645. *Acid–Base Properties of Hydrogen Peroxide–Water Mixtures*

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The dissociation constants of a number of weak acids in hydrogen peroxide–water mixtures have been redetermined. These acids fall into two categories typified by picric acid and acetic acid, respectively. It is shown that the difference between these groups is not due to the formation of per-acids, but may be explained in terms of the solvation properties of the undissociated acids resulting in widely different molar free energies of transfer from water to hydrogen peroxide–water mixtures. The solubility of picric acid and the solubility products of a number of salts have been measured over a range of hydrogen peroxide concentrations, and molar free energies of transfer estimated. If certain extrathermodynamic assumptions are accepted, it is shown that all values of free energy of transfer are small except for those of the H_3O^+ and O_2H^- ions, and the undissociated acids in the acetic class.

THE acid–base properties of hydrogen peroxide–water mixtures have been extensively studied by Wynne-Jones and his school. They were the first to use the glass electrode in this solvent system,[1] determining its standard potential at concentrations over the entire range from 0 to 100% hydrogen peroxide and using these values to measure the ionic product ($K_M = [H_3O^+][O_2H^-]$) over the same solvent range.[2] They also measured the dissociation constants of various weak acids in these solvent mixtures, and found that they fell into two groups.[3] The first, typified by picric acid, exhibits a rapid decrease in dissociation constant on addition of hydrogen peroxide to the aqueous solution, whilst the second, typified by acetic acid, shows only a small decrease in dissociation constant up to 0·6 mole-fraction of peroxide. Because the changes shown by the picric acid group of compounds could be related to the standard potentials of the glass–calomel electrode system in the same solvent mixtures, it was assumed that this group reflected the true basicity of the solvent mixtures, and it was concluded that water acted as the basic component and hydrogen peroxide as the acid.

Our interest in the acid–base properties of hydrogen peroxide–water systems developed from studies of the homogeneous catalytic decomposition of these mixtures by various ions.[4-8] In general, the ionisation constants of the various per-acids formed in these systems did not change with solvent composition in the picric acid pattern, but, like acetic acid, remained almost constant. This led to the present investigation into the reasons why acids fall into the two distinct groups described above. In the first place, Wynne-Jones's measurements of the dissociation constants of weak acids have been repeated and extended by spectrophotometric, potentiometric (glass electrode), and conductimetric techniques. Secondly, Wynne-Jones's suggestion that the acids in the acetic acid group form per-compounds under the conditions of the measurement has been examined and has not been confirmed by experiment. Lastly, in order to build up a self-consistent qualitative picture of the sign and magnitude of the molar free energies of transfer of various ion-pairs and molecules from water to hydrogen peroxide mixtures, the solubilities or solubility products of the relevant acids and salts have been measured over a wide range of solvent compositions.

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[1] A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1955, **51**, 1690.
[2] A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 824.
[3] W. F. K. Wynne-Jones, unpublished Ministry of Supply Report.
[4] T. J. Lewis, D. H. Richards, and D. A. Salter, *J.*, 1963, 2434.
[5] P. Flood, T. J. Lewis, and D. H. Richards, *J.*, 1963, 2446.
[6] A. J. Dedman, T. J. Lewis, and D. H. Richards, *J.*, 1963, 2456.
[7] A. J. Dedman, T. J. Lewis, and D. H. Richards, *J.*, 1963, 5020.
[8] P. Flood, T. J. Lewis, and D. H. Richards, *J.*, 1963, 5024.

EXPERIMENTAL

Spectrophotometric Measurements.—Measurements of the dissociation constants of acids having anions which absorb in the visible region were carried out with the aid of a Unicam S.P. 500 spectrophotometer. The method used, which has been described previously,[4] allows for any contribution to the optical density due to absorption of the undissociated acid.

Measurements of pH.—Measurements on colourless acids were performed with a glass electrode and measured against a calomel electrode. The technique was essentially that described by Mitchell and Wynne-Jones.[1,2]

Conductivity Measurements.—The cell used was similar to that described by Gill.[9] The electrodes were machined from tin rod (AnalaR), and fitted snugly into side-arms protruding from either side of the central cell compartment, being held there by cold-setting Araldite. Although Araldite is softened by continual contact with hydrogen peroxide, the fit of the electrodes into the glass sleeves was so tight that very little of the resin was in contact with the liquid, and no deterioration in stability of the peroxide or in strength of the seal was observed. In order to calculate dissociation constants from the observed conductivities, Gill's values [9] for $\Lambda_0(H^+)$ were taken and the values of $\Lambda_0(Ac^-)$ and so on were calculated from the equivalent conductivity of the same ions in water by means of the Walden rule.

Solubility Determinations.—Generally, the solubility of a material in a hydrogen peroxide–water mixture was determined by shaking excess of the material with a known volume of solvent in a thermostat until saturation had occurred, filtering through a Gooch crucible, drying, and weighing. Measurements were carried out at 22° and corrections were applied for dissociation when the solubilities of acids were determined.

Caution. Attempts were made to measure the solubility of silver acetate in hydrogen peroxide by shaking silver acetate with the solvent. However, each time the solvent and solid came into contact, an exceedingly violent decomposition occurred. It was shown that solvolysis occurred and AgO_2H, in a finely divided form, precipitated. This solid is an extremely active catalyst. The difficulty was overcome by carrying out the solubility determinations in acidified peroxide and correcting the results for the contribution of the added acid.

The solubility products of silver bromide are far too low to be determined by the method described above, and conductivity methods are impracticable because of the precipitation of silver on the tin electrodes. The solubility product was therefore determined by a radiochemical technique described by Ruka and Willard.[10] Our method differed only in that ^{110m}Ag ($t_{1/2}$ 253 days) was used as a tracer rather than ^{82}Br ($t_{1/2}$ 36 hr.), and a reproducibility of ±15% was obtained.

Peracetic Acid Determinations.—One per cent solutions of acetic acid and picric acid in 50% w/w hydrogen peroxide containing various amounts of sulphuric acid up to 1% v/v were prepared. Periodically, two drops of solution were removed, weighed, and transferred to a flask containing dilute sulphuric acid. The hydrogen peroxide was destroyed by the careful addition of 0·1N- and 0·01N-potassium permanganate solution. Excess of potassium iodide was added and any iodine liberated was titrated against 0·01N-sodium thiosulphate with starch as indicator. Throughout the titration a stream of nitrogen was bubbled through the solution.

RESULTS

Relative Dissociation Constants of Weak Acids.—The results are shown in Figure 1. Picric acid, *m*-Cresol Purple, Thymol Blue and the *o*- and *p*-nitroanilinium ions were measured spectrophotometrically. Acetic acid, phosphoric acid, and arsenic acid were measured conductimetrically, acetic acid being checked also by potentiometric measurements.

Relative Solubilities of Picric Acid, Potassium Picrate, and Potassium Perchlorate.—Curves A, B, and C of Figure 2 show the variation with solvent composition of the functions $\log r(S)_{\mathrm{HPic}}$, $\log r(S.P.)_{\mathrm{KPic}}$ and $\log r(S.P.)_{\mathrm{KClO_4}}$ which are defined as follows:

$$r(S)_{\mathrm{HPic}} = \frac{\text{solubility of picric acid in solvent}}{\text{solubility of picric acid in water}} = \frac{1}{\gamma_{\mathrm{HPic}}}$$

and $$r(S.P.)_{\mathrm{KPic}} = \frac{\text{solubility product of potassium picrate in solvent}}{\text{solubility product of potassium picrate in water}} = \frac{1}{\gamma_{\mathrm{K^+}}\gamma_{\mathrm{Pic^-}}}$$

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[9] R. A. Gill, Ph.D. Thesis, University of Durham, 1953.

[10] R. Ruka and J. E. Willard, *J. Phys. Colloid Chem.*, 1949, **53**, 351.

where γ represents the degenerate activity coefficient of the species concerned.

(By the term degenerate activity coefficient we mean the activity coefficient based on a scale with infinite dilution in water as unity. The activity coefficient of the species in a solvent other than water will then be the product of two factors. The first is a measure of the free energy of transfer of the species from infinite dilution in water to infinite dilution in the solvent, and the second describes the change of activity with concentration in that solvent. In the case of peroxide–water mixtures there is evidence that the latter is small compared with the former. The e.m.f. of a glass electrode in any one hydrogen peroxide–water mixture may be accurately described by the equation $E = E_0 + 0{\cdot}059 \log [H^+]$. The activity coefficients described in this paper are assumed to be governed predominantly by the composition of the solvent. However, in some measurements of solubility, notably potassium picrate, the concentrations of the solutes involved are so high that the second effect must also be significant.)

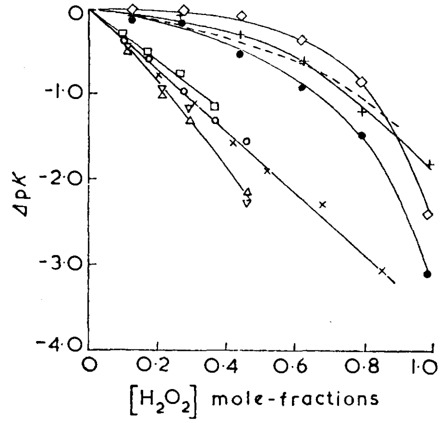

FIGURE 1. Change in relative dissociation constants with solvent composition

◇ Orthophosphoric acid (K_1), + arsenic acid (K_1), ● acetic acid, □ *m*-Cresol Purple, ○ Thymol Blue, × picric acid, △ *o*-nitroaniline, ▽ *p*-nitroaniline. Dotted curve log a_{H_2O}

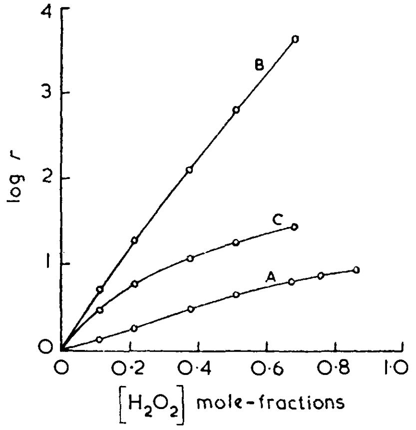

FIGURE 2. Relative solubility and solubility product changes in water–hydrogen peroxide mixtures

Curves A, log r_0 (S) picric acid; B, log r_1 (*S.P.*) potassium picrate; C, log r_2 (*S.P.*) potassium perchlorate

Relative Solubility Products of Silver Acetate and Silver Bromide.—The variations of log $r(S.P.)_{AgAc}$ and log $r(S.P.)_{AgBr}$ with solvent are shown in Figure 3. Log $r(S.P.)_{AgO_2H}$, based on the data of Maggs and Sutton,[11] is also shown for reasons given in the discussion section. It can be seen from the graph that log $r(S.P.)_{AgAc}$/log $r(S.P.)_{AgBr}$ is very much less than log $r(S.P.)_{AgO_2H}$/log $r(S.P.)_{AgBr}$, and that whilst in 0·7 mole-fraction of hydrogen peroxide $\gamma_{Br^-}/\gamma_{Ac^-}$ is not greater than a factor of about 4, $\gamma_{Br^-}/\gamma_{O_2H}$ is of the order of 1000.

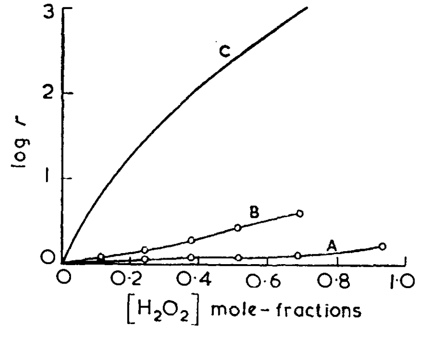

FIGURE 3. Relative solubility product changes in water–hydrogen peroxide mixtures

Curves A, log r (*S.P.*) silver bromide; B, log r (*S.P.*) silver acetate; C, log r (*S.P.*) AgO_2H (Maggs and Sutton, ref. 11)

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[11] F. T. Maggs and D. Sutton, *Trans. Faraday Soc.*, 1958, **54**, 1861.

Peracetic Acid Determinations.—With acetic acid solutions containing no sulphuric acid, no increase in the value of the thiosulphate titre, over and above that of the blank was observed during several days. In the presence of 0·1% v/v sulphuric acid, conversion was complete after 10 days, and with 1% v/v acid in 4 hr. Thus peracetic acid could be detected by this method, and the negative results on solutions containing no mineral acid indicate that under these conditions peracetic acid is not formed.

No peroxy-compound was detected in a solution of picric acid in hydrogen peroxide even in the presence of 1% v/v sulphuric acid.

DISCUSSION

Four conclusions may be drawn from the present investigation: (*a*) Wynne-Jones's observation that acids may be divided into two groups according to their behaviour in hydrogen peroxide–water mixtures is corroborated; (*b*) the difference between the two classes of acids is not due to the formation of per-acids; (*c*) the difference between the two classes does not appear to be due to a property of the anions. Although our solubility measurements have compared the picrate ion with the perchlorate ion and the acetate ion with the bromide ion, there is evidence that the free energies of transfer for many inorganic ions such as perchlorate, chloride, or bromide from water to hydrogen peroxide are similar. This comes from the fact that the standard potential of the glass electrode/calomel electrode cell is independent of the nature of the strong acid used in its measurement and hence $\gamma_{H^+}\gamma_{ClO_4^-} = \gamma_{H^+}\gamma_{Cl^-}$ etc. Solubility measurements show that variations of activity coefficient of the acetate ion are similar to those of the bromide ions, and although $\gamma_{ClO_4^-}/\gamma_{Pic^-}$ increases fairly rapidly with increasing peroxide concentration, this ratio would have to *decrease* in order to explain the variation in the dissociation constant of picric acid; (*d*) the fall in the dissociation constant of picric acid with increasing peroxide concentration cannot be due to changes in the degenerate activity coefficient of the undissociated acid. If the primary solvation shell of the hydrogen contains only one water molecule (this will be shown later to be the case), and neglecting the composition of the secondary shells, the ionisation of a weak acid is given by

$$HA + H_2O \overset{K}{\rightleftharpoons} H_3O^+ + A^-$$

From this it may be deduced that

$$K/K_0 = \frac{\{H_2O\}\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}} \qquad (1)$$

where K_0 is the concentration ionisation constant in water, γ is the degenerate activity coefficient, and H^+ represents the solvated hydrogen ion.

The value of γ_{HA} for picric acid is available from solubility measurements and its values do not approach those required to explain the variation observed in the K/K_0 term of equation (1). This contrasts with the conclusion of workers on the dioxan–water system that here the variation in the dissociation of weak acids with solvent composition is due largely to changes in the activity coefficients of the undissociated acids.[12, 13]

An argument is presented below to show that (1) the decrease in the ionisation constant of picric acid on increasing the hydrogen peroxide component of the solvent is due to an increase in $\gamma_{H^+}\gamma_{Pic^-}$ compared with $\gamma_{M^+}\gamma_{Pic^-}$; (2) there is a corresponding decrease in the ratio of $\gamma_{M^+}\gamma_{O_2H^-}$ compared with $\gamma_{M^+}\gamma_{X^-}$ so that $\gamma_{H^+}\gamma_{O_2H^-} \approx 1$ throughout the solvent range; (3) for the acetic acid group of acids, an increase in the degenerate activity coefficient of the undissociated acid compensates for the increase in $\gamma_{H^+}\gamma_{X^-}$ and leaves the dissociation constant relatively unaffected by solvent composition; (4) at least one water molecule is necessary in the solvation shell of the hydrogen ion.

It has already been shown that the thousand-fold lowering of K/K_0 for the picric acid group cannot be due to a decrease in γ_{HA}. Not only are the solubility changes of picric acid

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[12] H. S. Dunsmore and J. C. Speakman, *Trans. Faraday Soc.*, 1954, **50**, 236.

[13] R. P. Bell and R. R. Robinson, *Trans. Faraday Soc.*, 1961, **57**, 965.

too small to give the required change in activity coefficient, but it is highly significant that the ionisation changes of positively charged acids such as the *o*- and *p*-nitroanilinium ions, follow the same curve as picric acid. Here the uncharged acid, HA, appears on the right-hand side of the dissociation equation and, if activity-coefficient changes of this species were critical, the dissociation constant would change in a direction opposite to that of picric acid. Clearly the changes must be principally due to changes in the term $\gamma_{H^+}\gamma_{A^-}$. For the acetic acid group, the term $\gamma_{HA}/\gamma_{H^+}\gamma_{A^-}$ is relatively constant. Since γ_{H^+} is common to both groups of acids there must be a difference in the behaviour of the term γ_{HA}/γ_{A^-}. But the solubility results have shown that the changes which occur in the ratio $\gamma_{Pic^-}/\gamma_{Ac^-}$ are in a direction opposite to that which would explain the difference between the two classes of acids. Thus in both instances the difference must be due to changes in γ_{HA}; that of acetic acid must increase much more rapidly than that of picric acid.

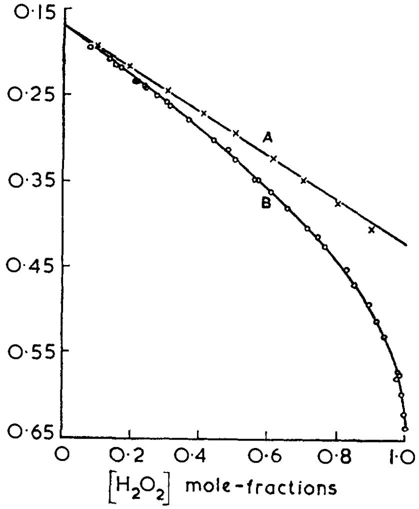

FIGURE 4. Variation of E_0 with solvent composition

×, $E^\circ + (\boldsymbol{RT/F}) \ln a_{H_2O}$; ○, experimental results of Mitchell and Wynne-Jones (ref. 1)

Similar conclusions come from the study of the glass electrode, the calomel electrode being used as reference. The electrode is reversible to hydrogen ions and may be simply treated as a hydrogen electrode. The counter-ion to the hydrogen is ion A^-, here perchlorate, chloride, or nitrate.

If the liquid junction potential is ignored, the single electrode potential in water may be written

$$E = E^\circ + (\boldsymbol{RT/F}) \ln [H^+]$$

and in a mixture $$E = E_1^\circ + (\boldsymbol{RT/F}) \ln ([H^+] \,.\, \gamma_{H^+}\gamma_{A^-}/\{H_2O\})$$

from which $$E_1^\circ - E^\circ = \Delta E^\circ = (\boldsymbol{RT/F}) \ln (\gamma_{H^+}\gamma_{A^-}/\{H_2O\}) \qquad (2)$$

The increase in ΔE° with peroxide concentration is much too large to be explained by the decrease in $\{H_2O\}$ and must be due to an increase in the term $\gamma_{H^+}\gamma_{A^-}$. Indeed, if the term $(\boldsymbol{RT/F}) \ln \{H_2O\}$ is subtracted from ΔE° (adopting the thermodynamic data of Scatchard, Kavanagh, and Ticknor [14]), a straight line is obtained (Figure 4). It would appear that if one water molecule is *essential* to the solvation of the proton, evidence for which is given below, then $\ln \gamma_{H^+}$ bears a linear relation to the mole fraction of peroxide present.

Equation (1) may be combined with equation (2) to give

$$-\Delta E^\circ = (\boldsymbol{RT/F}) \ln (K/K_0\gamma_{HA}) \qquad (3)$$

[14] G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715.

Beck and Wynne-Jones[15] have shown that if $-\Delta E^\circ$ is plotted against $(\boldsymbol{RT}/\boldsymbol{F}) \ln K/K_0$ for picric acid, a straight line at 45° passing through the origin is obtained. This indicated once again that $\gamma_{\text{HA}} \approx 1$ for this acid.

This interpretation of the glass-electrode measurements implies a large positive molar free energy of transfer (ΔG_t) for strong acids from water to hydrogen peroxide–water mixtures. For $HClO_4$, HCl, and HNO_3, ΔG_t from water to 0·5 mole fraction H_2O_2 is in each case about **3700** cal. From the solubility measurements, ΔG_t values for similar transfers are: AgBr, −130; Ag acetate, −500; picric acid, −700; $KClO_4$, −1500; and AgO_2H, −3100 cal. The figure for potassium picrate is not quoted since its very high solubility makes quantitative interpretation dubious, although it may be said to be rather more negative than that for $KClO_4$. Other ΔG_t values calculated from previously published solubility data,[16,17] again for the transfer from water to 0·5 mole fraction H_2O_2, include $LiNO_3$, +1600; $NaNO_3$, −880; KNO_3, −1050; $RbNO_3$, −1200; $CsNO_3$, −1800; NaCl, −440; KCl, −520 cal. Quantitative self-consistency is not to be expected in the ΔG_t values calculated from solubility data, since the solutions are at various concentrations and some are in the range where activity coefficients, other than those due to the transference of an infinitely dilute electrolyte from one solvent to another, are probably important. However, the glass-electrode measurements were carried out in dilute solution, and the ΔG_t values calculated from these should approximate more closely to ΔG_t°, the value at infinite dilution.

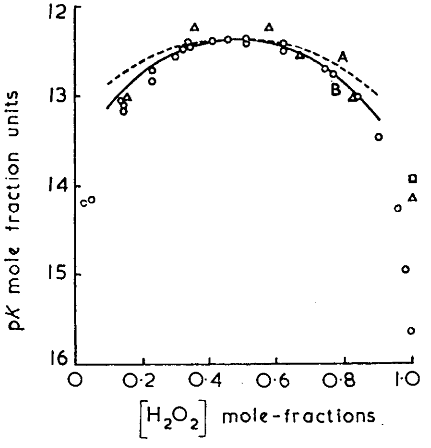

FIGURE 5. Variation of ionic product with solvent composition

Curve A, $K[H_2O_2][H_2O]$; Curve B, $K'\{H_2O\}\{H_2O\}$; both curves corrected for ε changes. ○, Mitchell and Wynne-Jones (ref. 2) e.m.f. method; Gill and Wynne-Jones (ref. 9) conductivity method. Δ, Kolczynski, Roth, and Shanley (average) e.m.f. method. □, Lewis, e.m.f. method, unpublished results

Any evaluation of single-ion molar free energies of transfer involves extra thermodynamic assumptions. In particular there have been several recent attempts to list ΔG_t° values for single ions in the water to methanol–water transfer.[18,19] For hydrogen peroxide, in view of the similarity of the ΔG_t figures for $HClO_4$, HNO_3, and HCl, we postulate that the molar free energy of transfer of the anions is low and that the **3700** cal. observed for these acids approximates to the value of ΔG_t for the hydrogen ion. It follows that the molar free energy of transfer for Ag^+ is small, and that for the O_2H^- ion about −**3000** cal. Values of ΔG_t for the other ions are comparatively small, although the larger ions of the alkali metals do tend to show negative values.

The fact that $\Delta G_t^\circ(H_3O^+) + \Delta G_t^\circ(O_2H^-) \approx 0$ may be shown by an analysis of the ionic-product measurements by Mitchell and Wynne-Jones.[2] They determined the value of $K_M = [H_3O^+][O_2H^-]$ over the complete range of solvent concentrations, but attempts to

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[15] N. H. Beck and W. F. K. Wynne-Jones, *J. Chim. phys.*, 1956, **49**, 97.

[16] J. D. Floyd and P. M. Gross, *J. Amer. Chem. Soc.*, 1955, **77**, 1435.

[17] M. E. Everhard, Ph.D. Thesis, University of Virginia, 1959.

[18] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.

[19] D. Feakins and P. Watson, *J.*, 1963, 4734.

relate these values to the concentration product $[H_2O][H_2O_2]$ resulted in a poor fit. However, we have obtained better agreement by replacing concentration terms by activities in the above equation.

Consider the relationship $n\mathrm{H_2O} + \mathrm{H_2O_2} = \mathrm{H_3O^+(H_2O)}_{n-1} + \mathrm{O_2H^-}$. Then K_M, the ionic product measured, is given by

$$K_M = \frac{K\{H_2O_2\}\{H_2O\}^n}{\gamma_{H^+}\gamma_{O_2H^-}} \tag{4}$$

where K is the thermodynamic equilibrium constant of the above equation. When K_M/K is calculated from this equation, a reasonable fit with the experimental points is obtained only if $n = 1$ and $\gamma_{H^+}\gamma_{O_2H^-} = 1$. This is shown in Figure 5. Corrections have been made for the small changes in dielectric constant with composition [20] by use of the Born equation:

$$\Delta G = -\boldsymbol{RT} \ln (K_1/K_2) = e^2 (1/\varepsilon_1 - 1/\varepsilon_2)/r$$

where ε_1 and ε_2 are the dielectric constants of the two different solvent compositions, $e =$ the electronic charge, and $r =$ ionic radius, taken as 2×10^{-8} cm.

It is therefore concluded that (1) the minimum number of water molecules necessary to solvate the proton is one, and (2) $\gamma_{H^+}\gamma_{O_2H^-} \approx 1$, confirming the conclusions drawn from the glass-electrode and solubility measurements.

Further evidence that the activity coefficient of the hydrogen ion changes rapidly with solvent concentration may be drawn from our study of vanadium complexes in hydrogen peroxide–water mixtures.[8] Three species were identified and inter-related by the following equations:

$$K = \frac{[H^+]^2[H_2VO_5^-]}{[H_4VO_5^+]} \text{ and } K' = \frac{[H^+][HVO_5^{2-}]}{[H_2VO_5^-]}$$

These equilibrium constants varied with solvent composition in a manner which could be described by the equation $\Delta pK = 2\Delta pK'$. This relationship is most easily explained in terms of changes in the activity coefficient of the hydrogen ion which appears as a square term in K but as a linear term in K'.

The result that only one water molecule appears to be essential in the solvation of the proton in these systems is in apparent conflict with the results of a number of studies on the variation of Hammett functions with water concentration in strong acids.[21] These have shown that the experiments at high acidity can best be interpreted when the hydrogen ion is regarded as a proton solvated by four molecules of water. Wicke *et al.* have suggested [22] that this entity consists of a central H_3O^+ ion with each hydrogen bonded to the oxygen of a neighbouring water molecule. Furthermore, Aazam [23] suggests that in dilute aqueous solutions the hydrogen ion is best represented by the formula $H_3O^+(H_2O)_3(H_2O)_9$, which involves a further solvation shell for the H_3O^+ ion.

Our results are reconciled with these observations as follows: it is well established that the basicity of water is far greater than that of hydrogen peroxide, but this basicity refers specifically to the solvation of a proton and cannot be extended to the more general field of cation solvation, since it has been shown that hydrogen peroxide can replace water in the solvation shell of metal ions.[4-6,24] The departure of the hydrogen ion from this behaviour probably originates from the greater resonance stabilisation of H_3O^+ over $H_3O_2^+$ but there seems to be no *a priori* reason why the ion H_3O^+, once formed, should be exclusively hydrogen-bonded to water rather than hydrogen peroxide molecules—indeed the degrees of hydrogen-bonding in peroxide and its aqueous solutions are similar to that

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[20] P. M. Gross and R. C. Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 2075.

[21] R. P. Bell, " The Proton in Chemistry," Methuen, p. 81.

[22] E. Wicke, M. Eigen, and T. Ackerman, *Z. phys. Chem.* (*Frankfurt*), 1954, **1**, 340.

[23] A. M. Azzam, Meeting held at Bradford on " Solvation of Molecules and Ions," 26th—27th September 1963.

[24] M. H. Gorin, *J. Amer. Chem. Soc.*, 1935, **57**, 1975.

in water.[25] The observed changes in γ_{H^+} indicate, however, that hydrogen-bonding to water molecules is preferred, and the measured γ_{H^+} can be represented as being determined by the summation of a series of equilibria of the type

$$H^+ + H_2O + (n - m)H_2O + mH_2O_2 \overset{K_m}{\rightleftharpoons} H_3O^+(H_2O)_{n-m}(H_2O_2)_m \qquad (5)$$

where m lies between 0 and n, and K_m is an inverse function of m. The observed rapid increase in γ_{H^+} requires that n is of the order of ten, which compares reasonably with Aazam's formula.

An argument similar to the foregoing can explain the decrease in the activity coefficient of the hydroperoxyl ion with increase in peroxide, if the solvation of the O_2H^- is similar to that of the H_3O^+ ion, except that hydrogen peroxide rather than water molecules are preferred. Thus a series of equilibria similar to equation (5) may be written

$$O_2H^- + (n - m)H_2O + mH_2O_2 \overset{K_m}{\rightleftharpoons} O_2H'(H_2O)_{n-m}(H_2O_2)_m$$

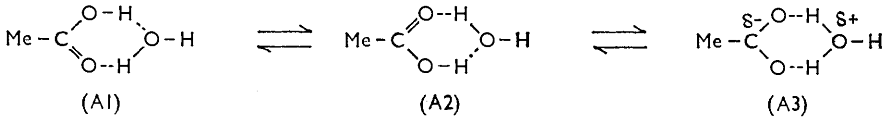
where K_m is now a direct function of m.

If the changes in K_m and K_m' with m are of similar magnitude, but of opposite sense, then the condition $\gamma_{H^+}\gamma_{H_2O^-} \approx 1$ is realised.

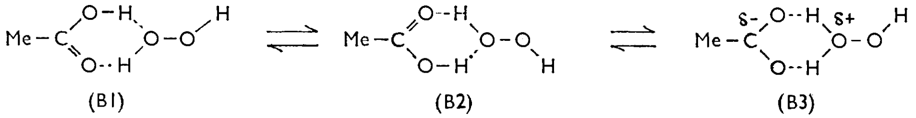
The division of acids into two groups, typified by picric acid and acetic acid, respectively, is tentatively explained as follows.

The acids which fall into the acetic acid category are oxyacids which are highly intermolecularly hydrogen-bonded in the pure state, *e.g.*, acetic acid forms dimers and sulphuric acid a three-dimensional network analagous to water. Probably then, on dilution with a hydrogen-bonding solvent, these acids are almost completely hydrogen-bonded by the solvent molecules, *i.e.*, solvation of the undissociated acid occurs. This would occur only to a much smaller extent with the intramolecularly hydrogen-bonded picric acid.

The possible modes of solvation of acetic acid are given below



(A1) (A2) (A3)



(B1) (B2) (B3)

Similar models could be drawn for the other oxyacids in the acetic acid group. As the hydrogen-bonding capacities of hydrogen peroxide and water are similar, modes B1 and B_2 are as likely to occur as modes A1 and A2. However, mode A3 is far more likely than B_3 because the stability of the $H_3O^{\delta+}$ component is greater than that of $H_3O_2^{\delta+}$. It seems reasonable to assume, therefore, that the undissociated acid is preferentially solvated with water so that, if A3 is the predominating structure, changes in its stability will largely determine the activity-coefficient changes of the undissociated acid. The stability changes of A3 should parallel those of the hydrogen ion, since the H_3O^+ entity is involved in both and is probably solvated further in a manner analagous to the hydrogen ion. Changes in γ_{H^+} will then balance changes in γ_{HA^+}, and variation in dissociation constant should be measured by $\{H_2O\}$ only. The variation of log $\{H_2O\}$ with peroxide concentration is seen as the dotted curve in Figure 1 and in fact it does exhibit a trend similar to the acetic acid group.

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[25] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, " Hydrogen Peroxide," Reinhold Monograph Series 128, p. 345.