19. Giauque, W. F., Hornung, E. W., Kunzler, J. E. and Rubin, T. R. *J. Am. Chem. Soc.* **82** (1960) 62.
20. Hamer, W. J. *Structure of Electrolytic Solutions*, John Wiley, New York 1959, a) Young, T. F., Maranville, L. F. and Smith, M. M., p. 35, b) Hamer, W. J., p. 236.
21. Högfeldt, E. and Bigeleisen, J. *J. Am. Chem. Soc.* **82** (1960) 15.
22. Wyatt, P. A. H. *Discussions Faraday Soc. No 24* (1957) 162.
23. Kirkbride, B. T. and Wyatt, P. A. H. *Trans. Faraday Soc.* **54** (1958) 483.
24. Gillespie, R. J., Hughes, E. D. and Ingold, C. K. *J. Chem. Soc.* **1950**, 2473.
25. Gillespie, R. J. and Oubridge, J. V. *J. Chem. Soc.* **1956** 80.
26. Young, T. F. *Private communication*, June 1959.
27. Hammett, L. P. and Deyrup, A. J. *J. Am. Chem. Soc.* **55** (1933) 1900.
28. Brand, J. C. *J. Chem. Soc.* **1950** 997.
29. Gillespie, R. J. and Cole, R. H. *Trans. Faraday Soc.* **52** (1956) 1325.
30. Seward, R. P. *J. Am. Chem. Soc.* **67** (1945) 1189.

Received April 13, 1960.