# 842. *Solutions in Sulphuric Acid. Part XXXI.*[1] *Temperature-dependence of the Self-dissociation Equilibria and the Heats of Autoprotolysis and Ionic Self-dehydration.*

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The conductivity data given in the previous paper and the position of the minimum conductivity of the $H_2O$–$SO_3$ system at 10°, 25°, and 40° are used to obtain values of the self-dissociation constants of sulphuric acid at 25° and 40° and to confirm previously determined values at 10°. The ratio of the mobilities of $H_3SO_4^+$ and $HSO_4^-$ is also derived.

IN order to interpret the conductivities of electrolyte solutions given in the preceding paper[1] it is necessary to have values of the equilibrium constants of the self-dissociation reactions at 25°. These values are derived in the present paper from the previous values[2] at 10°, the position of minimum conductivity of the $H_2O$–$SO_3$ system,[3] and some of the conductivity data of the preceding paper. Values are also obtained for 40° together with values for the heats of autoprotolysis and ionic self-dehydration.

*Ratio of the Mobilities of* $H_3SO_4^+$ *and* $HSO_4^-$.—We need first the ratio of the mobilities of the ions $H_3SO_4^+$ and $HSO_4^-$. This may be obtained at 10° from the ratio of the conductivities of solutions of water and disulphuric acid of equal ionic strengths, it being assumed that the mobilities of these ions depend only on the total ionic strength of the solution and not, at least to a first approximation, on the nature of the other ions present.

For any solution of univalent ions we have

$$\kappa = 10^{-3}\sum c_i\lambda_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\kappa$ is the specific conductance, $c_i$ the concentration of the ionic species $i$, and $\lambda_i$ the ion conductance (or mobility) of this species. As the concentrations of all the species in various sulphuric acid systems have been previously calculated[2] by use of molal concentrations it is also convenient to use these units here. For the relatively low concentrations with which we are concerned it is a reasonable approximation to write

$$c_i = \rho m_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[1] Part XXX, Bass, Flowers, Gillespie, Robinson, and Solomons, preceding paper.

[2] Bass, Gillespie, and Robinson, Part XXVII, *J.*, 1960, 821.

where $\rho$ is the density of the solution and $m_i$ the molality of species $i$. Hence for any solutions in the $H_2O$–$SO_3$ system

$$\kappa = 10^{-3}\rho(m_{H_3SO_4^+}\lambda_{H_3SO_4^+} + m_{HSO_4^-}\lambda_{HSO_4^-} + m_{H_3O^+}\lambda_{H_3O^+} + m_{HS_2O_7^-}\lambda_{HS_2O_7^-}) \quad . \quad (3)$$

Since we are interested particularly in the conductivity due to the ions $H_3SO_4^+$ and $HSO_4^-$ it is convenient to define a " corrected " conductivity in the following manner

$$\kappa' = \kappa - 10^{-3}\rho(m_{H_3O^+}\lambda_{H_3O^+} + m_{HS_2O_7^-}\lambda_{HS_2O_7^-}) = 10^{-3}\rho(m_{H_3SO_4^+}\lambda_{H_3SO_4^+} + m_{HSO_4^-}\lambda_{HSO_4^-}) \quad (4)$$

For many purposes it is sufficiently accurate to put $\kappa' = \kappa$ since the contribution of $H_3O^+$ and $HS_2O_7^-$ to the conductivity is very small. When necessary their contribution to the conductivity can be allowed for approximately. Thus, on the basis of the transport numbers determined by Gillespie and Wasif [3] a value of $\lambda_{H_3O^+} = \lambda_{HSO_7^-} = 3$ was estimated. This is only an approximation but in view of the very small mobilities of these ions is sufficiently accurate for our purposes.

If the concentration of $HSO_4^-$ in any aqueous sulphuric acid is $m^a_{HSO_4^-}$, and if the concentration of $H_3SO_4^+$ in an oleum of the same total ion concentration (*i.e.*, same ionic strength) is $m^o_{H_3SO_4^+}$, then it may be shown that $m^a_{HSO_4^-} = m^o_{H_3SO_4^+}$, and similarly that $m^a_{H_3SO_4^+} = m^o_{HSO_4^-}$, $m^a_{H_3O^+} = m^o_{HS_2O_7^-}$, and $m^a_{HS_2O_7^-} = m^o_{H_3O^+}$. Thus, for any given stoicheiometric concentrations of $H_2S_2O_7$ the corresponding ion concentrations can be obtained from Table 5 of Part XXVII.[2] The ion concentrations in the corresponding aqueous solutions of equal ionic strength can then be obtained from the above relations. The stoicheiometric concentration of $H_2O$ is readily calculated (equation 7 of Part XXVII [2]) and the corresponding conductivity obtained from the data in Part XXX.[1] Values of ion concentrations and conductivities obtained in this way are given in Table 1. For such points of equal ionic strength in aqueous and oleum solutions respectively the corresponding " corrected " conductivities ($\kappa'$) are given by

TABLE 1. *Ion concentrations and conductivities at 10° of aqueous and oleum solutions of equal ionic strengths.*

| $m^s_{H_2S_2O_7}$ | $m_{H_3SO_4^+}$ | $m_{HSO_4^-}$ | $m_{H_3O^+}$ | $m_{HS_2O_7^-}$ | $m_{H_2S_2O_7}$ | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) |
|---|---|---|---|---|---|---|
| 0·0150 | 0·0158 | 0·0108 | 0·0039 | 0·0089 | 0·0100 | 0·617 |
| 0·0200 | 0·0171 | 0·0099 | 0·0033 | 0·0105 | 0·0128 | 0·638 |
| 0·0300 | 0·0199 | 0·0086 | 0·0025 | 0·0138 | 0·0186 | 0·673 |
| 0·0400 | 0·0220 | 0·0078 | 0·0021 | 0·0163 | 0·0256 | 0·712 |
| 0·0600 | 0·0263 | 0·0065 | 0·0016 | 0·0214 | 0·0402 | 0·784 |
| 0·0800 | 0·0302 | 0·0056 | 0·0013 | 0·0259 | 0·0558 | 0·855 |
| 0·1000 | 0·0335 | 0·0050 | 0·0012 | 0·0297 | 0·0711 | 0·922 |
| 0·1200 | 0·0368 | 0·0046 | 0·0011 | 0·0333 | 0·0875 | 0·986 |

| $m^s_{H_2O}$ | $m_{H_3SO_4^+}$ | $m_{HSO_4^-}$ | $m_{H_3O^+}$ | $m_{HS_2O_7^-}$ | $m_{H_2S_2O_7}$ | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) |
|---|---|---|---|---|---|---|
| 0·0020 | 0·0108 | 0·0158 | 0·0089 | 0·0039 | 0·0029 | 0·580 |
| 0·0049 | 0·0099 | 0·0171 | 0·0105 | 0·0033 | 0·0023 | 0·580 |
| 0·0098 | 0·0086 | 0·0199 | 0·0138 | 0·0025 | 0·0015 | 0·587 |
| 0·0130 | 0·0078 | 0·0220 | 0·0163 | 0·0021 | 0·0012 | 0·598 |
| 0·0191 | 0·0065 | 0·0263 | 0·0214 | 0·0016 | 0·0007 | 0·632 |
| 0·0241 | 0·0056 | 0·0302 | 0·0259 | 0·0013 | 0·0005 | 0·666 |
| 0·0281 | 0·0050 | 0·0335 | 0·0297 | 0·0012 | 0·0004 | 0·697 |
| 0·0318 | 0·0046 | 0·0368 | 0·0333 | 0·0011 | 0·0004 | 0·728 |

The ion concentrations were calculated on the basis of the following values for the self-dissociation constants: $K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_{id} = 3{\cdot}5 \times 10^{-5}$, and $K_a = 0{\cdot}014$.

$$(\kappa')^o = 10^{-3}\rho(m^o_{H_3SO_4^+}\lambda_{H_3SO_4^+} + m^o_{HSO_4^-}\lambda_{HSO_4^-}) \quad . \quad . \quad . \quad . \quad (5)$$

$$(\kappa')^a = 10^{-3}\rho(m^a_{H_3SO_4^+}\lambda_{H_3SO_4^+} + m^a_{HSO_4^-}\lambda_{HSO_4^-}) \quad . \quad . \quad . \quad . \quad (6)$$

For simplicity we will write $m_{H_3SO_4^+} = m_+$, $m_{HSO_4^-} = m_-$, $\lambda_{H_3SO_4^+} = \lambda_+$, and $\lambda_{HSO_4^-} = \lambda_-$.

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

Hence

$$\frac{(\kappa')^{\mathrm{o}}}{(\kappa')^{\mathrm{a}}} = \frac{m^{\mathrm{o}}_{+}\lambda_{+} + m^{\mathrm{o}}_{-}\lambda_{-}}{m^{\mathrm{a}}_{+}\lambda_{+} + m^{\mathrm{a}}_{-}\lambda_{-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Substituting $\mu = \lambda_{+}/\lambda_{-}$, $k = (\kappa')^{\mathrm{o}}/(\kappa')^{\mathrm{a}}$, and $r = m^{\mathrm{o}}_{+}/m^{\mathrm{a}}_{-} = m^{\mathrm{a}}_{-}/m^{\mathrm{o}}_{+}$ we have

$$\mu = (k - r)/(1 - kr) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Values of $(\kappa')^{\mathrm{o}}$ and $(\kappa')^{\mathrm{a}}$ and the corresponding values of $\mu$ are given in Table 2. The values of $\mu$ are reasonably constant and the mean is 1·45. It appears therefore that $\mu$ is independent of concentration. This is consistent with the fact that both ions conduct by essentially the same proton-transfer mechanism and the mobilities might therefore be expected to depend on the ionic strength in the same manner.

TABLE 2. *Conductivities ($\kappa'$) of aqueous acids and oleums at equal ionic strengths.*

| $m^{s}_{H_2S_2O_7}$ | $(\kappa')^{\circ} \times 10^2$ | $m^{s}_{H_2O}$ | $(\kappa')^{a} \times 10^2$ | $\mu$ | $m^{s}_{H_2S_2O_7}$ | $(\kappa')^{\circ} \times 10^2$ | $m^{s}_{H_2O}$ | $(\kappa')^{a} \times 10^2$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|
| 0·015 | 0·610 | 0·0020 | 0·571 | 1·43 | 0·060 | 0·771 | 0·0191 | 0·619 | 1·44 |
| 0·020 | 0·631 | 0·0049 | 0·571 | 1·46 | 0·080 | 0·841 | 0·0241 | 0·652 | 1·45 |
| 0·030 | 0·664 | 0·0098 | 0·578 | 1·42 | 0·100 | 0·906 | 0·0281 | 0·681 | 1·47 |
| 0·040 | 0·701 | 0·0130 | 0·587 | 1·46 | 0·120 | 0·968 | 0·0318 | 0·710 | 1·49 |
|  |  |  |  |  |  |  |  | Mean | 1·45 |

*The Composition at Minimum Conductance.*—A minimum in the conductivity–concentration curve of the $H_2O$–$SO_3$ system occurs very slightly on the aqueous side of the composition $H_2SO_4$.[4] The position of this minimum depends primarily on the concentrations of $H_3SO_4^{+}$ and $HSO_4^{-}$ and on the ratio of their mobilities ($\mu$). If we neglect the contribution of $H_3O^{+}$ and $HS_2O_7^{-}$ to the conductivity, as this has a negligible influence on the position of minimum conductivity, we may write

$$\kappa = \kappa' = 10^{-3}\rho(m_{+}\lambda_{+} + m_{-}\lambda_{-}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= 10^{-3}\rho\lambda_{-}(m_{+}\mu + K_{\mathrm{ap}}/m_{+}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $K_{\mathrm{ap}} = m_{+}\cdot m_{-}$. Hence

$$\partial\kappa/\partial m_{+} = 10^{-3}\rho\lambda_{-}(\mu - K_{\mathrm{ap}}/m_{+}^{2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and at the composition of minimum conductivity $\partial\kappa/\partial m_{+} = 0$, hence $\mu = K_{\mathrm{ap}}/m_{+}^{2}$ or

$$m_{+} = (K_{\mathrm{ap}}/\mu)^{\frac{1}{2}} \quad \text{and} \quad m_{-} = (K_{\mathrm{ap}}\mu)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

provided that $\mu$ and $\lambda_{-}$ are constant over the composition region near the minimum. The constancy of $\mu$ has been demonstrated above. In the region of the composition 100% $H_2SO_4$ the total ion concentration only changes slowly with the stoicheiometric composition.[1] Since it is likely that the mobility of $HSO_4^{-}$ is primarily dependent on the total ion concentration it seems reasonable to suppose that $\lambda_{-}$ will remain approximately independent of composition in this region.

Thus at the composition of minimum conductivity the concentrations of $H_3SO_4^{+}$ and $HSO_4^{-}$ may be obtained from (11) and if $(m_{H_3SO_4^{+}}) - (m_{HSO_4^{-}}) = a$, the concentration of $H_3O^{+}$ is given by [2]

$$m_{H_3O^{+}} = \tfrac{1}{2}[a + (a^{2} + 4K_{\mathrm{id}})]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and $m_{HS_2O_7^{-}}$ is obtained from $K_{\mathrm{id}} = m_{H_3O^{+}} \,.\, m_{HS_2O_7^{-}}$, $m_{H_2S_2O_7}$ from $K_{\mathrm{a}} = m_{H_3SO_4^{+}} \,.\, m_{HS_2O_7^{-}}/m_{H_2S_2O_7}$, and finally the stoicheiometric concentration of water at the minimum is given by $m^{s}_{H_2O} = m_{H_3O^{+}} - m_{HS_2O_7^{-}} - m_{H_2S_2O_7}$. Thus the composition of minimum conductance may be calculated from a knowledge of the equilibrium constants for self-dissociation and $\mu$, the ratio of the mobilities of $H_3SO_4^{+}$ and $HSO_4^{-}$. It may be

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

seen in Table 3 that, for the previously deduced values at 10° of $K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_{id} = 3{\cdot}5 \times 10^{-5}$, $K_a = 1{\cdot}4 \times 10^{-2}$, and $\mu = 1{\cdot}45$, the predicted position of the minimum specific conductance at $m^s{}_{H_2O} = 0{\cdot}0019$ agrees well with the observed minimum at $m^s{}_{H_2O} = 0{\cdot}0023$. The agreement can, in fact, be further improved by using $K_{id} = 3{\cdot}0 \times 10^{-5}$ and this value is perhaps to be preferred to the value $3{\cdot}5 \times 10^{-5}$ deduced earlier from cryoscopic measurements. Since $\lambda_+$ and $\lambda_-$ have the same temperature coefficient (Table 4), $\mu$ would be expected to be independent of temperature. Thus, although a value of $\mu = 1{\cdot}5$ is consistent with the observed conductivity minimum at 10°, it can be rejected as it is not also consistent with the position of the minimum at 25° and 40° (Table 3). The value $\mu = 1{\cdot}4$ is unlikely as it necessitates a value of $K_{id}$ less than $2{\cdot}5 \times 10^{-5}$ and this is quite inconsistent with the cryoscopic data.[2]

TABLE 3. *Dependence of the calculated composition of minimum conductance (stoicheiometric concentration of water, $m^s{}_{H_2O}$) on $\mu$ and $K_{id}$.*

| $10^2K_{id}$ | $\mu$<br>1·4 | <br>1·45 | <br>1·5 | Exptl.[3] |
|---|---|---|---|---|
| | 10° ($K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_a = 0{\cdot}014$) | | | |
| 2·5 | 0·0021 | 0·0025 | 0·0030 | |
| 3·0 | 0·0017 | 0·0022 | 0·0027 | |
| 3·5 | 0·0014 | 0·0019 | 0·0024 | 0·0023 |
| 4·0 | 0·0011 | 0·0016 | 0·0021 | |
| 4·5 | 0·0008 | 0·0013 | 0·0018 | |

| $10^2K_{id}$ | $\mu$<br>1·4 | <br>1·45 | <br>1·5 | Exptl. |
|---|---|---|---|---|
| | 25° ($K_{ap} = 2{\cdot}4 \times 10^{-4}$, $K_a = 0{\cdot}014$) | | | |
| 3·5 | 0·0016 | 0·0023 | 0·0032 | |
| 4·0 | 0·0012 | 0·0020 | 0·0029 | 0·0019 |
| 4·5 | 0·0009 | 0·0017 | 0·0026 | |
| | 40° ($K_{ap} = 3{\cdot}2 \times 10^{-4}$, $K_a = 0{\cdot}014$) | | | |
| 4·5 | 0·0014 | 0·0022 | 0·0031 | |
| 5·0 | 0·0010 | 0·0018 | 0·0028 | 0·0015 |
| 5·5 | 0·0007 | 0·0015 | 0·0025 | |
| 6·0 | 0·0004 | 0·0012 | 0·0022 | |

*Self-dissociation Constants at* 25° *and* 40°.—(i) *The autoprotolysis constant.* For solutions of a hydrogen sulphate at concentrations at which the autoprotolysis has been largely repressed, the conductivity is given to a good approximation by

$$\kappa = 10^{-3}\rho\lambda_{HSO_4^-} \, . \, m_{HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that for two temperatures $t'$ and $t''$ we have

$$\frac{\kappa^{t'}}{\kappa^{t''}} = \frac{\rho^{t'}\lambda_-{}^{t'}}{\rho^{t''}\lambda_-{}^{t''}} = \alpha_- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Similarly for solutions of an acid

$$\frac{\kappa^{t'}}{\kappa^{t''}} = \frac{\rho^{t'}\lambda_+{}^{t'}}{\rho^{t''}\lambda_+{}^{t''}} = \alpha_+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Values of $\alpha_+$ and $\alpha_-$ calculated from the data in the preceding paper are given in Table 4 for $H_3O{\cdot}HSO_4$, $KHSO_4$, $H_2S_2O_7$, and $HB(HSO_4)_4$. After autoprotolysis has been repressed these ratios become constant. For 10—25° the constant values are in the range 1·50—1·55,

TABLE 4. *Conductivity temperature coefficients $\alpha_+$ and $\alpha_-$.*

| | $(\alpha_-)^{2}_{1}$ | | $(\alpha_+)^{25}_{10}$ | | $(\alpha_-)^{40}_{10}$ |
|---|---|---|---|---|---|
| *m* | $H_3O{\cdot}HSO_4$ | $KHSO_4$ | $H_2S_2O_7$ | $HB(HSO_4)_4$ | $KHSO_4$ |
| 0·000 | 1·81 | 1·81 | 1·81 | 1·81 | 2·96 |
| 0·010 | 1·80 | 1·78 | 1·78 | 1·75 | 2·92 |
| 0·02 | 1·75 | 1·74 | 1·73 | 1·70 | 2·81 |
| 0·04 | 1·65 | 1·63 | 1·69 | 1·57 | 2·63 |
| 0·06 | 1·60 | 1·58 | 1·66 | 1·53 | 2·51 |
| 0·10 | 1·57 | 1·53 | 1·63 | 1·52 | 2·29 |
| 0·14 | 1·56 | 1·51 | 1·64 | — | 2·17 |
| 0·18 | — | 1·49 | 1·62 | — | 2·13 |
| 0·24 | — | 1·49 | 1·58 | — | 2·14 |
| 0·32 | — | 1·51 | 1·59 | — | 2·13 |
| 0·40 | — | — | 1·59 | — | — |
| 0·50 | — | — | 1·59 | — | — |

except in the case of $H_2S_2O_7$ which more slowly approaches the slightly larger limiting value of 1·59, and to a good approximation $\alpha_+ = \alpha_-$. The slightly higher value given by $H_2S_2O_7$ may be attributed to incompleteness in the repression of the self-dissociation even at rather high concentrations and to the temperature coefficient of the dissociation constant of $H_2S_2O_7$ which although certainly small may not be quite negligible. That $\alpha_+$ should be equal to $\alpha_-$ is reasonable in view of the similarity in the mechanism of conduction by these two ions. In the following we write $\alpha_+ = \alpha_- = \alpha$.

The conductivity for any solution in the $H_2O$–$SO_3$ system is given by equation (9) and at the minimum

$$m_{H_3SO_4^+} = (K_{ap}/\mu)^{\frac{1}{2}} \quad \text{and} \quad m_{HSO_4^-} = (K_{ap}\mu)^{\frac{1}{2}}$$

Therefore for any two temperatures $t'$ and $t''$ we have

$$\frac{\kappa_{\text{min.}}^{t'}}{\kappa_{\text{min.}}^{t''}} = \frac{\lambda_+^{t'}(K_{ap}^{t'}/\mu)^{\frac{1}{2}} + \lambda_-^{t'}(K_{ap}^{t'}\mu)^{\frac{1}{2}}\rho^{t'}}{\lambda_+^{t''}(K_{ap}^{t''}/\mu)^{\frac{1}{2}} + \lambda_-^{t''}(K_{ap}^{t''}\mu)^{\frac{1}{2}}\rho^{t''}} \quad . \; . \; . \; . \; . \quad (17)$$

and hence

$$\frac{\kappa_{\text{min.}}^{t'}}{\kappa_{\text{min.}}^{t''}} = \left\{\frac{K_{ap}^{t'}}{K_{ap}^{t''}}\right\}^{\frac{1}{2}} \cdot \frac{\lambda_+^{t'}\rho^{t'}}{\lambda_+^{t''}\rho^{t''}} = \alpha\left\{\frac{K_{ap}^{t'}}{K_{ap}^{t''}}\right\}^{\frac{1}{2}} \quad . \; . \; . \; . \; . \quad (18)$$

and

$$K_{ap}^{t''}/K_{ap}^{t'} = (\alpha\kappa_{\text{min.}}^{t''}/\kappa_{\text{min.}}^{t'})^2 \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

Substituting $(\alpha)_{10}^{25} = 1·5$, $\kappa_{\text{min.}}^{25}/\kappa_{\text{min.}}^{10} = 1·81$,[3] and $K_{ap}^{10} = 1·7 \times 10^{-4}$, we find $K_{ap}^{25} = 2·4 \times 10^{-4}$. Similarly, if we take $(\alpha)_{10}^{40}$ and $\kappa_{\text{min.}}^{40}/\kappa_{\text{min.}}^{10}$ from the values for $KHSO_4$ solutions in Table 4, we find $K_{ap}^{40} = 3·2 \times 10^{-4}$. From these values the heat of autoprotolysis $\Delta H_{ap}$ may be calculated to be 3·8 kcal. mole$^{-1}$. Values of $K_{ap}$ and $\Delta H_{ap}$ are summarised in Table 5.

TABLE 5. *Self-dissociation constants at* 10°, 25°, *and* 40° *and the heats of self-dissociation.*

| Temp. | $10^4K_{ap}$ (mole$^2$ kg.$^{-2}$) | $\Delta H_{ap}$ (kcal.) | $10^5K_{id}$ (mole$^2$ kg.$^{-2}$) | $\Delta H_{id}$ (kcal.) |
|---|---|---|---|---|
| 10° | 1·7 | 3·4 | 3·0 | 3·6 |
| 25 | 2·4 | | 4·2 | |
| 40 | 3·2 | | 5·5 | |

(ii) *The ionic self-dehydration constant.* It has been shown above that the position of the minimum conductivity at 10° is consistent with the values of the self-dissociation constants and the value of the ratio $\mu$ that had been previously and independently determined. The value of the ionic self-dehydration constant, $K_{id}$, at 25° and 40° can be calculated from the observed composition of minimum conductance at these temperatures by using the values of $K_{ap}$ derived above and assuming that $K_a$ is independent of temperature. The latter assumption is reasonable in view of the negligible temperature coefficient found for the dissociation constants of a number of weak bases in sulphuric acid * and the generally rather small temperature coefficient of the dissociation constants of weak acids in aqueous solution.[6] The position of minimum conductance was calculated as described above for various assumed values of $K_{id}$ and $\mu$, and values were chosen which predicted a minimum in closest agreement with the observed values. The results of these calculations are summarised in Table 3. Only $\mu = 1·45$ gives satisfactory predictions of the position of minimum conductivity. With this value, $K_{id} = 4·0 \times 10^{-5}$ gives the

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* Good agreement is obtained between dissociation constants determined cryoscopically at 10° and conductometrically at 25°.[5]

[5] Gillespie and Robinson, *J.*, 1957, 4233.

[6] Gurney, " Ionic Processes in Solution," McGraw-Hill, New York, 1953.

minimum at $m^{s}_{\rm H_2O} = 0{\cdot}0020$, and $K_{\rm id} = 4{\cdot}5 \times 10^{-5}$ gives it at $m^{s}_{\rm H_2O} = 0{\cdot}0017$ compared with the observed value of $m^{s}_{\rm H_2O} = 0{\cdot}0019$ at 25°. The intermediate value of $4{\cdot}2 \times 10^{-5}$ gives an exact fit, but it cannot of course be regarded as having been determined with greater accuracy than $\pm 0{\cdot}05 \times 10^{-5}$. At 40° $\mu = 1{\cdot}45$ again gives reasonable values, and $K_{\rm id} = 5{\cdot}5 \times 10^{-5}$ gives the position of minimum conductance at $m^{s}_{\rm H_2O} = 0{\cdot}0015$ in agreement with experiment.[3] Table 5 summarises the " best " values of $K_{\rm id}^{25}$ at 10°, 25°, and 40° as determined from the composition of minimum conductance. The corresponding value of the heat of ionic self-dehydration is $\Delta H_{\rm id} = 3{\cdot}6$ kcal. mole$^{-1}$.

Earlier estimates[7] of $K_{\rm ap}{}^{25} = 2{\cdot}9 \times 10^{-4}$ and $\Delta H_{\rm ap} = 4$ kcal. mole$^{-1}$ were made on the basis of a more approximate treatment of conductivity data than that given above and they may be regarded as in reasonable agreement with the present values. Unfortunately, there is not such good agreement with the more recent values given by Kirkbride and Wyatt[8] which are as follows: $K_{\rm ap}{}^{25} = 3{\cdot}4 \times 10^{-4}$, $K_{\rm id} = 1{\cdot}8 \times 10^{-4}$, $\Delta H_{\rm ap} = 4{\cdot}8$ kcal. mole$^{-1}$ and $\Delta H_{\rm id} = 6{\cdot}2$ kcal. mole$^{-1}$. These were obtained from the heats of solution of potassium, ammonium, barium, and oxonium hydrogen sulphate and acetic acid in sulphuric acid at 25° on the assumption that the autoprotolysis and ionic self-dehydration are independent and that the solutions behave ideally up to at least 0·2m. Neither of these assumptions is in fact correct, but the latter is likely to lead to the greatest errors. Cryoscopic measurements[9] have shown that solutions of hydrogen sulphates deviate from ideal behaviour mainly because of cation solvation. These differences between different electrolytes would be expected to show up in the heat of solution measurements and are indeed reflected in the different values (varying from 3·1 to $4{\cdot}5 \times 10^{-4}$) obtained by Kirkbride and Wyatt for $K_{\rm ap}$ from heats of solution of different electrolytes. These authors state that " the specific deviations from ideality may be large enough in some cases to give unreliable results and this is probably the case for $\rm Ba(HSO_4)_2$," and they therefore rejected the value derived from the heats of solutions of $\rm Ba(HSO_4)_2$. Solutions of $\rm Ba(HSO_4)_2$ do indeed show considerable deviations from ideal behaviour[9] which are larger than shown by other hydrogen sulphates with simple monatomic cations, but all the electrolytes that have been investigated show similar, if smaller, deviations, so it seems likely that this method does not in fact give reliable results for any electrolyte. Of the electrolytes studied by Kirkbride and Wyatt, ammonium hydrogen sulphate shows the smallest deviations from ideal behaviour[9] and so it might be expected to give the most nearly correct value of $K_{\rm ap}$: the value of $3{\cdot}1 \times 10^{-4}$ obtained in this case was in fact the lowest value obtained by these authors and the closest to our value of $2{\cdot}4 \times 10^{-4}$. Kirkbride and Wyatt's values for $K_{\rm ap}$ and $K_{\rm id}$ are, moreover, not consistent with the position of minimum conductivity. Thus, by taking $K_{\rm ap} = 3{\cdot}4 \times 10^{-4}$, $K_{\rm id} = 1{\cdot}8 \times 10^{-4}$, and $\mu = 1{\cdot}45$ it may be shown that the conductivity minimum would be predicted to occur on the oleum side of the composition $\rm H_2SO_4$ at $m^{s}_{\rm H_2S_2O_7} = 0{\cdot}0060$ rather than as observed on the aqueous side at $m^{s}_{\rm H_2O} = 0{\cdot}0019$. We consider that our values of the self-dissociation constants which are consistent with both cryoscopic and conductometric measurement and depend primarily on measurements at low concentrations are more accurate than any previous values.

*Thermodynamic Constants for the Self-dissociation of Protonic Solvents.*—From the data in Table 5 values of the standard free energies and entropies of autoprotolysis and ionic self-dehydration were calculated and are given in Table 6. It is of interest to compare these thermodynamic data for the autoprotolysis of sulphuric acid with those for the autoprotolysis of other protonic solvents. The latter data have been collected by Jolly[10] and are given in Table 7 together with the present values for sulphuric acid.

Jolly discussed the entropy of autoprotolysis of protonic solvents and pointed out that

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

[8] Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483.

[9] Bass, Gillespie, and Oubridge, Part XXVIII, *J.*, 1960, 827.

[10] Jolly, *J. Amer. Chem. Soc.*, 1952, **74**, 6199.

the relatively small negative value for water is consistent with a previous suggestion[11] that ionic entropies in water are abnormally high because of the considerable structure-breaking caused by an ion when it enters the strongly hydrogen-bonded structure of water. The still smaller negative value of the entropy of autoprotolysis of sulphuric acid could similarly be attributed to ions having a relatively greater disruptive effect on the very strongly hydrogen-bonded structure of sulphuric acid. It is possible, however, that the characteristic ions formed by the autoprotolysis of a protonic solvent do not have the same effect on the structure of the solvent as other ions. Since they differ from a solvent molecule only by possessing one more or one less proton, they will fit easily into the structure of the solvent, and it is likely that they will cause little if any disruption of this structure. Indeed, it seems probable that the charge of the ions will cause a strengthening of the hydrogen bonds around the ion and an increase in the amount of solvent structure. This would be accompanied by a decrease in entropy and this is consistent with the fact that all the observed entropies of autoprotolysis are negative. The most negative values of the entropy of autoprotolysis are given by weakly hydrogen-bonded solvents such as ethanol, in which the characteristic ions resulting from the autoprotolysis can presumably cause a considerable increase in the strength and the amount of hydrogen bonding. On the other hand, in strongly hydrogen-bonded solvents such as water and sulphuric acid the effect of the characteristic ions on the structure of the solvent will be relatively much smaller, and the entropies of autoprotolysis correspondingly small.

TABLE 6. *Thermodynamic constants for the self-dissociation of sulphuric acid at* 25°.

| | $\Delta G^\circ$ (cal./mole) | $\Delta H^\circ$ (cal./mole) | $\Delta S^\circ$ (cal./deg. mole) |
|---|---|---|---|
| Autoprotolysis | 4730 | 3400 | −4·5 |
| Ionic self-dehydration | 6010 | 3600 | −8·1 |

TABLE 7. *Thermodynamic constants for autoprotolysis at* 25°.

| Solvent | $-\log K_{ap}$ | $\Delta H^\circ$ (cal./mole) | $\Delta S^\circ$ (cal./deg. mole) | $\Delta S^\circ_{unitary}$ (cal./deg. mole) |
|---|---|---|---|---|
| $H_2SO_4$ | 3·47 | 3,400 | −4·5 | −13·7 |
| $H_2O$ | 14·00 | 13,360 | −19·2 | −35·2 |
| AcOH | 12·6 | 5,700 | −38·6 | −49·9 |
| MeOH | 16·6 | 11,200 | −38·6 | −52·6 |
| EtOH | 18·9 | 11,500 | −48·0 | −60·2 |
| $NH_3$ | 29·8 | 26,200 | −49 | −65·3 |

It should be pointed out that it is not strictly correct to compare the conventional standard entropies of autoprotolysis $\Delta S^\circ$ since these include a *cratic* term[6] but we should compare values of $\Delta S^\circ_{unitary}$ where

$$\Delta S^\circ_{unitary} = \Delta S^\circ - 2\boldsymbol{R} \ln M$$

where $M$ is the number of moles of solvent in 1000 g. These values are given in the last column of Table 7, and although they differ from the conventional $\Delta S^\circ$ values, this does not affect our qualitative discussion above.

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[*Received, January* 13*th*, 1960.]

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[11] Jolly, *Chem. Rev.*, 1952, **50**, 351.