# 355. *The Dissociation Constants of Thiosulphuric Acid.*

By F. M. PAGE.

The second dissociation constant of thiosulphuric acid has been measured at several ionic strengths by means of a glass electrode. The value extrapolated to zero ionic strength is 0·019. The first dissociation constant has been estimated.

THE rate of the reaction between ferric salts and sodium thiosulphate is affected by the hydrogen-ion concentration (Holluta and Martini, *Z. anorg. Chem.*, 1925, **144**, 321). One factor contributing to this effect is the incomplete dissociation of thiosulphuric acid. It was expected that a significant amount of the total thiosulphate in a reaction mixture would be present as $HS_2O_3^-$, and, if the solution were sufficiently acid, as undissociated thiosulphuric acid $H_2S_2O_3$. The concentration of free thiosulphate ion in the reaction mixture can be calculated if the two dissociation constants of thiosulphuric acid are known. The first dissociation constant has never been measured, although its magnitude has been estimated by analogy with sulphuric acid (Jellinek, *Z. physikal. Chem.*, 1911, **76**, 257). Since values reported for the second dissociation constant are widely scattered, it was decided to make a fresh determination of the dissociation constants of thiosulphuric acid under the same experimental conditions as in the kinetic investigation of the ferric–thiosulphate reaction (Page, in the press).

The dissociation constant of a monobasic acid can be determined by measuring the concentrations of dissociated and undissociated forms of the acid in equilibrium in a solution of known hydrogen-ion concentration. This is conveniently done by adding a known amount of a strong acid, which can be considered as completely dissociated, to a known amount of a salt of the acid under investigation, and determining the hydrogen-ion concentration in the resulting mixture with a glass electrode. If the acid is polybasic, this method leads to an " apparent dissociation constant " which is a function of the hydrogen-ion concentration. The various dissociation constants of the polybasic acid can be measured by determining this apparent dissociation constant over a wide range of hydrogen-ion concentration.

*Decomposition of Thiosulphuric Acid.*—Acid solutions of sodium thiosulphate rapidly decompose, forming the sulphite ion and free sulphur; $HS_2O_3^- \longrightarrow S + HSO_3^-$. The sulphur is visible as a faint opalescence when its amount exceeds the limit set by its solubility ($10^{-4}$ g.-atom/l.). If the initial concentration of thiosulphate ion exceeds $10^{-2}$M, the proportion lost by undetected decomposition will be less than 1%, but it may be substantial in more dilute solutions.

The sulphurous acid produced during the decomposition will also affect the hydrogen-ion concentration. If a small amount of the completely dissociated acid is added to the thiosulphate solution, most of the added hydrogen ions will go to form bisulphite ions, since the dissociation constant of this ion ($10^{-5}$) is very much smaller than that of the ion $HS_2O_3^-$. It was found that in solutions of pH 4·5—6·0, thiosulphuric acid appeared to have a dissociation constant of the order of $10^{-5}$. This value rose rapidly with increasing acidity, reaching $5 \times 10^{-2}$ at pH 3·5. The effect of traces of sulphurous acid will be less important in more acid solutions, because all the sulphurous acid will be in the undissociated form, and hydrogen ion thus lost will be a negligible fraction of the total acid added.

*Calibration of the Glass Electrode.*—The glass electrode measures the activity of the hydrogen ions in a solution. The algebraic equations derived below involve the concentration of hydrogen ions, and it is necessary to convert the measured activities into concentrations before calculating the dissociation constants. This can be done by using estimated activity coefficients, but the necessity for the conversion can be avoided by a suitable calibration of the glass electrode.

The measurement of hydrogen-ion activity by the glass electrode is essentially a series of measurements of the potential of the cell

$$\text{Glass electrode} \quad \underset{A}{\Big|} \quad \begin{matrix}\text{Solution}\\ \text{X}\end{matrix} \quad \underset{B}{\Big\|} \quad \text{Satd. KCl} \quad \Big| \quad \text{Calomel electrode}$$

There are two unknown junction potentials in this cell—at *A* and *B*. The usual calibration of the glass electrode with a standard buffer solution allows for the asymmetry potential of the glass electrode at junction *A*, but may overcompensate for the liquid-junction potential at *B*. If the glass electrode is calibrated with a solution whose ionic strength is the same as that of the solution under examination, then the liquid-junction potential at *B*, and any salt effect on the asymmetry potential at *A*, will be the same during the experiment as during the calibration, and the difference between the observed potentials will be given by

$$E_{\text{exp.}} - E_{\text{calib.}} = (RT/F) \log_e a_{\text{H}^+,\,\text{exp.}}/a_{\text{H}^+,\,\text{calib.}}$$

where $a_{\text{H}^+}$ is the activity of the hydrogen ion, and $E_{\text{exp.}}$ and $E_{\text{calib.}}$ refer respectively to the experimental and the calibrating cell. In this equation, each activity can be replaced by the product of the appropriate concentration and activity coefficient. The two solutions used during the calibration and the experiment have similar compositions and the activity coefficients of the ions will be the same. The difference in the potentials of the experimental and the calibrating cell is therefore a measure, not only of the ratios of the activities of the hydrogen ions in the two cells, but also of the ratios of the concentrations.

It is important that the calibrating solution should differ from the experimental solution as little as possible. In the present work the electrode was calibrated with solutions containing perchloric acid and sodium perchlorate, and in the experimental solutions a portion of the sodium perchlorate was replaced by sodium thiosulphate, the total ionic strength being kept constant.

*Experimental.*—All materials used were of the best available grade of analytical reagent. The sodium thiosulphate solution was standardised against potassium iodate, and the perchloric acid by reference to potassium hydrogen phthalate. The pH of the sodium perchlorate solution lay within the range 6·8—7·2, showing that no important quantities of free acid or alkali were present. All water had been distilled from a Pyrex-glass still, and was freshly boiled to expel dissolved gases. All solutions were brought to the required ionic strength by addition of the calculated amount of sodium perchlorate.

A measured volume of the perchloric acid solution was added to a known quantity of the sodium thiosulphate solution in a small beaker, and the pH was measured with a glass electrode and valve potentiometer. Several successive additions of small quantities of perchloric acid could sometimes be made before the opalescence showed that a significant amount of decomposition had occurred; more usually each mixture had to be made up afresh. All measurements were repeated five times; the observed values of the pH did not differ from the mean by more than 0·01 unit except in the most dilute solutions, where the scatter was about twice as great.

The electrodes were kept in distilled water between measurements and were well drained before each measurement. They were calibrated frequently with an M/20-solution of potassium hydrogen phthalate, whose pH was taken to be 4·01. All measurements were carried out in a thermostat kept at 25·00° ± 0·02° and the solutions were stored in the same thermostat.

A parallel series of experiments was made, in which the sodium thiosulphate solution was replaced by a solution of sodium perchlorate of the same ionic strength. The results of this series were used to calibrate the glass electrode in terms of the concentration of hydrogen ion in the mixed solution, thus avoiding errors due to the liquid-junction potential and enabling all calculations to be carried out with concentrations instead of activities.

*Calculation of the Dissociation Constants of a Dibasic Acid.*—Consider the solution obtained by mixing a volume $V_A$ ml. of a solution of a fully dissociated acid of concentration $A$ with $V_B$ ml. of a solution of the salt of a weak dibasic acid of concentration $B$. Then, if we denote the concentrations of undissociated weak acid and singly and doubly dissociated anions by $b_0$, $b_1$, and $b_2$ respectively, and the hydrogen-ion concentration of the mixed solution by $h$, we have

$$V = V_A + V_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Vh + 2V_BB = Vb_1 + 2Vb_2 + V_AA \quad \text{(electrical neutrality)} \quad . \quad . \quad . \quad . \quad (2)$$

$$V_BB = V(b_0 + b_1 + b_2) \quad \text{(conservation of weak acid anion)} \quad . \quad . \quad . \quad . \quad (3)$$

These can be combined with the expressions for the dissociation constants of the weak acid, *viz.*, $K_1 = b_1h/b_0$ and $K_2 = b_2h/b_1$, to give the relation

$$(V_AA - Vh)/V_BB = h(K_1 + 2h)/(h^2 + K_1h + K_1K_2)$$

Inversion of this equation gives

$$\frac{V_BB}{V_AA - Vh} = \frac{h^2 + K_1h + K_1K_2}{h(K_1 + 2h)} = \frac{K_1K_2 - h^2}{h(K_1 + 2h)} + 1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and, putting

$$K' = (K_1K_2 - h^2)/(K_1 + 2h) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

we have

$$K' = V_AB/(V_AA - Vh) - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which depends only on known or measurable quantities.

Equation (5) can be rearranged to give

$$K_2 = K' + h(h + 2K')/K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When a sufficiently extensive range of measurements is available, the separate values of $K_1$ and $K_2$ can be obtained graphically from equation (7). In other cases, only $K'$ can be calculated with accuracy, and it is assumed that $K'$ is equal to $K_2$, the last term in equation (7) being negligible if $h \ll K'$.

*Results.—Ionic strength,* $I = 0{\cdot}094$. This concentration is the lowest which it is convenient to use, and the results are comparable with those of Yui and Hagisawa (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1942, **21**, 5) and Denney and Monk (*Trans. Faraday Soc.*, 1951, **47**, 992) whose experiments were carried out under roughly the same conditions.

The measurements are collected and analysed in detail in Table 1. Only abbreviated Tables will be given for the results at other ionic strengths, as the details of the analysis are the same in each case. The value of $K'$, the apparent dissociation constant, falls as the hydrogen-ion concentration rises, in accord with equation (5). The results lead to the values $K_1 = 0{\cdot}52$, $K_2 = 0{\cdot}0573$, which become $K = 0{\cdot}65$ and $K = 0{\cdot}0517$, respectively, when corrected for the effect of sodium in forming $NaS_2O_3^-$.

TABLE 1.

| $10^4[H^+]$ | Total thio-sulphate | Total Na ion | $10^4[H^+]$ con-sumed | $K'$ (eqn. 5) | $[S_2O_3^{--}]$ | $10^4 \times [NaS_2O_3]$ | $[Na^+]$ | $[HS_2O_3^-]$ | $K'$, corr. | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 15·4 | 0·0325 | 0·0650 | 9·0 | 0·0540 | 0·0285 | 30·8 | 0·0619 | 0·00090 | 0·0487 | 0·0959 |
| 24·9 | 0·0320 | 0·0640 | 13·6 | 0·0560 | 0·0277 | 29·5 | 0·0610 | 0·00136 | 0·0507 | 0·0956 |
| 40·9 | 0·0313 | 0·0626 | 21·9 | 0·0544 | 0·0263 | 27·5 | 0·0598 | 0·00219 | 0·0491 | 0·0952 |
| 60·4 | 0·0303 | 0·0606 | 30·5 | 0·0540 | 0·0248 | 25·1 | 0·0581 | 0·00305 | 0·0491 | 0·0944 |
| 90·0 | 0·0290 | 0·0580 | 40·3 | 0·0558 | 0·0228 | 22·2 | 0·0358 | 0·00403 | 0·0509 | 0·0938 |
| 135 | 0·0270 | 0·0540 | 54 | 0·0540 | 0·0198 | 18·1 | 0·0522 | 0·0054 | 0·0494 | 0·0927 |
| 220 | 0·0238 | 0·0476 | 66 | 0·0513 | 0·0159 | 12·9 | 0·0463 | 0·0066 | 0·0530 | 0·0921 |
| 258 | 0·0222 | 0·0444 | 75 | 0·0506 | 0·0137 | 10·4 | 0·0434 | 0·0075 | 0·0471 | 0·0914 |
| 350 | 0·0191 | 0·0382 | 79 | 0·0497 | 0·0105 | 6·9 | 0·0375 | 0·0079 | 0·0465 | 0·0916 |
| 420 | 0·0167 | 0·0333 | 80 | 0·0458 | 0·0082 | 4·7 | 0·0328 | 0·0080 | 0·0430 | 0·0915 |
| 527 | 0·0133 | 0·0267 | 73 | 0·0433 | 0·0057 | 2·7 | 0·0264 | 0·0073 | 0·0411 | 0·0924 |

This Table calls for certain comments. It is not correct, even in solutions as dilute as these, to ignore the effects of undissociated thiosulphuric acid, and to equate the hydrogen ions consumed to the $HS_2O_3^-$ formed, as has been done here. The correction for the formation of $NaS_2O_3^-$ was made by using a value $K_{NaS_2O_3^-} = 0{\cdot}57$. This value, although obtained by application of Davies's activity relation (see below), is probably fairly accurate, as the experimental work upon which it is based was carried out at an ionic strength of about 0·11, and the same relation used to extrapolate to zero ionic strength. The mean value of the ionic strength had been taken as 0·094.

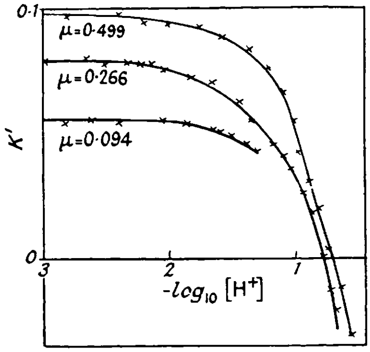
*Ionic strengths* $I = 0{\cdot}27$ *and* 0·50. The results at these ionic strengths followed the same pattern as those at the lower ionic strength, except that the more concentrated solutions enabled measurements to be made under slightly more acid conditions, and the value of $K'$ could be followed much further, until it became negative. The measurements are shown graphically in the Figure. The results are in agreement with the values for the two dissociation constants shown below. These values have not been corrected for the effect of $NaS_2O_3^-$.

| $I$ | $K_1$ | $K_2$ | $I$ | $K_1$ | $K_2$ |
|---|---|---|---|---|---|
| 0·27 | 0·35 | 0·0816 | 0·50 | 0·45 | 0·0970 |

*Ionic strengths* $I = 0{\cdot}78$ *and* 0·91. The measurements at these strengths were hampered by rapid precipitation of sulphur, and the accessible range of hydrogen-ion concentration was small. It was possible to make sufficient measurements to determine the values of both dissociation constants, but the accuracy was lower than in the previous experiments. A number of results are collected in Table 2.

TABLE 2.

| $[H^+]$ | Total thio-sulphate | $[H^+]$ con-sumed | Total Na | $K'$ | $I$ |
|---|---|---|---|---|---|
| 0·00589 | 0·0909 | 0·00363 | 1·000 | 0·141 | 0·916 |
| 0·00891 | 0·0869 | 0·0047 | 1·000 | 0·147 | 0·914 |
| 0·0138 | 0·0800 | 0·0072 | 0·999 | 0·141 | 0·912 |
| 0·0155 | 0·0769 | 0·0087 | 0·998 | 0·136 | 0·910 |
| 0·0407 | 0·0500 | 0·0117 | 0·996 | 0·133 | 0·906 |
| 0·0515 | 0·0333 | 0·0723 | 0·994 | 0·098 | 0·908 |
| 0·0190 | 0·278 | 0·0400 | 0·640 | 0·113 | 0·784 |
| 0·0299 | 0·256 | 0·0518 | 0·619 | 0·118 | 0·782 |
| 0·0400 | 0·239 | 0·0611 | 0·627 | 0·116 | 0·782 |
| 0·0504 | 0·222 | 0·0676 | 0·641 | 0·115 | 0·780 |
| 0·0648 | 0·278 | 0·112 | 0·556 | 0·096 | 0·777 |
| 0·102 | 0·256 | 0·193 | 0·512 | 0·082 | 0·778 |
| 0·135 | 0·238 | 0·171 | 0·476 | 0·057 | 0·776 |
| 0·162 | 0·222 | 0·191 | 0·444 | 0·026 | 0·779 |
| 0·231 | 0·055 | 0·064 | 0·348 | 0·031 | 0·781 |



The concentration of sodium ion in the solutions studied is so high that it is essential to take into account the ion $NaS_2O_3^-$. The dissociation constant of this ion has been determined by Denney and Monk (*loc. cit.*), but their results were obtained at relatively low ionic strengths, and considerable uncertainly must occur in any extrapolation to the ionic strength used in the present work.

Davies (*J.*, 1938, 2093) has pointed out that the mean activity coefficients of many electrolytes can be represented over a considerable range of ionic strengths by the equation

$$\log \gamma_{\pm} = 0{\cdot}505 Z_1 Z_2 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0{\cdot}2I \right\} = 0{\cdot}505 Z_1 Z_2 \, \mathrm{f}(I)$$

where $Z_1$, $Z_2$ are the charges of the ions and $I$ is the ionic strength. Davies also suggested that this relation was generally applicable, provided that the ionic strength was not too great. This equation, applied to the dissociation of $NaS_2O_3^-$, gives for the dissociation constant at an ionic strength of $I$: $\log K_1 = \log K_0 + 2{\cdot}02\mathrm{f}(I)$. The dissociation constant of $NaS_2O_3^-$ has been calculated by this equation for each ionic strength, and the dissociation constants thus obtained have been used to correct the observed dissociation constants of $HS_2O_3^-$ for the errors due to the formation of $NaS_2O_3^-$.

The second dissociation constant of thiosulphuric acid is shown by equation (7) to be the limit of $K'$ as the hydrogen-ion concentration tends to zero. Inserting this in equation (6), we obtain

$$K_2 = \underset{h \to 0}{\mathrm{Lt}}\,(K') = \underset{h \to 0}{\mathrm{Lt}} \left\{ \frac{V_B B h}{V_A A - V h} - h \right\}$$

In the limit, $V_A = 0$ and $V = V_B$. The correction for formation of $NaS_2O_3^-$ in the solution is made by multiplying the observed value of $K_2$ by the fraction of thiosulphate in the solution of sodium thiosulphate which is in the free state, *i.e.*,

$$K_2 = \left[ \underset{h \to 0}{\mathrm{Lt}}\,(K') \right] \times \left[ \frac{[S_2O_3{}^{--}]}{[S_2O_3{}^{--}] + [NaS_2O_3{}^{-}]} \right]$$

The latter factor can be computed from the dissociation constant of the ion $NaS_2O_3^-$. It is necessary to use successive approximations, since the ionic strength involves a knowledge of the concentration of $NaS_2O_3^-$ present. The computed dissociation constants of $NaS_2O_3^-$ at the various ionic strengths are given in Table 3, together with the observed and corrected dissociation constants of $HS_2O_3^-$ at each ionic strength and the value at zero ionic strength calculated from each result by Davies's equation.

TABLE 3.

| Ionic strength | | 0 | 0·094 | 0·266 | 0·949 | 0·775 | 0·910 |
|---|---|---|---|---|---|---|---|
| $K_{NaS_2O_3^-}$ | | 0·21 | 0·57 | 0·79 | 0·87 | 0·90 | 0·90 |
| $K_{HS_2O_3^-}$ | obs. | — | 0·0573 | 0·0816 | 0·0970 | 0·143 | 0·118 |
| | corr. | — | 0·0517 | 0·0673 | 0·0776 | 0·0788 | 0·0759 |
| | $I = 0$ | 0·0184 | 0·0191 | 0·0179 | 0·0187 | 0·0187 | 0·0177 |

The value of $K_1$ is obtained from the hydrogen-ion concentration at which $K'$ is zero. At this point $K_1K_2$ is equal to the square of the hydrogen-ion concentration, and the concentrations of sodium ion and free thiosulphate ion are so small that the concentration of $NaS_2O_3^-$ may be neglected. The values of $K_1$ obtained in this way are collected in Table 4, together with the values at zero ionic strength obtained by applying Davies's formula.

TABLE 4.

| Ionic strength | 0 | 0·094 | 0·266 | 0·499 | 0·775 | 0·910 |
|---|---|---|---|---|---|---|
| Critical hydrogen-ion concentration | — | 0·142 | 0·169 | 0·209 | 0·197 | 0·185 |
| $K_1$ | — | 0·53 | 0·49 | 0·45 | 0·49 | 0·45 |
| $K_1$ ($I = 0$) | 0·25 | 0·32 | 0·25 | 0·22 | 0·24 | 0·22 |

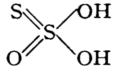
*Discussion.*—The use of an empirical activity equation to correlate equilibrium constants at different ionic strengths is only valid if it is known that the equation applies in the region studied. Davies's equation was proposed to cover the range $I = 0$ to $I = 0{\cdot}1$, and the results obtained in this work lies well outside this range. If the results of Davies and Righellato (*Trans. Faraday Soc.*, 1930, **26**, 592) for the conductivity of potassium sulphate are examined, it is found that the empirical equation expresses these measurements even at 0·2M ($I = 0{\cdot}6$). From this, it appears that any errors introduced by the use of this equation will be less than the errors of experiment. Furthermore, the errors thus introduced are likely to be the same in the dissociation constants of both $HS_2O_3^-$ and $NaS_2O_3^-$, and will tend to cancel, particularly in those experiments where the corrections for the effect of sodium are important. The use of this empirical equation brings the varied results at different ionic strengths to a common value and, as the equation may reasonably be expected to apply at the lowest ionic strength studied, it can be taken to apply throughout the range of the experiments.

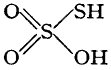
The value of the second dissociation constant now obtained is somewhat lower than the values obtained by previous workers (Denney and Monk, Yui and Hagisawa, *locc. cit.*) and the difference cannot be entirely ascribed to the use of perchloric acid instead of hydrochloric acid. A more probable explanation of the difference lies in the method by which the hydrogen-ion concentration is calculated. The use of activity coefficients predicted by general formulæ is always open to criticism, particularly so when, as in the present work, the numerical result is very sensitive to slight changes in the value of the activity coefficient. The method of calibration used in the present work avoids this source of error, and at the same time reduces to a minimum the difference between the liquid-junction potentials in the calibrating and experimental cells.

The structure of the thiosulphate ion has frequently been compared to that of the sulphate ion, and Jellinek (*loc. cit.*) on these grounds estimated the first dissociation constant of thiosulphuric acid. It is instructive to compare the values for the dissociation constants of thiosulphuric acid obtained here with those measured or estimated for sulphuric acid.

The comparison of the second dissociation constants shows that $HS_2O_3^-$ ($K_2 = 0{\cdot}018$ at 25°) is a slightly stronger acid than is $HSO_4^-$ ($K_2 = 0{\cdot}012$ at 25°; Hamer, *J. Amer. Chem. Soc.*, 1936, **58**, 2126) in agreement with many observations on salts and complex ions of the two acids. There is no such agreement between the first dissociation constants; indeed, the value obtained in this paper contravenes all the relations observed between first and second dissociation constants of acids. A dibasic acid with two equivalent ionising groups should have a first and second dissociation constant differing by a factor of $10^5$ (Pauling, " General Chemistry," 1947, p. 394) or $10^{5{\cdot}1}$ (MacGowan, *Chem. and Ind.*, 1948, 632), so that sulphuric and thiosulphuric acids should have a dissociation constant of about 1000, and the curvature to be seen in the figure should be unobservable. The classification adopted by Ricci (*J. Amer. Chem. Soc.*, 1948, **70**, 109) would indicate a much smaller value, but, as he remarks, the group into which sulphuric acid falls is not sufficiently homogeneous to enable any conclusion to be drawn.

(I)





(II)

Two structures have been proposed for thiosulphuric acid—the symmetric structure (I) in which the ionisable hydrogen are both attached to oxygen atoms, and the asymmetric structure (II) in which one hydrogen is attached to the sulphur atom. The estimation of the difference between the dissociation constants outlined above is only valid when the ionisable hydrogen atoms are equivalent, *i.e.*, for the structure (I). The asymmetric formula is strongly supported by studies on the formation of organic thiosulphates from thiols and chlorosulphonic acid (Mellor, " Inorganic Chemistry ") and the strongly coloured ferric thiosulphate complex ion is typical of the complexes formed between $Fe^{3+}$ and compounds containing the thiol group. The physical evidence is not decisive, though the S–S internuclear distance of 2·1 Å (Gupta and Guha, *Proc. Nat. Inst. Sci. India*, 1941, **7**, 267) suggests a single covalent bond.

The dissociation constants of phenol and thiophenol have been measured under similar conditions (Fletcher, *J. Amer. Chem. Soc.*, 1946, **68**, 2726) and thiophenol is the stronger acid by 3·3 units of p$K$. If thiosulphuric acid has the asymmetric formula, the usual empirical rules will not apply, since the two ionisable hydrogen atoms are not equivalent, but the S–H bond should be the first to break. The resulting ion closely resembles the $HSO_4^-$ ion, and may be compared with it.

In the absence of comparable measurements on sulphuric acid by the technique used here, the possibility that the abnormally low first dissociation constant of thiosulphuric acid is fictitious cannot be completely ruled out, but the consistency of the results from widely different conditions of experiment strongly suggests that the value reported here is of the correct order of magnitude, and the explanation of the low value must be sought in the detailed structure of thiosulphuric acid itself.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
BUTTERWICK RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[*Received, September* 10*th*, 1952.]