497. *Dielectric Dispersion in Sulphuric Acid.*

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The complex dielectric constant of anhydrous sulphuric acid has been measured at six frequencies between 100 and 3000 Mc. The results are compatible with a small distribution of relaxation times and are analysed by the semi-empirical equation (Cole and Cole, *J. Chem. Phys.*, 1941, **9**, 341)

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = \varepsilon_\alpha + (\varepsilon_0 - \varepsilon_\alpha)/\{1 + (i\omega\tau_0)^{1-\alpha'}\} \quad . \quad . \quad . \quad (1)$$

wherein ε_0 and ε_α are, respectively, the low- and the high-frequency limiting dielectric constants, τ_0 is the most probable relaxation time, and α' is a parameter governing the spread of relaxation times. The parameters which best fit the experimental results are, at 20°: $\varepsilon_\alpha = 5$ (assumed), $\varepsilon_0 = 110$, $\tau_0 = 4{\cdot}8 \times 10^{-10}$ sec., and $\alpha' = 0{\cdot}085$. The high electrolytic conductance introduces considerable experimental difficulties, and the extrapolation of ε_0 is uncertain to several units. The significance of the dielectric constant is discussed in relation to the thermodynamic properties of solutions in sulphuric acid.

It is well known that electrolyte solutions in sulphuric acid are thermodynamically nearly ideal, even at very high ionic strengths. This property was first appreciated by Hammett and Deyrup who suggested, as the most rational explanation, that the dielectric constant of the acid must be " extremely high " (Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940). More recently it has been found that solutions of non-electrolytes in sulphuric acid are, on the whole, *less* nearly ideal than the electrolytic solutions, and opinion has veered towards the view that the dielectric constant is so very high that electrostatic forces between ions are negligible. On this hypothesis (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473) the need to consider electrolytes and non-electrolytes as separate classes disappears and only solvation, or other equilibria, are considered to cause the small but measurable defects from ideality.

Walden, in 1903 (*Z. physikal. Chem.*, **46**, 182), reported that the dielectric constant of " concentrated " sulphuric acid was higher than that of water. However, this conclusion involved the tacit assumption that the dielectric was lossless, a condition very far indeed from being fulfilled. Assuming that Walden used 96% acid we can estimate from our results that the loss tangent was not lower than 10 at the operating frequency (417 Mc., 72 cm.) and that the dielectric constant was probably only 30—40, considerably less than in water; but no optical method would give an accurate value of the dielectric constant of a liquid with so high a loss. By using *anhydrous* sulphuric acid, which has a much lower electrolytic conductance, it is possible to make reasonably accurate measurements at high frequencies, and hence to extrapolate the limiting low-frequency dielectric constant within a few units; the uncertainty of the extrapolation is still due mainly to the residual d.c. conductance of the anhydrous acid.

The theory of an ideal polar dielectric in an alternating field was developed by Debye (" Polar Molecules," Chemical Catalogue Co., New York, 1929). Except for the assumption of a single relaxation time, the basic equations (2) are independent of the dielectric model.

$$\left.\begin{aligned} &\varepsilon = \varepsilon_1 - i\varepsilon_2 = \varepsilon_\alpha + (\varepsilon_0 - \varepsilon_\alpha)/(1 + i\omega\tau) \\ \text{where}\quad &\varepsilon_1 = (\beta^2 - \alpha^2)/\beta_0^2 \\ \text{and}\quad &\varepsilon_2^{\mathrm{T}} = 2\alpha\beta/\beta_0^2 = \varepsilon_2 + \varepsilon_2^{\mathrm{C}} = \varepsilon_2 + 4\pi\kappa/\omega \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

In eqn. (2), ε_1 is the dielectric constant (variable with frequency) and $\varepsilon_2^{\mathrm{T}}$ is the total dielectric loss factor, ε_2 and $\varepsilon_2^{\mathrm{C}}$ being the loss factors relating to dipole orientation and d.c. conductance, respectively, ε_0 and ε_α are the limiting low- and high-frequency dielectric constants, and ε is the complex dielectric constant at the angular frequency ω, τ is the relaxation time corresponding to the wave-length $\lambda_m = 2\pi c\tau$ at which ε_2 is a maximum, and κ is the d.c. conductance in e.s.u. α and β are, respectively, the attenuation constant and the phase constant of classical electromagnetic theory, β_0 being the phase constant for propagation *in vacuo*; α, β, and β_0, and hence ε_1 and ε_2^T, are experimentally measurable quantities. Although the assumption of a single relaxation time is verifiable for some dielectrics, real systems are often better described by the modified, semi-empirical expression (1) (see Summary), where the symbols have the same meaning except that the relaxation process is specified by τ_0 and α' in place of τ.

Measurements with sulphuric acid were made in the decimetre and metre wave-bands at a single temperature (20°). Different experimental methods were used in the two regions, but the general principle was to determine β and α in a coaxial wave-guide from the phase and power of the wave transmitted through a column of the dielectric. The mode in the guide was purely transverse. The derived values of ε_1 and ε_2 were more consistent with eqn. (1) than with the Debye equations, although the spread of relaxation times was quite small. ε_0, τ_0, and α' were obtained as parameters, the maximum loss due to dipole reorientation being at 330 ± 30 Mc ($\lambda_m = 90$ cm.).

EXPERIMENTAL

Measurements at 100—300 Mc.—The generator was a conventional variable-frequency oscillator incorporating a miniature triode (Mullard EC53), a tuned crystal detector being used to monitor the relative power levels. The rectified current from the crystal is proportional to (voltage)^2, and hence is proportional to power if the voltage is developed across a constant impedance. The tuning of the detector by a variable reactance (an adjustable short-circuited length of concentric line at 300 Mc and a lumped circuit at 250—100 Mc) discriminates against the rectification of harmonics.

The "square-law" characteristic of the crystals was tested by measurements on the standing-wave in a slotted guide with a short-circuit termination (Birks, *Proc. Phys. Soc.*, 1948, **60**, 282). The voltage distribution on the line is

$$V^2 = V_0^2 \sin^2 (2\pi x/\lambda)$$

where V_0 is the maximum voltage, and V is the voltage at a distance x from the minimum. If the "square-law" characteristic holds accurately the crystal current, i, must be proportional to $\sin^2 (2\pi x/\lambda)$, and this was verified with a probable error of less than 1% over a complete quarter wave-length, *i.e.*, for the voltage range zero to V_0. The proportionality found in this experiment also proves that harmonics present in the output of the generator are not rectified by the crystal. In actual measurements the crystal current was always <1 μa, and was measured by a galvanometer previously calibrated against a standard microammeter.

Dielectric Cells.—These were telescopic sections of coaxial wave-guide, and two such cells were employed. In one, the outer conductor (diam. 4·43 cm.) was of copper and the inner conductor (1·28 cm.) of brass, the surfaces being gold-plated (0·004 cm.); the length was 30 cm. The inner conductor was held centrally by a "Polythene" disc which also provided a liquid-tight seal. The telescopic section of the cell, which did not come into contact with sulphuric acid and was unplated, was in sliding contact with the gold-plated surfaces and was moved by hand. Connections were made by flexible coaxial cable (Uniradio 21) through G.E.C. coaxial sockets. Control measurements with aqueous electrolyte solutions showed that there was no interference from subsidiary modes. The second cell was similar, but was constructed of stainless steel which is not attacked by sulphuric acid. The outer and inner conductor diameters were, respectively, 3·81 and 1·27 cm. The expectation that this cell might prove appreciably resistive to high-frequency current, owing to the surface film of oxide, was not realised and the results with the two cells were indistinguishable. Preliminary measurements were made with a gold-plated cell 14 cm. long; this was designed in the expectation of a much higher dielectric constant and in practice did not provide a sufficiently long "optical path" of dielectric.

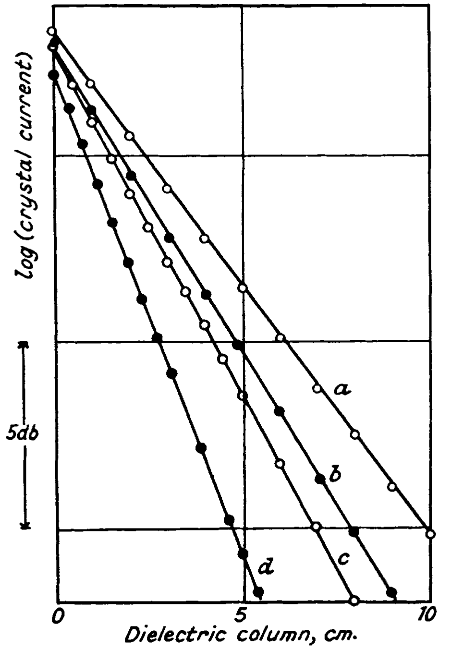
Measurement of Attenuation Coefficient.—The measurement of α (cf. Turner, *J. Inst. Elect. Eng.*, 1946, IIIA, **93**, 1474) is the same in principle as the measurement of percentage transmission at optical and infra-red frequencies with a cell of variable thickness. Power is the analogue of intensity, the relation between transmitted power, P, and the dielectric path, l, being

$$P = P_0 \exp(-2\alpha l) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

α is obtained by plotting the logarithm of the crystal current ($i \propto P$) against the length of the dielectric column (Table 1 and Fig. 1).

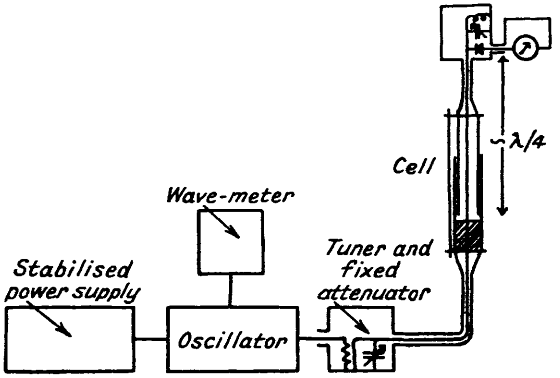
The arrangement of the apparatus is shown in Fig. 2. At radio-frequencies certain conditions need to be fulfilled which do not have an optical analogy. First, on the side of the crystal detector the electrical length from the surface of the dielectric to the short circuit must remain constant, or eqn. (3) is not fulfilled : * a constant length was maintained by raising the telescopic section of the cell after each addition of sulphuric acid. Secondly, the power level sent from the generator into the cell must remain constant as the dielectric path changes. This is achieved if the *initial* length of the dielectric column is such that at least 90% of the incident power is absorbed by the column, because the power reflected to the generator from the upper surface of the dielectric is then negligible and additions to the dielectric column do not change the impedance of the load as seen from the generator. The generator was tuned to the load by a small variable condenser.

FIG. 1. *Power attenuation in* H_2SO_4



	λ, cm.	α, decibels cm.$^{-1}$	κ_{20}, ω^{-1} cm.$^{-1}$
Curve *a*	304	1·35	0·00866
,, *b*	198	1·64	0·00857
,, *c*	157	1·86	0·00860
,, *d*	108	2·69	0·00875

FIG. 2. *Measurement of attenuation coefficient.*



The sulphuric acid was added to the cell from a burette, the height of the liquid in the cell being calculated from the volume and the cross-sectional area. The acid in the burette was protected by phosphoric oxide guard tubes, and a stream of dry nitrogen was passed over the surface of the liquid in the cell to minimise absorption of moisture. The d.c. conductance of the acid in the cell was measured at the conclusion of the experiment.

Measurement of the Phase Constant.—The phase constant $\beta = 2\pi/\lambda_d$ was determined by measuring λ_d, the wave-length of the radiation in the dielectric. An interferometric method was employed (Fig. 3). Power from the generator was sent partly through the dielectric cell, and partly into a correctly-terminated slotted guide which was a reference source of radiation of varying phase at constant amplitude. The resultant power from the top of the dielectric cell and from a probe on a travelling detector in the slotted guide was monitored by a crystal. When the wave through the dielectric is out-of-phase with the wave from the slotted line the power registered at the crystal termination is a minimum. In operation, the depth of sulphuric acid

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* Because α is defined in terms of voltage, $E = E_0 \exp(-\alpha l)$; power is proportional to E^2 only if the impedance is constant.

in the cell was increased stepwise and the position of the travelling probe which minimised the crystal current found after each addition. The wave-length in the dielectric was given by:

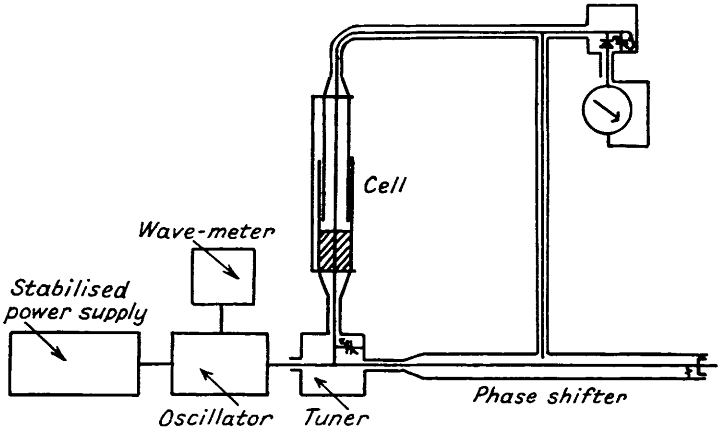
$$\frac{\lambda_d}{\lambda_0} = \frac{\beta_0}{\beta_d} = \frac{\text{Added height of dielectric column}}{\text{Probe movement along slotted line}}$$

λ_0 being the free-space wave-length (Table 1).

As in the measurement of α, the initial path of the dielectric must be sufficiently attenuative effectively to isolate the two halves of the apparatus. The sensitivity of the apparatus is optimal if the power load in the two arms is equal, so that the power received by the crystal is zero when the waves are exactly out of phase; this was achieved by adjusting the depth of the probe in the slotted guide. The telescopic cell was extended after each addition of sulphuric acid. The free-space wave-length was measured on a section of short-circuited line, very loosely coupled to the generator; tests showed no pulling of the oscillator under load.

Measurements at 1120 *and* 3000 Mc.—A reflection method was used. At the face of the dielectric sample partial reflection occurs, and interference between the incident and the reflected waves sets up a standing-wave in the line above the dielectric. An attenuator (20—50 db.) was inserted to prevent the reflected wave from reaching the oscillator. The voltage distribution along the standing-wave and the position of the voltage minima were determined by a crystal probe in a travelling detector.

FIG. 3. *Measurement of phase constant.*



The calculation of ε_1 and $\varepsilon_2^{\mathrm{T}}$ from the standing-wave pattern is straightforward if the dielectric column quantitatively absorbs the incident radiation. With sulphuric acid, which has a high loss at these frequencies, this condition is easily satisfied, and it can then be shown (Willis Jackson, *Trans. Faraday Soc.*, 1946, **42**, *A*, 91) that the voltage–standing-wave ratio, $s = V_{\mathrm{max.}}/V_{\mathrm{min.}}$, is equal to $|\varepsilon|^{\frac{1}{2}}$, where $|\varepsilon|$ is the modulus of the complex dielectric constant,

$$\varepsilon = \varepsilon_1 - i\varepsilon_2^{\mathrm{T}} = |\varepsilon| \exp(-i\delta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

s was evaluated from the probe positions at which the power level was $2V_{\mathrm{min.}}$ by the equation $s^2 = 1 + \operatorname{cosec}^2 \beta_0 x_0$, $2x_0$ being the distance between points on each side of the minimum at which $i/i_{\mathrm{min.}} = (V/V_{\mathrm{min.}})^2 = 2$ (Birks, *loc. cit.*). The phase angle δ (eqn. 4) was calculated from the distance x of the first voltage minimum from the surface of the dielectric by the expression $\delta \simeq 2 \tan^{-1} [(s - 1/s) \tan \beta_0 x]$.

Also, from eqn. (4), $\delta = \tan^{-1} (\varepsilon_2^{\mathrm{T}}/\varepsilon_1)$. Hence ε_1 and $\varepsilon_2^{\mathrm{T}}$ can be calculated from the measurements of s and x. ε_2 is obtained from $\varepsilon_2^{\mathrm{T}}$ by subtracting the electrolytic conductance, $4\pi\kappa/\omega$.

Owing to the meniscus on the liquid surface, the value of x is unsharp. x was measured from the voltage minimum to the liquid surface at a standard distance (1 mm.) from the centre conductor. Control experiments with aqueous electrolyte solutions showed that the values of $\tan \delta$ calculated from the measurement of x were uncertain to 20%. The derived results for ε_1 and ε_2 (Table 1) must be regarded as qualitative.

At 3000 Mc a standard reflex klyston was used, very loosely coupled to the wave-guide system through a coaxial cable. The coaxial wave-guide, which was silver-and-rhodium-plated, had inner and outer conductor diameters of 0·775 and 2·225 cm. and a slot length of 16 cm. The cells had the same cross-section and were of various lengths up to 10 cm. The centre conductor of the slotted line was held by a " Polythene " plug at the upper end and by the central pillar of the dielectric cell at the foot. The movement of the detector carriage was measured (to 0·002 cm.) by a micrometer dial gauge, and the free-space wave-length was observed between successive voltage minima in the slotted guide, a short-circuit termination being used. At 1120 Mc the oscillator was a 446 tube with concentric line tuning; the slotted line was the same element used in measurement of the phase constant, and the position of the detector carriage was read on a 0·1-mm. vernier scale.

Alternation Coefficient of Aqueous Sulphuric Acid at 30—100 Mc.—These measurements were undertaken to determine whether the electrolytic conductance of sulphuric acid is variable with frequency. The cells described on p. 2448 were used. At low frequencies it was advantageous to have a coaxial line connection, approx. $\lambda/4$, from the surface of the dielectric to the crystal detector; a lumped circuit sufficed for the line termination. The components of the lumped circuit were varied according to the measuring frequency. The free-space wave-length at 60—100 Mc was measured on a short-circuited line. At 30 Mc (experiments by J. HOSSACK) the wave-length was measured by a heterodyne wave-meter calibrated against a crystal oscillator. The results for the aqueous acids (96—99·5% H_2SO_4) and for a solution of potassium nitrate in sulphuric acid are in Table 3.

Conductivity Measurements and Temperature Control.—The composition of the sulphuric acid was determined by conductivity measurement. The anhydrous acids were initially 100·01—100·04% H_2SO_4; some moisture was absorbed during the dielectric measurements, corresponding to a composition change of 0·005—0·01% of H_2SO_4, but the error introduced in this way is negligible. The conductivity was measured at 20° ± 0·01° in a U-shaped cell with bright platinum electrodes, with a screened a.c. bridge (James and Knox, *Trans. Faraday Soc.*, 1950, **46**, 254) at frequencies from 1000 to 3000 c. sec.$^{-1}$. The cell was calibrated by means of Jones and Bradshaw's data for potassium chloride. The dielectric measurements were made at 20° ± 1° in a constant-temperature room.

DISCUSSION

High-frequency radiation is attenuated in sulphuric acid by two independent mechanisms, dipole reorientation and electrolytic conductance. The reorientation process is a classical model of the rotational absorption spectrum, and is necessarily accompanied by dispersion of the dielectric constant. The rotational absorption in a pure polar liquid is a weak, very broad band covering about two decades of frequency, the intensity of absorption being described by the dielectric loss factor (ε_2) which is proportional to the power attenuation per wave-length. The conductance also causes power attenuation, expressed in the same units by $\varepsilon_2^{C} = 4\pi\kappa/\omega$, and to obtain ε_2 the term ε_2^{C} must be subtracted from the total loss factor ($\varepsilon_2^{T} = \varepsilon_2 + \varepsilon_2^{C}$) measured experimentally. κ is assumed not to vary with frequency, and this assumption is discussed later.

The relation between dispersion and dipolar absorption is brought out by plotting ε_1 and ε_2 on perpendicular axes, each point referring to one frequency (Fig. 4). If there is a single relaxation time the Debye equations (2) are valid, and the theoretical locus of the points is a semicircle on the abscissa with intercepts ε_0 and ε_α; in this case the dispersion ($\varepsilon_0 - \varepsilon_\alpha$) equals twice the maximum value of ε_2. Real dielectrics are often better described by eqn. (1), which is an empirical modification of eqn. (2) and introduces a new parameter α' to define the distribution of relaxation times (Cole and Cole, *J. Chem. Phys.*, 1941, **9**, 341). Other forms of distribution function have been proposed but they are indistinguishable experimentally, particularly when the distribution of times is small (Kauzmann, *Review Mod. Phys.*, 1942, **14**, 12). With a distribution of relaxation times the (ε_1, ε_2) points fall on a circular arc with intercepts ε_0 and ε_α, the centre of the circle lying below the horizontal axis. The axis is now a chord and not a diameter of the circle and the dispersion, enclosed by the two intersections with the axis, is greater than twice the maximum value of ε_2. The results for sulphuric acid are more consistent with the Cole–Cole expression than with the Debye equation although, owing to the correction for electrolytic conductance, the experimental uncertainty is rather high. The required distribution of relaxation times is small.

The parameters α' and τ_0 are evaluated by the equation

$$(\varepsilon_1 - \varepsilon_\alpha)/\varepsilon_2 - \tan(\alpha'\pi/2) = (\lambda_m/\lambda)^{1-\alpha'};\ \lambda_m = 2\pi c\tau_0$$

obtained by rearrangement of eqn. (1). The two sides of this expression are plotted logarithmically in Fig. 5. α' determines the gradient but also contributes a small term to the ordinate, and the best value is found by trial and error; λ_m, and hence τ_0, is then found from the intercept with $\log [(\varepsilon_1 - \varepsilon_\alpha)/\varepsilon_2 - \tan (\alpha'\pi/2)] = 0$. In this calculation we have assumed $\varepsilon_\alpha = 5$, a value which seems to be typical of associated liquids, including water and the lower alcohols (Lane and Saxton, *Proc. Roy. Soc.*, 1952, *A*, **213**, 400, 473; Cole and Davidson, *J. Chem. Phys.*, 1952, **20**, 1389). The assumed value of ε_α is not critical because α' and τ_0 are mainly determined by the results at 1—3 m. where $\varepsilon_1 - \varepsilon_\alpha$ is large, but the overall uncertainty, *e.g.*, in τ_0, must be estimated at not less than 10%. α' from Fig. 5 was used to construct the arc in Fig. 4. The parameters describing the dispersion are summarised in Table 2, and the calculated values of the attenuation coefficient and phase constant are given in Table 1. Table 1 is a better test of agreement than the graphical representation in Fig. 4 because the circular arc plot, where frequency does not appear explicitly, does not show whether the (ε_1, ε_2) points are consistent with ω.

FIG. 4. *Complex dielectric constant of* H_2SO_4 (20°).

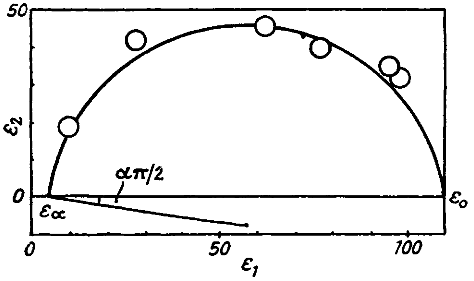


FIG. 5. *Evaluation of* α' *and* λ_m.

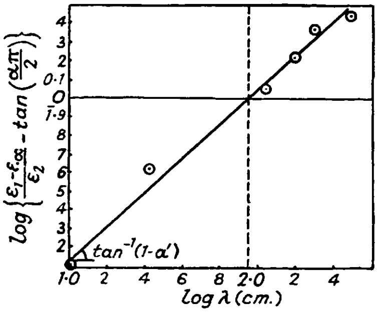


TABLE 1. *Dispersion and dielectric loss in anhydrous* H_2SO_4 (20°).

Frequency (Mc)	κ_{20} (ω^{-1} cm.$^{-1}$)	Attenuation coeff. (nepers cm.$^{-1}$) exp.	Attenuation coeff. (nepers cm.$^{-1}$) calc.	Phase constant (radians cm.$^{-1}$) exp.	Phase constant (radians cm.$^{-1}$) calc.	ε_2^T	ε_2^C	ε_2	ε_1
99·0	0·00866	0·157	0·155	0·258	0·256	190	158	32	98
151·5	0·00875	0·190	0·199	0·364	0·357	139	104	35	95
191·5	0·0095	0·240	0·240	0·428	0·432	128	88	40	77
296	0·00870	0·310	0·314	0·553	0·564	102·4	56·5	45·6	62·5
1120	—	—	—	—	—	—	—	42	28
2940	—	—	—	—	—	—	—	19	10

Columns headed " calc. " are evaluated by eqn. (1) from the parameters in Table 2.

The molecular relaxation time for a spherical molecule rotating in a medium with an " inner " viscosity η is (Debye, *loc. cit.*):

$$\tau_m = 3\pi\eta V/kT$$

η is usually identified with the macroscopic viscosity coefficient. The relation between the dielectric relaxation time (τ_0) and τ_m depends upon the assumption made for the local field in the dielectric. For the Mosotti field $\tau_m = (\varepsilon_\alpha + 2)/(\varepsilon_0 + 2)\tau_0$, while for the Onsager field $\tau_m \simeq \tau_0$ (Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486; Cole, *J. Chem. Phys.*, 1938, **6**, 385). An Onsager field being assumed, the hypothetical molecular volume, *V*, calculated from τ_0 is 29×10^{-24} ml., compared with the value from the density of 87×10^{-24} ml. With this agreement there are no grounds for suggesting that the reorientating unit is smaller than the whole molecule. The Onsager field is recognised as a poor approximation for an associated liquid like sulphuric acid, but to apply the Kirkwood theory (*J. Chem. Phys.*, 1939, **7**, 911; Oster and Kirkwood, *ibid.*, 1943, **11**, 175) it is essential to know the local liquid structure, or at least the crystal structure, and this has not been measured. It may be noted that Kirkwood's treatment does not automatically predict a high dielectric constant for an associated liquid, because the short-range forces do not necessarily favour parallel orientation of the dipoles, and in an intermediate case the theory leads to the same result as Onsager's. The small value of the distribution parameter α' might be explained by the fact that the sulphuric acid molecule is not far from spherical (a general correlation between α' and the molecular shape can be established in some systems : Hennelly, Heston, and Smyth, *J. Amer. Chem. Soc.*, 1948, **70**, 4102), but it is equally probable that the distribution of times arises from non-uniformity in the local liquid structure. If the relaxation is interpreted as a rate process (Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941) in which the rotating molecule crosses a potential barrier from one equilibrium position to another, the usual expression for the free energy of activation can be written

TABLE 2. *Dispersion and polar relaxation parameters for* H_2SO_4 (20°).

$\varepsilon_0 = 110$; $\varepsilon_a = 5$; $\tau_0 = 4{\cdot}8 \times 10^{-10}$ sec.; $\lambda_m = 90$ cm.; $\alpha' = 0{\cdot}085$

$$\tau_0 = 1/k = (\boldsymbol{h}/\boldsymbol{k}T) \exp (\Delta G_D{}^{\ddagger}/\boldsymbol{R}T)$$

Similar treatment of viscous flow leads to the relation

$$\eta = (\boldsymbol{h}/v) \exp (\Delta G_v{}^{\ddagger}/\boldsymbol{R}T) \quad (v = \text{volume per mol.})$$

and from these equations we find $\Delta G_D{}^{\ddagger} \simeq \Delta G_v{}^{\ddagger} = 4{\cdot}6$ kcal. per mole at 20°. The agreement probably has no quantitative significance but it supports other evidence for a close relation between the mechanisms of dipole reorientation and viscous flow.

Electrolytic Conductance at High Frequency.—The conductance of anhydrous sulphuric acid is due mainly to the autoprotolysis

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4{}^+ + HSO_4{}^-$$

Both the ions released by this equilibrium have abnormal mobilities (Hammett and Lowenheim, *J. Amer. Chem. Soc.*, 1934, **56**, 2620; Schwab, Zentelis, and Kassapoglou, *Chem. Ber.*, 1952, **85**, 508). Normal ion mobilities are low in sulphuric acid on account of the high viscosity (Hammett and Lowenheim, *loc. cit.*) and there is, therefore, a strong possibility of a large decrease of conductivity if the frequency of the applied field is of the same order of magnitude as the velocity of the proton-exchange process underlying the abnormal mechanism. According to Hückel (*Z. Elektrochem.*, 1928, **34**, 546) the fall occurs at a wave-length

TABLE 3. *High-frequency conductivity of aqueous sulphuric acid.*

Medium, H_2SO_4, %	Temp.	λ_0 (cm.)	κ_{20} (ω^{-1} cm.$^{-1}$)	ε_1 *	ε_2 *	Attenuation coeff. (nepers cm.$^{-1}$) exp.	calc.
99·5	21°	304	0·0343	97	28	0·359	0·355
96	21	304	0·1034	97	28	0·642	0·638
100 + KNO_3 (0·27M)	20	304	0·0662	97	28	0·500	0·495
99·5	20	504	0·0345	103	19	0·268	0·273
96	20	504	0·1031	103	19	0·485	0·486
98·7	20	887	0·0554	107	13	0·264	0·267
98·7	20	933	0·0553	107	10	0·267	0·261

$$\lambda_c = (4\pi)^2 \boldsymbol{c} a^3 \eta / \boldsymbol{k}T \quad (a = \text{ionic radius}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The average value of a for $H_3SO_4{}^+$ and $HSO_4{}^-$ being estimated at 3 Å, λ_c for sulphuric acid is approx. 7 m. A direct test of the theory is possible because the expression for λ_c does not involve an ionic concentration, and λ_c will be primarily unaffected by the addition of a solute. Table 3 contains results for the solutes water (H_3O^+, $HSO_4{}^-$) and potassium nitrate (K^+, $NO_2{}^+$, $2HSO_4{}^-$) in the frequency range 30—100 Mc. It will be seen that the electrolytic conductance of these solutions greatly exceeds the dielectrical conductance, so that any dispersion of κ with frequency will be disclosed by an almost proportionate change of the attenuation coefficient. Actually no variation is detected within the experimental limits of accuracy (1—2%).* Similar but less accurate results were obtained at 3000 Mc.

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* Values of ε_1 and ε_2 appropriate to the anhydrous acid have been used in calculations of the attenuation coefficient in Table 3 (col. 8). This is not quantitatively correct because the presence of solute will somewhat alter both these quantities (cf. Collie, Hasted, and Ritson, *loc. cit.*) but the changes are secondary compared with the effect of the increased electrolytic conductance, and they also work in opposite directions and tend to cancel.

It is noteworthy that the Hückel effect does not occur in aqueous solutions containing H_3O^+ or OH^- ions at a wave-length of 1·25 cm. although, according to eqn. (5) $\lambda_c =$ 5—8 cm. A possible explanation (Collie, Hasted, and Ritson, *J. Chem. Phys.*, 1948, **16**, 1) is that the Mosotti field assumed by Hückel should be replaced by an Onsager field, and in sulphuric acid this substitution yields $\lambda_c \simeq 25$ cm. The question of whether the effect occurs at higher frequencies is therefore still open.

A second possibility is the rise of conductivity at high frequency predicted by the Debye–Falkenhagen theory (Falkenhagen, "Electrolytes," Oxford Univ. Press, 1934). Unlike the position with the Hückel effect only a small dispersion of κ is involved and rough calculations indicate that it may be within experimental error. The onset of the dispersion occurs at a wave-length

$$\lambda_f \text{ (cm.)} = 16{\cdot}7\varepsilon_0/\gamma\Lambda_\infty$$

where γ is the electrolyte concentration (g.-equiv./l.) and Λ_∞ is the equivalent conductivity at infinite dilution; the dispersion of conductivity is spread over two decades of frequency, the limiting equivalent conductivity at high frequency being approximately midway between the stationary field value and Λ_∞. Calculations based on the measurements by Schwab and his collaborators (*loc. cit.*) yield $\lambda_f = 170$ cm. for anhydrous sulphuric acid, the total dispersion of κ, effective at 1—2-cm. wave-length, being about 1·2%. Moreover, the theoretical Debye–Falkenhagen treatment sets only an upper limit to the dispersion at the ionic strength ($I > 0{\cdot}01$) prevailing in the anhydrous acid; the real effect is probably much smaller (cf. Collie, Hasted, and Ritson, *loc. cit.*).

Electrolyte Solutions in Sulphuric Acid.—Allowance being made for the change of dielectric constant, the thermodynamic properties of electrolyte solutions appear to be essentially the same in sulphuric acid as in water. The semblance of ideality, noted by many workers, is due partly to experimental difficulties (the defects from ideality are never large) and partly to limitations imposed by the solvent, some of which are noted below.

The freezing-point depression constant has been a recurrent difficulty in the interpretation of cryoscopic measurements. A recent determination of the heat of fusion gives $k = 6{\cdot}118$ cal. mole^{-1} deg.$^{-1}$ (Rubin and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 800) and this figure is used throughout the calculations in this section. Gillespie, Hughes, and Ingold (*loc. cit.*) adopted a value of 5·98, calculated from freezing-point data for several electrolytes and non-electrolytes on the assumption that the solutes were solvated but otherwise ideal. Hammett and Deyrup (*loc. cit.*) used 6·154, from Brönsted's measurement of the heat of fusion, and earlier workers usually employed higher values, up to 7·0. Cryoscopic measurements in sulphuric acid generally refer to ionic strengths in the range 0·05—0·20, water being added initially to repress the self-ionisation equilibria of the anhydrous acid. The fact that the ionic strengths are high and the range rather limited undoubtedly fosters the impression that the activity coefficients are independent of concentration. Another levelling factor is that the anion in these solutions is necessarily always HSO_4^-.

The most accurate freezing-point data, due to Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 5271), are for solutions of water in sulphuric acid. Osmotic coefficients calculated from these results in the range of water molality 0·048—0·247 are shown in Fig. 6. The values of g refer to an unsolvated binary electrolyte, allowance being made for the removal of sulphuric acid by the reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

All the points lie higher than predicted by the limiting law, as would be expected for the ionic strengths involved; the important question is whether g is intelligible in terms of one of the extensions of the limiting law valid for aqueous solutions at comparable values of I. For the case of a single 1 : 1 electrolyte the generalised expression proposed by Guggenheim is (*Phil. Mag.*, 1935, **19**, 588)

$$g = 1 - (1/3)am^{\frac{1}{2}}\sigma(m^{\frac{1}{2}}) + \beta m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where m is the electrolyte molality and β is an empirical parameter. For sulphuric acid at 10° ($\varepsilon_0 \sim 115$) the limiting law coefficient is given by

$$(1/3)a = \left(\frac{2\pi N_0 d}{9}\right)^{\frac{1}{2}}\left(\frac{e^2}{\varepsilon_0 kT}\right)^{\frac{3}{2}} = 0{\cdot}324$$

and the limiting law is simply $g = 1 - 0{\cdot}324m^{\frac{1}{2}}$. The full line in Fig. 6 is calculated from eqn. (6) with $\beta = 0$, *i.e.*, with eqn. (6) reduced to the Güntelberg form (*Z. physikal. Chem.*, 1926, **123**, 243), and gives a fairly good representation of the experimental points. Water can therefore be regarded as a " standard " 1 : 1 electrolyte in sulphuric acid; the osmotic coefficients of the solution are quantitatively in agreement with an especially simple extension of the Debye–Hückel theory containing no adjustable parameter. There appear to be no grounds for assuming that a dilute solution of water in sulphuric acid is incompletely ionised, as claimed by Gillespie, Hughes, and Ingold.

Cryoscopic measurements with solutes other than water relate to mixed electrolyte solutions because the depressions are referred to a slightly aqueous sulphuric acid. In the case where the second solute (R_iHSO_4) is a 1 : 1 electrolyte Guggenheim's equation is

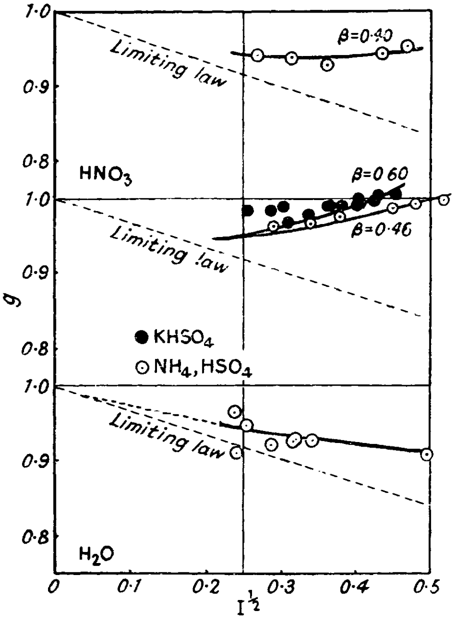

FIG. 6. *Osmotic coefficients of electrolyte solutions in sulphuric acid.*

$$g = 1 - (1/3)aI^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) + \beta_i m_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

it being remembered that β is zero for the first component, $H_3O^+ \; HSO_4^-$. In eqn. (7) m_i is the molality (as hydrogen sulphate) of the solute R_iHSO_4. Fig. 6 shows the application of eqn. (7) to the cryoscopic results for potassium sulphate, ammonium sulphate, and nitric acid obtained by Gillespie, Hughes, Ingold, and their collaborators. It may be emphasised that the results are given here in the form of *thermodynamic* osmotic coefficients, assumptions regarding solvation or incomplete ionisation being eliminated. The ionisation of nitric acid occurs according to the equation

$$NO_2{\cdot}OH + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

and m_i in eqn. (7) refers to the molality of nitronium hydrogen sulphate. Positive values of β are required to represent the behaviour of these electrolytes but the parameters are within the limits encountered in aqueous solutions. Few, if any, electrolytes in sulphuric acid yield negative values of β. Differences between the osmotic coefficients of the several electrolytes at constant ionic strengths may be due to changes in either solvation or heat of dilution. The interaction parameters, β, and the deviation of the experimental osmotic coefficients from the eqns. (6) and (7) are summarised below.

Electrolyte	H_3O,HSO_4	NO_2,HSO_4	NH_4HSO_4	$KHSO_4$
β	0·00	0·40	0·46	0·60
Standard deviation (*g*)	+0·009	0·004	0·004	0·008
No. of points	8	5	6	15

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