700. *Comparison of Some Properties of Anhydrous Sulphuric Acid and Dideuterosulphuric Acid over a Range of Temperature.*

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Anhydrous dideuterosulphuric acid has been prepared and its properties have been compared with those of sulphuric acid. Substitution of deuterium for hydrogen raises the m. p. and density of the compound, leaves the molar volume and viscosity almost unchanged, and lowers the specific electrical conductivity. The activation energies of viscous flow and electrical conduction are almost identical, and neither is affected by deuterium substitution. The conductivity decreases more than 300-fold on solidification though this factor is markedly dependent on the purity of the acid. These results are compared with those observed for deuterium substitution in other systems and the effects are discussed in terms of the proton-jump theory of electrical conduction in sulphuric acid.

Two of the most characteristic features of anhydrous sulphuric acid are its self-dissociation into ionic products [1] and its ability to conduct electricity by a proton-switch mechanism.[2] These factors combine to give sulphuric acid a higher electrical conductivity at room temperature than any other compound except nitric, phosphoric, and selenic acids and the

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[1] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

[2] Hammett and Lowenheim, *ibid.*, 1934, **56**, 2620.

hydrates of boron trifluoride. The cryoscopic and thermodynamic consequences of self-dissociation of a solvent by autoprotolysis and ionic dehydration are now well established but, despite numerous experimental and theoretical investigations, there remains some uncertainty about the factors which facilitate electrical conduction by a chain mechanism involving proton jumps. Indeed, it is still difficult to predict whether a given solvent will show abnormal conduction or not. No theory is completely successful in interpreting why the solvated hydrogen ion has an anomalous mobility in water,[3] methanol,[4,5] ethanol,[4] and anhydrous sulphuric acid [6] but not in liquid ammonia, hydrogen fluoride, or ethylene glycol, and why the anions characteristic of the solvents water, sulphuric acid, and possibly hydrogen fluoride [7] (OH^-, HSO_4^-, and F^-) have abnormally high mobilities whereas those characteristic of methanol, ethanol, and ammonia (OMe^-, OEt^-, NH_2^-) have not. Nor do the theories agree on whether the rate-determining process in water is (i) the frequency of proton jumps over a potential energy barrier, (ii) the quantum-mechanical tunnelling frequency through the barrier, (iii) the prior reorientation of the ion and solvent molecule into positions which facilitate the proton transfer, or (iv) the subsequent rotation of the molecule after proton transfer into a position favourable for the next transfer.[8,9]

Because of the difficulties involved in developing a satisfactory theory of abnormal ionic mobilities for water itself and the still more formidable problem of extending such a theory to other solvents, it seemed that further understanding of these effects might come more readily from an experimental approach which extended the number of liquids showing abnormal conduction and which investigated the effect of substituting hydrogen by deuterium in these systems. As a result of such work, phosphoric acid [10] and selenic acid can now be added to the above list of four compounds which conduct by a proton-jump mechanism, and this paper reports results of the complementary study of the influence which deuterium substitution has on the electrical and other physical properties of sulphuric acid. The measurements were made over a wide range of temperature to enable activation energies to be calculated and to determine how these energies varied with temperature. During the course of this work an independent study of some properties of dideuterosulphuric acid at its m. p. and at two other temperatures was published; [11] where the two investigations overlap there is substantial agreement on the properties of dideuterosulphuric acid.

EXPERIMENTAL AND RESULTS

Sulphuric acid was prepared and handled on the same scale as, and in apparatus identical with, that used for dideuterosulphuric acid. This had the double advantage of (i) proving the reliability of the experimental techniques by reproducing the most accurate published data on sulphuric acid, and (ii) increasing the precision of comparison of the two compounds by eliminating the effect of slight errors in the absolute values of calibration constants.

The anhydrous acids were prepared on a 30 g. scale in a vacuum line by transferring the stoicheiometric amount of water or heavy water on to a known weight of sulphur trioxide which had previously been purified by repeated distillation *in vacuo*.[12] One batch of sulphuric acid was also prepared by titrating "AnalaR" sulphuric acid with dilute oleum until a minimum in conductivity was obtained. The results on the two samples were the same to within experimental error.

Electrical conductivity was measured after the acids had been subjected to final purification by repeated fractional freezing under vacuum in an all-glass apparatus attached directly to

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[3] Danneel, *Z. Elektrochem.*, 1905, **11**, 249.

[4] Uhlich, *Trans. Faraday Soc.*, 1927, **23**, 288; Walden, *Z. phys. Chem.*, Bodenstein Festband, **1931**, 19.

[5] Hartley and Raikes, *Trans. Faraday Soc.*, 1927, **23**, 393.

[6] Gillespie and Wasif, *J.*, 1953, 209.

[7] Kilpatrick and Lewis, *J. Amer. Chem. Soc.*, 1956, **78**, 5186.

[8] Conway, Bockris, and Linton, *J. Chem. Phys.*, 1956, **24**, 835, and refs. therein.

[9] Eigen and de Maeyer, *Proc. Roy. Soc.*, 1958, **247**, *A*, 505.

[10] Greenwood and Thompson, following paper.

[11] Flowers, Gillespie, Oubridge, and Solomons, *J.*, 1958, 667.

[12] Greenwood and Thompson, " Inorganic Syntheses," Vol. VI, in the press.

the conductivity cell. In this process the acid was reduced to about one-tenth of its original volume. Two independent concordant sets of results were obtained on using cells with bright platinum electrodes. The cell constants were 85·33 cm.$^{-1}$ and 48·15 cm.$^{-1}$. The cell resistances, which were of the order of 10^3—10^4 ohm, were measured with a precision of about 1 part in 3000 on an earthed A.C. network at 1000 cycles/sec.[13] Variation of frequency from 500 to 3000 cycles/sec. left the resistance unchanged and results were reproducible during several thermal cycles up to 70°.

Viscosity was measured in a sealed glass viscometer which used the Wier principle to maintain a constant mean head of liquid over a range of temperature.[14] It was calibrated with aniline and 60% aqueous sucrose solution by means of an intermediate viscometer, and the kinematic viscosity (ν cs) was found to be related to the outflow time (t sec.) by the equation $\nu = \eta d^{-1} = 0{\cdot}0840t - 6{\cdot}56t^{-1}$. Here η (cP) is the dynamic viscosity and d (g.ml.$^{-1}$) the density. Because of the difficulties inherent in the measurement of the absolute viscosity of highly viscous liquids it would be rash to claim more than 1% for the absolute accuracy of these measurements but the relative viscosity of the two compounds and their comparative values at different temperatures are precise to 2 parts per thousand.

Density, which was corrected for buoyancy of the air, was measured in a Pyrex-glass dilatometer having a volume of 11·7 ml. and a capillary radius of 1 mm. Temperatures were measured on N.P.L. calibrated mercury-in-glass thermometers; the accuracy on an absolute scale was ±0·02° and the precision with which a given temperature could be reproduced was ±0·005°.

Results.—The m. p. of our anhydrous sulphuric acid was 10·35° ± 0·02°, close to the accepted value of 10·371°.[15] The highest m. p. observed for dideuterosulphuric acid was 14·10°, but an extrapolation of the values obtained as a function of the number of fractional crystallisations indicates a limiting value somewhere between 14·3° and 14·4°, in agreement with the recently published value of 14·35° ± 0·02° which was obtained in experiments using a larger initial volume of acid.[11]

The density ($d_4{}^t$), dynamic viscosity (η), and specific conductivity (κ) of the two acids were determined at 5° intervals from 10° to 60° and typical results are summarized in Table 1. The conductivity was also measured at 7·5° and 70° but viscosities at these temperatures (in parentheses) were found by extrapolation

Values of the molar conductivity ($\mu = \kappa V_{\mathrm{M}}$) and reduced conductivity ($\mu\eta$) given in the last four columns of Table 1 will be mentioned in the Discussion.

Density varied linearly with temperature (t°):

$$\mathrm{H_2SO_4}:\ d_4{}^t = 1{\cdot}8516 - 1{\cdot}000 \times 10^{-3}t;\quad \mathrm{D_2SO_4}:\ d_4{}^t = 1{\cdot}8816 - 0{\cdot}980 \times 10^{-3}t$$

TABLE 1. *Density, viscosity, and conductivity between* 7·5° *and* 70°.

Temp.	$d_4{}^t$ (g. cm.$^{-3}$)		η (cP)		$10^2\kappa$ (ohm^{-1} cm.$^{-1}$)		μ (ohm^{-1} cm.^{2} mole^{-1})		$\mu\eta$ (ohm^{-1} cm.^{2} cP mole^{-1})	
	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4
7·5°	1·8441	1·8743	(50·1)	(51·5)	0·5166	0·1440	0·2746	0·0738	(13·76)	(3·80)
10·0	1·8416	1·8718	44·88	45·65	0·5769	0·1598	0·3071	0·0854	13·78	3·90
15·0	1·8359	1·8670	36·07	37·79	0·7110	0·1948	0·3795	0·1046	13·70	3·84
20·0	1·8318	1·8620	29·56	30·08	0·8671	0·2351	0·4641	0·1263	13·72	3·80
25·0	1·8267	1·8572	24·55	24·88	1·044	0·2832	0·5602	0·1524	13·74	3·79
30·0	1·8212	1·8522	20·62	20·74	1·242	0·3356	0·6681	0·1812	13·77	3·76
35·0	1·8162	1·8473	17·24	17·44	1·465	0·3963	0·7903	0·2146	13·63	3·74
40·0	1·8117	1·8422	14·67	14·87	1·712	0·4637	0·9260	0·2517	13·59	3·75
45·0	1·8066	1·8373	12·62	12·81	1·985	0·5425	1·072	0·2952	13·54	3·78
50·0	1·8017	1·8324	10·93	11·12	2·279	0·6243	1·239	0·3407	13·56	3·79
60·0	1·7921	1·8228	8·50	8·55	2·929	0·8079	1·602	0·4433	13·61	3·79
70·0	1·7816	1·8134	(6·78)	(6·79)	3·683	1·0280	2·025	0·5558	(13·70)	(3·78)

The usual activation energy plots of log κ, log μ, and log η *versus* $1/T$ (°K) were curved, but when $1/T^2$ was used as abscissa the plots were linear, indicating that the data can be represented by equations of the form:

$$\kappa = \kappa_0 \exp\left(-C_\kappa/\boldsymbol{R}T^2\right);\ \mu = \mu_0 \exp\left(-C_\mu/\boldsymbol{R}T^2\right);\ \eta = \eta_0 \exp\left(C_\eta/\boldsymbol{R}T^2\right)$$

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[13] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

[14] Greenwood and Wade, *ibid.*, p. 349; *J. Sci. Instr.*, 1957, **34**, 288.

[15] Gable, Betz, and Maron, *J. Amer. Chem. Soc.*, 1950, **72**, 1445; Kunzler and Giauque, *ibid.*, 1952, **74**, 5271.

The validity of these equations is illustrated in Fig. 1, the values of the constants being summarized in Table 2. The most striking feature of these results is the great similarity in the 6 values of the exponential constant C. It will be shown later that this implies a similarity in the activation energies of the various processes occurring.

The conductivity of solid sulphuric acid was less than that of the supercooled liquid by a factor which depended on the purity of the acid and on the temperature of comparison. Fig. 2 illustrates that, whilst small amounts of water have comparatively little effect on the conductivity of the liquid, they increase the conductivity of the solid by nearly two orders of magnitude at 7°. Hence, at this temperature, the ratio of the conductivity of the supercooled liquid to that of the solid, which was 310 for the pure acid, decreased to 116, 82, 39, 10, and 6·6 for the five concentrations of water indicated in Fig. 2. At 10° the conductivity of the liquid was 68·3 times that of the solid but this factor dropped to 3·5 for acid containing 36 millimoles of water per kg. of solution. (Concentrations of water were estimated by measuring the specific conductivity at 25·0° and then interpolating from recent precise data relating the conductivity to water content.[16]) The curves for solid sulphuric acid showed a premelting increase in conductivity very similar to that observed for ice,[17] and at 10° (0·35° below the m. p.) there was also a slow drift to higher conductivities, the equilibrium value being approached after about 1 hr. During this process there was no visible sign of melting. Below 7° the curves became almost linear; the slope was virtually independent of water content and corresponded to an exponential constant $C_\kappa \sim 2910$ kcal. deg. mole.$^{-1}$ (cf. liquid: $C_\kappa = 927$ kcal. deg. mole.$^{-1}$; ratio 3·14).

FIG. 1. *Conductivity and fluidity of* H_2SO_4 *and* D_2SO_4.

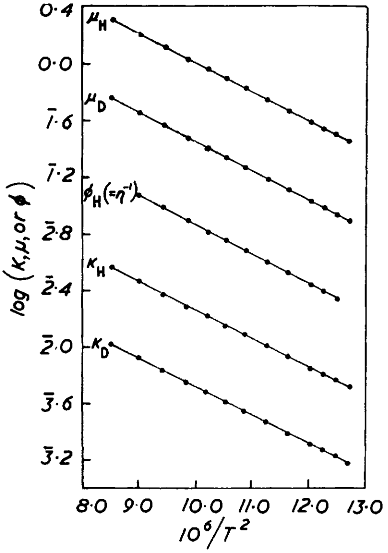
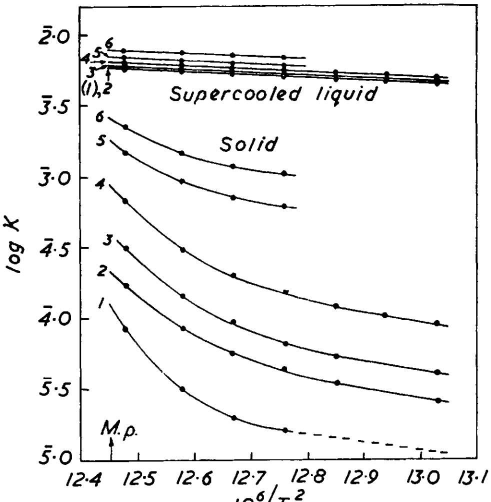


FIG. 2. *Conductivity of solid and supercooled sulphuric acid between 3° and 10° as a function of concentration.*



1, Anhydrous H_2SO_4; 2, 8 mmoles of H_2O per kg. of soln.; 3, 13 mmoles of H_2O per kg. of soln.; 4, 20 mmoles of H_2O per kg. of soln.; 5, 26 mmoles of H_2O per kg. of soln.; 6, 36 mmoles of H_2O per kg. of soln.

TABLE 2. *Conductivity and viscosity constants.*

Constant	H_2SO_4	D_2SO_4	Constant	H_2SO_4	D_2SO_4
κ_0 (ohm^{-1} cm.$^{-1}$)	1·990	0·543	C_κ (kcal. deg. mole^{-1})	927	928
μ_0 (ohm^{-1} cm.^{2} mole^{-1})	121·5	32·75	C_μ (kcal. deg. mole^{-1})	950	950
η_0 (cP)	0·1066	0·1068	C_η (kcal. deg. mole^{-1})	960	963 *

* Varies from 990 at 10° to 937 at 60°.

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[16] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.

[17] Bradley, *Trans. Faraday Soc.*, 1957, **53**, 687.

DISCUSSION

Three general aspects of the results arise for discussion: (i) The absolute values of the density, viscosity, and conductivity of sulphuric acid, and a comparison of these with values in the literature. (ii) The influence of deuterium substitution on the properties of sulphuric acid as compared with the effect of isotopic substitution in other systems. (iii) The temperature variation of viscosity and conductivity and the interpretation of the activation energies of viscous flow and electrical conduction. These points are best considered by discussing the density, viscosity, and conductivity separately [sections (i), (ii), (iii)]. The results are relevant to theories on the mechanism of electrical conduction in sulphuric acid [section (iv)] and, in particular, the proton-jump theory is examined. Implications of the conductivity of solid sulphuric acid [section (v)] are also discussed.

(i) *Density*.—The industrial and economic importance of sulphuric acid ensured the early determination of accurate values for the density as a function of temperature and composition. Nearly a century ago Marignac [18] represented the density of the anhydrous acid as $d_4^t = 1{\cdot}85289 - 0{\cdot}0010654t + 0{\cdot}000001321t^2$; this differs from our values by 7 parts in 10^4 at 0° and by only 2 parts in 10^4 at 25°. Little point would be served in enumerating the many intervening concordant determinations but a recent precise value [19] of $d_4^{25} = 1{\cdot}8269$ can be mentioned to illustrate the agreement with our value of $d_4^{25} = 1{\cdot}8267$. The density of dideuterosulphuric acid ($d_4^{25} = 1{\cdot}8572$) is 1·64% greater, and agrees closely with the only published value [11] for this compound, $d_4^{25} = 1{\cdot}8573$. The equations on p. 3476 can therefore be taken to represent the density accurately between 0° and 70°.

Of more interest is the molar volume. Deuterium substitution almost invariably increases the molar volume of a liquid, the only two exceptions being the special case of deuterium itself, whose molar volume at −253° is 12·9% less than that of liquid hydrogen because of a zero-point energy effect,[20] and hexadeuterobenzene where the change in molar volume compared with benzene at 25° is −0·21%.[21] For all other isotopic pairs of liquids investigated deuterium substitution causes only a very slight increase in molar volume. At 25° the molar volumes of the two sulphuric acids are $53{\cdot}69_0$ and $53{\cdot}89_2$ ml. mole^{-1}, the increase being $0{\cdot}20_2$ ml. (0·38%). This is unexpectedly large, since the deuterium atom is the same size as the hydrogen atom and, in the gas phase, bond distances involving the two isotopes are virtually identical. Differences in the molar volumes of isotopic pairs of liquids must therefore be ascribed primarily to differences in intermolecular forces rather than to differences in molecular size. For non-hydrogen-bonded liquids at 20° the increase in molar volume of a deutero-compound compared with its hydrogen analogue seems to be less than 0·1%; *e.g.*, tetradeuterothiophen, C_4D_4S, 0·0%,[22] deuterochloroform, $CDCl_3$, 0·07%,[23] boron trifluoride dideuterate, $D_3O[BF_3{\cdot}OD]$, 0·08%,[24] boron trifluoride monodeuterate, $D[BF_3{\cdot}OD]$, 0·1%,[25] tetrachlorodideuteroethane, $(CDCl_2)_2$, 0·1%.[26] On the other hand, when strong hydrogen bonding contributes to the liquid structure the increase in molar volume attending deuteration is significantly larger. Deuterium peroxide, D_2O_2, appears to be an intermediate case (increase at 20°, 0·13% [27]), but for heavy water the increase at 25° is 0·38%,[28] which is similar to the value found for dideuterosulphuric acid

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[18] Landolt–Börnstein, " Physikalisch-Chemische Tabellen," 5th Edn., 1923, p. 307.

[19] Gillespie and Wasif, *J.*, 1953, 215.

[20] Itterbeck and Paemel, *Physica*, 1941, **8**, 133.

[21] Ingold, Raisin, Wilson, Bailey, and Topley, *J.*, 1936, 915; see also Klit and Langseth, *Z. phys. Chem.*, 1936, *A*, **176**, 65 (−0·22% at 20°); Bowman, Benedict, and Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 960 (−0·07% at 25°); Erlenmeyer, Lobeck, Gartner, and Epprech, *Helv. Chim. Acta*, 1936, **19**, 336 (−0·04% at 20°).

[22] Steinkopf and Böetius, *Annalen*, 1941, **546**, 208.

[23] Breuer, *J. Amer. Chem. Soc.*, 1935, **57**, 2236.

[24] Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **5**, 229.

[25] *Idem, ibid.*, p. 224.

[26] Breuer, *J. Amer. Chem. Soc.*, 1936, **58**, 1289.

[27] Phibbs and Giguère, *Canad. J. Chem.*, 1951, **29**, 173.

[28] Stokland, Ronaess, and Tronstad, *Trans. Faraday Soc.*, 1939, **35**, 312; Wirtz, *Phys. Z.*, 1942, **43**, 465.

at the same temperature (0·38%), and for trideuterophosphoric acid, D_3PO_4, the molar volume is 0·93% higher than for normal phosphoric acid.[9] It is tempting to conclude that the deuterium bridge is longer than the hydrogen bridge in these liquids.[29] Moreover, since the temperature coefficient of the density of dideuterosulphuric acid is less than that of sulphuric acid, the disparity in molar volume decreases with rise in temperature and is only 0·24% at 70°. A similar decrease is observed with water and implies that the degree of hydrogen bonding diminishes as the temperature rises. This is consistent with the concurrent decrease in activation energy of viscous flow to be discussed in the next section.

(ii) *Viscosity.*—The viscosity of anhydrous sulphuric acid at 25° has only recently been determined accurately and no reliable data exist on the variation of viscosity with temperature. The following values appear in the literature for η_{25} though not all refer to precisely 100·0% acid: 19·15,[30] 19·85,[31] 23·5,[32] 23·57,[33] 24·0,[34] 24·19,[35] 24·20,[36] 24·68,[37] 24·77,[38] and 25·33.[39] To these have recently been added two others, 24·53 [40] and 24·54,[19] in excellent agreement with our value of 24·55 CP, and it is recommended that this be accepted as the viscosity of anhydrous sulphuric acid at 25°. The literature is equally confused about values at other temperatures. This is illustrated in Table 3 which summarizes values at even temperatures between 10° and 60° and, as values at other temperatures show a similar spread, no reliable deductions could previously be made about the detailed dependence of viscosity on temperature. The present measurements resolve this difficulty and give a consistent set of values over a range of 50°. The viscosity of dideuterosulphuric acid, which had not previously been recorded, was measured over the same temperature range.

TABLE 3. *Viscosity (in* CP) *of sulphuric acid at selected temperatures.*

Temp.	This work	Lutschinski [a]	Other values
10·0°	44·88	—	35·17 [b]
20·0	29·56	25·4	21·93,[c] 24·22,[b] 28·21,[d] 28·40 [d]
30·0	20·62	15·68	19·69,[d] 19·84,[d] 21·34 [e]
40·0	14·67	11·45	13·07,[b] 14·80 [f]
50·0	10·93	8·82	10·55,[g] 10·6,[h] 10·69,[d] 10·78,[d] 10·80 [i]
60·0	8·50	7·22	8·32,[j] 8·78 [k]

[a] Ref. 31. [b] Bingham and Stone, *J. Phys. Chem.*, 1923, **27**, 701. [c] Graham, *Phil. Trans.*, 1861, **151***A*, 373. [d] Schwab and Kolb, *Z. phys. Chem.* (*Frankfurt*), 1955, **3**, 52. [e] Pound, *J.*, 1911, **99**, 708. [f] Tutunzic and Liler, *Bull. Soc. chim. Belgrade*, 1953, **18**, 521. [g] Ref. 34. [h] Ref. **32**. [i] Ref. 36. [j] Ref. 37. [k] Ref. 38.

The viscosity of sulphuric acid as a function of temperature can be represented accurately by the expression $\eta = \eta_0 \exp (C_\eta/\boldsymbol{R}T^2)$. This implies that the activation energy E_η varies inversely as the absolute temperature because

$$\log \eta = \log \eta_0 + \frac{C_\eta}{2{\cdot}303\boldsymbol{R}}\left(\frac{1}{T}\right)^2$$

hence

$$\frac{\mathrm{d}\,(\log \eta)}{\mathrm{d}\,(1/T)} = \frac{2C_\eta}{2{\cdot}303\boldsymbol{R}}\cdot\frac{1}{T} = \frac{E_\eta}{2{\cdot}303\boldsymbol{R}}$$

Further, $\dfrac{\mathrm{d}\,(\log \eta)}{\mathrm{d}\,(1/T^2)} = \dfrac{C_\eta}{2{\cdot}303\boldsymbol{R}}$, so that $E_\eta = 2C_\eta/T$.

[29] Wirtz, *Z. Elektrochem.*, 1958, **62**, 389.
[30] Bergius, *Z. phys. Chem.*, 1910, **72**, 338.
[31] Lutschinski, *ibid.*, 1934, *A*, **169**, 269.
[32] Dunstan, *Proc. Chem. Soc.*, 1914, **30**, 104.
[33] Schwab, *Chem. Ber.*, 1957, **90**, 221.
[34] Rhodes and Hodge, *Ind. Eng. Chem.*, 1929, **21**, 142.
[35] Tutunzic, Liler, and Kosanovic, *Bull. Soc. chim. Belgrade*, 1955, **20**, 363.
[36] Rhodes and Barbour, *Ind. Eng. Chem.*, 1923, **15**, 850.
[37] Dunstan and Wilson, *J.*, 1907, **91**, 85, as corrected in ref. 32.
[38] Bright, Hutchison, and Smith, *J. Soc. Chem. Ind.*, 1946, **65**, 385.
[39] Brun, *Univ. i Bergen Årbok*, 1952, *Naturvitenskap. Rekke* No. 12, 1953, 1.
[40] Hetherington, Nichols, and Robinson, *J.*, 1955, 3141.

The activation energy at any temperature is therefore best computed by first plotting log η as a function of $1/T^2$ (Fig. 1) to obtain C_η (Table 2), and then applying the relation $E_\eta = 2C_\eta/T$, rather than by plotting log η against $1/T$ and drawing a tangent to the curve at the required temperature. Activation energies calculated in this way for three temperatures are listed in the last two columns of Table 4 which show clearly the decrease in energy as the temperature rises. Normally the process which requires the smaller activation energy predominates at lower temperatures and the opposite trend for the activation energy of viscous flow in sulphuric acid implies some structural change in the liquid (such as the progressive breaking of hydrogen bonds) which increasingly facilitates the flow of the liquid as the temperature is raised. A similar effect is well known for water, although for that liquid log η is a linear function of $1/T^2$ only above 20°, the slope at lower temperatures increasing by about 7%.

TABLE 4. *Activation energies for viscous flow and electrical conduction.*

	E_κ (kcal. mole^{-1})		E_μ (kcal. mole^{-1})		E_η (kcal. mole^{-1})	
Temp.	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4	H_2SO_4	D_2SO_4
10°	6·55	6·55	6·71	6·71	6·78	6·99
25	6·22	6·22	6·37	6·37	6·44	6·64
60	5·56	5·57	5·70	5·70	5·76	5·62

If the decrease in the activation energy of viscous flow arises from a gradual reduction in the extent of hydrogen bonding, then the average size of the flow units involved in the transfer of momentum from one shear layer to the next will progressively diminish. This should be paralleled by a decrease in the value of Batschinski's constant B, since the magnitude of this constant (which is obtained from the relation $v = b + B\phi$ between specific volume, v, and fluidity, ϕ) is roughly proportional to the size of the kinetic units of flow in a liquid.[24] Such a decrease is, in fact, observed, the value of B falling from 0·28 cP ml. g.$^{-1}$ at 10° to 0·21 at 25° and 0·11 at 60°. The values for dideuterosulphuric acid are slightly smaller, being 0·26, 0·19, and 0·10 cP ml. g.$^{-1}$ at the same temperatures. On the assumption of direct proportionality between Batschinski's constant and the size of flow units, the figures suggest that the size of these structural units in sulphuric acid is halved when the temperature is raised from 25° to 60°.

The kinematic viscosity (ν) of the two compounds is the same to within experimental error, so that the difference in dynamic viscosity ($\eta = \nu d$) is due solely to the difference in density of the two liquids. At 25° the ratio of the dynamic viscosity of dideuterosulphuric acid to that of sulphuric acid itself is 1·014, which is a smaller ratio than for any other of the eight isotopic pairs of liquids yet investigated.[24,9,41] Again, deuterium substitution invariably increases the activation energy of viscous flow.[24,9,41] Whilst Table 4 indicates that this is also true for the present compounds, at least at the lower temperatures, the increase is probably not far outside experimental error, since the exponential constants C_η given in Table 2 differ by only 0·3%. Indeed, the main effect of deuteration seems to be the introduction of a slight non-linearity in the relation between log η and $1/T^2$.

(iii) *Conductivity.*—There is now general agreement that the conductivity of anhydrous sulphuric acid at 25° is $1{\cdot}044 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ as found in this work. The most precise figure in the literature [16] is $1{\cdot}0439 \pm 0{\cdot}0005 \times 10^{-2}$, which is identical with our value, and other recent determinations give $1{\cdot}045 \times 10^{-2}$ [42,43] and $1{\cdot}046 \times 10^{-2}$.[39] This variation may well represent a difference in calibration of temperature scales in the various laboratories since Table 1 indicates that $0{\cdot}001 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ is equivalent to a temperature change of 0·002°. The older literature on the conductivity of sulphuric acid at 25° has been reviewed several times [16,39,43,44] and requires no further comment. Less is known, however,

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[41] Greenwood and Thompson, *J.*, 1959, 3493.
[42] Trenner and Taylor, *J. Phys. Chem.*, 1931, **35**, 1336.
[43] Hetherington, Hub, Nichols, and Robinson, *J.*, 1955, 3300.
[44] Gillespie and Wasif, *J.*, 1953, 204.

about the temperature variation of the conductivity, the only measurements on reliable acid at temperatures other than 25° being at 9·66° and 40° where the values were $0{\cdot}570 \times 10^{-2}$ and $1{\cdot}711 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$, respectively, compared with our values of $0{\cdot}569 \times 10^{-2}$ and $1{\cdot}712 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ at the same temperatures.

Only one report of the conductivity of dideuterosulphuric acid has been published,[11] the values of $10^2\kappa$ (ohm^{-1} cm.$^{-1}$) at 10°, 25°, and 40° (compared with our values in parentheses) being 0·133 (0·1598), 0·2568 (0·2832), and 0·446 (0·4637). This suggests [11] that the dideuterosulphuric acid used in the present work contained 0·09 mole % excess of heavy water. Both sets of figures agree, however, that substitution of deuterium for hydrogen results in a substantial reduction in the electrical conductivity of sulphuric acid. Furthermore, the discrepancy in absolute values is unlikely to affect values of the temperature coefficient significantly, since Fig. 2 shows that the presence of even 0·36 mole % of water in sulphuric acid (curve 6) has but slight effect on the slope of the curve.

Treatment of the conductivity data in Table 1 by the methods used for viscosity in the preceding section leads to the conclusion that the activation energy for conduction in both acids varies inversely as the absolute temperature, *i.e.*, $E_\kappa = 2C_\kappa/T$. Values for these activation energies, and for the activation energy of molar conduction ($\mu = \kappa V_{\text{M}}$), are given in Table 4. The similarity at each temperature between values of E_μ and E_η for both compounds is particularly noteworthy. Usually,[45] such similarity is taken to imply that ionic migration is viscosity-controlled, the mobility of the ions being inversely proportional to viscosity as required by Stokes's law. Such an interpretation is at variance with the known mechanism of conduction in sulphuric acid which takes place predominantly by proton jumps rather than by normal ionic migration.[2,6,46] This problem is considered further in the next section.

(iv) *Mechanism of Electrical Conduction.*—In general, the magnitude of the electrical conductivity of an ionizing protonic solvent depends both on the extent of self-dissociation and on the mobility of the ions so formed. The mobility has two components, the normal Kohlrausch migration velocity and an excess of mobility due to a proton-jump mechanism. Increase in temperature alters the concentration of ions and also their mobility (by altering the viscosity and the extent of hydrogen bonding). Similarly, substitution of hydrogen by deuterium can affect the extent of self-dissociation as well as the viscosity and the extent and strength of hydrogen bonding. It is remarkable, therefore, that the activation energy of conduction in sulphuric acid (which reflects changes both in the number and in the mobility of the ions) should so exactly parallel the activation energy of viscous flow. It is still more remarkable that deuterium substitution, which lowers both the concentration of ions and their mobility, should also leave the activation energies unchanged. Various interpretations of these observations can be considered by examining in detail the factors contributing to the conductivity. If n_+ and n_- are the number of cations and anions per ml. formed by autoprotolysis ($2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$), and v_+ and v_- are the mobilities of these ions, then

$$\kappa = n_+ev_+ + n_-ev_- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the pure, anhydrous acid $n_+ = n_-$ ($=n$, say) and, since the minimum in the conductivity–composition plot occurs almost exactly at the stoicheiometric ratio H_2O,SO_3,[16,47] it follows that the mobilities of the two ions are very similar (*i.e.*, $v_+ = v_- = v$, say). Hence $\kappa = 2nev$. Further, $n = \sqrt{K_{\text{ap}}}$, where the autoprotolysis constant $K_{\text{ap}} = [H_3SO_4^+][HSO_4^-]$, so that

$$\kappa = 2ev\sqrt{K_{\text{ap}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[45] Greenwood and Martin, *J.*, 1953, 1427.
[46] Gillespie and Wasif, *J.*, 1953, 221.
[47] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 804.

By taking logarithms and differentiating with respect to $1/T$, one arrives at the relation

$$E_\kappa = \tfrac{1}{2}\Delta H_{ap} + E_v \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where E_κ is the activation energy for conduction, E_v is the activation energy for ionic migration, and ΔH_{ap} is the heat of autoprotolysis.

The following three interpretations of the similarities in the activation energies shown in Table 4 can be considered. (*a*) Sulphuric acid is completely dissociated into ions so that, by eqn. (1), changes in conductivity are due entirely to changes in ionic mobility. It follows that E_κ must equal E_v and, since E_κ is very similar to E_η, the activation energies of viscosity and ionic migration must also be almost equal. This implies that mobility is inversely proportional to viscosity (Walden's rule) and suggests normal ionic migration. Under such conditions the mobility of an ion is relatively insensitive to its mass (cf. the small range of ionic mobilities in water) and substitution of hydrogen by deuterium would leave the mobility and the activation energy of migration substantially unchanged, as observed. Furthermore, since the molar volume of sulphuric acid at 25° is 53·7 cm.^{3}, the calculated number of ions per cm.^{3} for complete dissociation is $1{\cdot}12 \times 10^{22}$; substitution of this figure, together with the value for the conductivity ($\kappa = 1{\cdot}044 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$) and the value of $\boldsymbol{e}$ ($1{\cdot}59 \times 10^{-19}$ coulomb), in equation (1) leads to an ionic mobility of $5{\cdot}84 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. This is of the same order of magnitude as the experimentally determined mobility of the hydrogen sulphate ion:[46] $\sim 150/\boldsymbol{F} = 15{\cdot}6 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. However, this interpretation cannot be accepted as it is completely at variance with the cryoscopically determined degree of ionic dissociation [48] which gives $K_{ap} = 1{\cdot}7 \times 10^{-4}$ g.-ion^2 kg.$^{-1}$ and $[HSO_4^-] = 0{\cdot}013$ molal, *i.e.*, $8{\cdot}0 \times 10^{19}$ ions/cm.^{3} at 10·4°.

(*b*) An alternative interpretation is that, though sulphuric acid is incompletely dissociated, the degree of dissociation remains almost constant, so that changes in ionic concentration are, as before, much smaller than changes in mobility. This implies that ΔH_{ap} is small and, by eqn. (3), E_κ is approximately equal to E_v. Since, experimentally, $E_\kappa \simeq E_\eta$, it follows that the activation energies of viscosity and ionic migration are similar and that mobility is inversely proportional to viscosity, etc., as in (*a*). However, this hypothesis is also untenable because the autoprotolysis constant has been shown [49] to increase from $1{\cdot}7 \times 10^{-4}$ at 10·4° to $2{\cdot}9 \times 10^{-4}$ at 25°. From the relation $\Delta H_{ap} = 2{\cdot}303\,\boldsymbol{R}\,\mathrm{d}(\log K_{ap})/\mathrm{d}(1/T)$, the heat of autoprotolysis can be calculated to be 6·1 kcal. mole^{-1}.* This is not negligible. A further argument against the implication that the mobilities of the $H_3SO_4^+$ and HSO_4^- ions are viscosity-controlled is that these ions have mobilities some 50 times greater than those of other ions in the system; that is, their mobility is far greater than would be expected in a solvent of such high viscosity. Thus, at 25° the mobility of the sulphate ion in water ($\eta = 0{\cdot}894$ cP) is $8{\cdot}26 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1} which, when corrected for the viscosity of sulphuric acid ($\eta = 24{\cdot}55$ cP), gives a calculated mobility of $0{\cdot}30 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. This is 52 times smaller than the observed mobility of the hydrogen sulphate ion in sulphuric acid ($15{\cdot}6 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}). It therefore appears that normal ionic migration constitutes but a small fraction of the total mobility and that the second component, the proton-switch contribution, is predominant. This is confirmed by transport measurements.[2,6]

(*c*) One is forced to conclude that the similarity in the activation energies of conduction and viscosity is fortuitous and that there is no necessary correlation in a proton-switch solvent between the activation energies of viscosity and ionic migration. This conclusion

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* This was erroneously given as 2·0 kcal. mole^{-1} in ref. 49. A more recent, unpublished estimate by Dr. Gillespie gives K_{ap} (25°) $= 2{\cdot}4 \times 10^{-4}$ and $\Delta H_{ap} = 3{\cdot}8$ kcal. mole^{-1}. These variations serve to illustrate the difficulty of fixing the heat of dissociation precisely but do not affect the main line of reasoning given above.

[48] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473; Gillespie, *J.*, 1950, 2516.

[49] Gillespie and Wasif, *J.*, 1953, 964.

is reinforced by the empirical observation [46] that, for a series of twelve electrolytes in sulphuric acid, there was a wide scatter of the curves when conductivity κ was plotted against concentration up to 1·5N, but that all the electrolytes fell on a common curve when the function $\kappa\eta^{\frac{1}{2}}$ was plotted against the concentration. As the concentration of ions formed by autoprotolysis of the solvent is only about 0·03N, virtually all the ions in the solution are due to the added electrolyte so that, at a given ionic concentration (n), variation in conductivity (eqn. 1) arises solely from variation in ionic mobility. It follows that in these solutions, mobility is inversely proportional to $\sqrt{\eta}$. This observation receives immediate interpretation on the present analysis for $E_\kappa = \frac{1}{2}\Delta H_{\text{ap}} + E_v$ by eqn. (3); from Table 4, E_κ is seen to have a mean value of 6·4 kcal. mole^{-1} in the range 10—25° and ΔH_{ap} was shown above to be 6·1 kcal. mole^{-1}. Hence E_v is calculated to be $3{\cdot}3_5$ kcal. mole^{-1}. From Table 4, the mean value of E_η is 6·6 kcal. mole^{-1}; thus $E_v = \frac{1}{2}E_\eta$. When the number of ions, n, is constant, then $\kappa = \kappa_0 \exp\,[-E_v/\boldsymbol{RT}]$ and $\eta = \eta_0 \exp\,[E_\eta/\boldsymbol{RT}]$. For the function $\kappa\eta^{\frac{1}{2}}$ to be constant, it is therefore necessary for $\kappa_0\eta_0^{\frac{1}{2}} \exp\,[(\frac{1}{2}E_\eta - E_v)/\boldsymbol{RT}]$ to be constant; *i.e.*, E_v must equal $\frac{1}{2}E_\eta$. This is the ratio just deduced. It is clear that no theoretical significance should be attached to the numerical value of the exponent $\frac{1}{2}$, as its value depends fortuitously on the values of E_κ, ΔH_{ap}, and E_η.† In particular, the semblance of a relation between viscosity and mobility should not be taken to imply a causal dependence of mobility on viscosity or to support [46] the assumption that molecular rotation rather than proton transfer is the rate-determining process in the switch mechanism. More positive evidence for this contention comes from a comparison of activation energies of conduction for sulphuric and dideuterosulphuric acids, since it is hard to imagine that the activation energy of the actual jump process would remain unaffected by substitution of the proton by a deuteron. The mechanism envisaged is a slow, rate-determining orientation of the ions and solvent molecules into positions favourable for proton jumps to occur, followed by rapid and recurring jumps in both directions across the hydrogen bridge once it is established.

(v) *Conductivity of Solid Sulphuric Acid.*—The conductivity of crystalline sulphuric acid is at least two powers of ten lower than that of the melt. The same difficulty arises here as was encountered in the preceding section in trying to apportion this decrease in conductivity between changes in the number and mobility of the ionic species present. In the case of water, it seems to be now well established [9, 51] that the slight drop in conductivity on solidification is the net result of a considerable decrease in the extent of self-dissociation and a compensating increase in the mobility. This increase in mobility presumably arises from the fact that, in the ice-structure, the positioning of the molecules by hydrogen bonds ensures that the species are correctly oriented for proton-transfer to occur, so that the rate-determining prior-orientation process is no longer necessary and the mobility depends only on jump frequency.[9] However, this mechanism is only expected to hold in those cases where the proton concentration is so small that the lattice has ample time to become reoriented before the same hydrogen bridge is passed by a proton-switch chain for a second time. Although the extent of autoprotolysis in crystalline sulphuric acid is not known it is relevant that the concentration of ions formed by self-dissociation of molten sulphuric acid at 25° is nearly 10^5 times greater than the equivalent ionic concentration in water. If this difference were carried over into the solids also, it would not be surprising to find that rotation now played some part in the conduction mechanism for sulphuric acid,

† This point is emphasized by a similar calculation made for water. From values of the conductivity [50] and autoprotolysis constant [9] in the range 0—18° we calculate $E_\kappa = 10{\cdot}1$ and $\Delta H_{\text{ap}} = 13{\cdot}5$; hence $E_v = 10{\cdot}1 - \frac{1}{2}(13{\cdot}5) = 3{\cdot}35$ kcal. mole^{-1}. This calculated value agrees with the figure determined directly from the change in the sum of the mobilities of H^+ and OH^- between 0° and 18°, *viz.*, 3·45 kcal. mole^{-1}. From the viscosity of water in the same temperature range $E_\eta = 4{\cdot}44$ kcal. mole^{-1}; the ratio E_v/E_η is thus 1/1·3 for water, compared with 1/2·0 for sulphuric acid. In water, of course, both normal ionic migration and proton switches contribute appreciably to the total mobility.

[50] Kohlrausch and Heydweiller, *Wied. Annalen*, 1894, **53**, 209.

[51] Conway and Bockris, *J. Chem. Phys.*, 1958, **28**, 354.

despite the fact that is was not rate-determining in ice. Further evidence on this point would be valuable for, even in the case of ice, there remain facts which are difficult to interpret. Thus, it is believed[9] that negligible activation energy is required for the proton jump itself, the protons residing, effectively, in a conduction band of the crystal. In addition, the similar dielectric properties of ice and water encourage the belief that molecular rotation in the solid can occur almost as freely as it does in the liquid and that the heat of ionic dissociation in the two phases will be similar.[17] Nevertheless, the activation energy for conduction in ice[17] ($E_\kappa = 12{\cdot}3$ kcal. mole^{-1}) is very similar to the heat of dissociation of water ($\Delta H_{\text{ap}} = 13{\cdot}5$ kcal. mole^{-1}), and application of equation (3) then gives the activation energy of mobility $E_v = 5{\cdot}6$ kcal. mole^{-1}. This is incompatible with a theory of rate-determining proton jumps of negligible activation energy unless the heat of ionic dissociation in ice is arbitrarily taken to be 24·6 kcal. mole^{-1}.

Applying this to crystalline sulphuric acid, we have $E_\kappa = 19{\cdot}5$ kcal. mole^{-1} (Fig. 2) and the heat of autoprotolysis, taken to be the same as that of the liquid, is 6·1 kcal. mole^{-1}. Hence by eqn. (3) the activation energy of the proton-switch is 16·4 kcal. mole^{-1}. In general, the switch mechanism involves (*a*) prior orientation of the molecules and ions, (*b*) the actual proton jump, and (*c*) subsequent rotation of the solvent molecules. As the solid is known to be rigidly ordered by hydrogen bonds,[52] the prior orientation into positions favourable for proton jumps to occur, which is the rate-determining step in liquid sulphuric acid, is unnecessary. Nor can the high activation energy be ascribed to the actual proton jump itself, for this will occur more readily in the solid than in the liquid owing to the slightly closer approach of the bridged species, and even in the liquid its value cannot exceed the total activation energy of mobility (3·3 kcal. mole^{-1}). It appears that the third process, (*c*) is rate-determining and that the activation energy for this process is 16·4 kcal. mole^{-1}. This process is not rate-determining in liquid sulphuric acid because rotation occurs more readily in the melt than in the rigidly bonded crystal; the process is not rate-determining in ice because the concentration of ions is so small that there is always sufficient time for rotation before the same water molecule is involved a second time in a conduction chain. The only other consistent interpretation of the observed energies (and this appears to be far less probable) is that rotation is not rate-determining in crystalline sulphuric acid and that the jump process has but a small energy of activation. This requires that $E_\kappa \simeq \frac{1}{2}\Delta H_{\text{ap}}$, which leads to a heat of autoprotolysis in the solid of about 39 kcal. mole^{-1}; this is 6—10 times greater than the value for the liquid.

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[52] Pascard, *Compt. rend.*, 1955, **240**, 2162; Bourre-Maladiere, *ibid.*, 1958, **246**, 1063.