# 500. *Cryoscopic Measurements in Sulphuric Acid. Part IV. Reactions of Ionised Sulphates in Sulphuric Oleum. Self-ionisation Equilibria in Sulphuric Acid, and Ionic Equilibria in Oleum. The Polysulphuric Acids.*

By R. J. GILLESPIE.

The variations of freezing point have been followed when, to an oleum, first ammonium sulphate, and thereafter water, are added. The nature of the results can be appreciated by reference to Fig. 1 on p. 2521. The freezing points of originally taken oleums lie on the limiting curve towards the right. The freezing-point curves obtained by adding ammonium sulphate run generally downward towards the left, but with a reduced initial slope, the initial reduction increasing, and leading eventually to an initial rise in the curve, as the concentration of the original oleum is increased. The curves for the addition of water are those which start upwards towards the left, then pass through a maximum, and then descend.

From these results the basicity constant of the hydrogen disulphate ion is deduced. From this, and the acidity constant of disulphuric acid, the autoprotolysis constant of sulphuric acid is calculated. By combining this value with the total concentration of self-dissociation products in sulphuric acid, as derived in Part II, the concentrations are computed of each of the four ionic species formed by self-dissociation of sulphuric acid. The dissociation consists of an autoprotolysis to $H_3SO_4^+$ and $HSO_4^-$, accompanied by a smaller amount of ionic self-dehydration to $H_3O^+$ and $HS_2O_7^-$.

Another set of conclusions relates to the presence in oleum, besides disulphuric acid, $H_2S_2O_7$, of higher polysulphuric acids. Trisulphuric acid, $H_2S_3O_{10}$, and tetrasulphuric acid, $H_2S_4O_{13}$, are definitely recognised. An equilibrium constant governing the formation of trisulphuric acid is deduced. The property of forming poly-acids, for which tungsten and molybdenum are notable, is thus extended to sulphur, to which it can be traced through the intermediate elements, chromium and selenium, as well as, in the other direction, to uranium. Therefore it appears as a somewhat general property of the elements in Group VI.

Further conclusions are drawn concerning the strengths of the polysulphuric acids. Disulphuric acid was shown in Part II to be a semi-strong acid. The hydrogen disulphate ion is, however, a very weak acid. It is very incompletely deprotonated to form a doubly charged ion, even by a large excess of hydrogen sulphate ion, the strongest available base in these solutions. Thus disulphuric acid does not undergo, to any marked extent, a second stage of ionisation, before the first stage is practically complete. On the other hand, the higher polysulphuric acids appear to be somewhat stronger than disulphuric acid with respect to first stages of ionisation, and to be very much stronger with respect to second stages. This is reasonable on structural and electrostatic grounds. Thus, on the progressive addition of hydrogen sulphate ions, the higher polysulphuric acids are deprotonated earlier than is the disulphuric acid; and the doubly charged anions of the higher poly-acids are formed in much greater proportion than is the doubly charged anion of disulphuric acid.

The reactions taking place during the titration of sulphur trioxide in oleum, or in solutions in oleum, with water to the cessation of fuming (Brand), are considered. The suggestion that one hydrogen sulphate ion removes half a molecule of titratable sulphur trioxide, for the reason that two hydrogen sulphate ions suffice for a stoicheiometrically quantitative removal of two protons from one molecule of disulphuric acid, is shown to be unfounded. The factor one-half is an approximation, and depends on an arbitrary adjustment (mainly through temperature control) of the sensitivity of the end-point of the titration, *i.e.*, it depends on an adjusted relation between the minimum concentration of disulphuric acid required to produce a visible fuming, and the basicity constant (which has the dimensions of concentration) of the hydrogen disulphate ion.

## (1) *Preliminary Statements about the Species Present in Sulphuric Acid and in Dilute Oleum.*

(1.1) *The Self-dissociation of Sulphuric Acid.*—The work to be reported was undertaken in order to obtain further information about the molecular and ionic species which are present, and about the equilibria in which they participate, in solvent sulphuric acid and in dilute sulphuric oleum. In order to simplify the following account of the relationships which the measurements reveal, it is convenient to commence with some statements which partly summarise results described in preceding papers, but partly also anticipate, or indicate, findings established later in this paper.

The rounding of the freezing-point curve of the system $H_2O$–$SO_3$ at compositions in the neighbourhood of $H_2SO_4$ was discussed in Part II (*J.*, 1950, 2493). It shows that sulphuric acid is considerably self-dissociated. Undoubtedly the self-dissociation is partly an autoprotolysis. The products of this process are the sulphuric acidium ion and the hydrogen sulphate ion :

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The process is thus quite analogous to the autoprotolyses that occur in other solvents, such as water and ammonia.

A part of the process of self-dissociation of sulphuric acid must, however, arise from the self-dehydration of the sulphuric acid to sulphur trioxide and water, each of which reacts with sulphuric acid to produce ions, as already described in Part II :

$$\left.\begin{array}{r}H_2SO_4 = H_2O + SO_3\\ H_2SO_4 + SO_3 = H_2S_2O_7\\ H_2SO_4 + H_2S_2O_7 = H_3SO_4^+ + HS_2O_7^-\\ H_2SO_4 + H_2O = H_3O^+ + HSO_4^-\end{array}\right\} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Qualitatively, the formation of sulphur trioxide is indicated by the fuming of pure sulphuric acid just above room temperature (cf. Brand, *J.*, 1946, 585). The formation of disulphuric acid from sulphur trioxide and sulphuric acid is well established, and so also are the ionisations of disulphuric acid and of water.

It will be shown later that sulphur trioxide and sulphuric acid can combine in molecular ratios other than 1 : 1, and that they are thus able to produce a whole series of ionising polysulphuric acids. However, these more complex ionogenic reactions of sulphur trioxide are not important at the low concentrations which are relevant to the self-dissociation of pure sulphuric acid. Furthermore, in the approximation to which one is limited by other considerations, it may be taken that, in accordance with equations (2), disulphuric acid is completely ionised as an acid, and water is completely ionised as a base, at the concentrations in which these substances are formed by self-dissociation. It follows that equations (2) can be reduced to the following approximate form :

$$2H_2SO_4 = H_3O^+ + HS_2O_7^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

In this approximation, the total self-dissociation of sulphuric acid can therefore be described by means of two equilibrium constants corresponding to equations (1) and (3). They are the autoprotolysis constant,

$$K_{ap} = [H_3SO_4^+][HSO_4^-]$$

and the ionic self-dehydration constant,

$$K_{id} = [H_3O^+][HS_2O_7^-]$$

It was established in Part II that, in pure sulphuric acid at its freezing point, the total concentration of all the products of dissociation is 0·43 molal, *i.e.*, enough to lower the freezing point by 0·26°. In Part I it was shown that the products of the autoprotolysis alone lower the freezing point by 0·16°; and hence it can be concluded that the concentration of the products of the self-dehydration is sufficient to cause a freezing-point lowering of 0·10°. The total self-dissociation is thus analysed into the following parts, and the manner in which they contribute to the lowering of the freezing point from 10·62°, as estimated for non-dissociated sulphuric acid, to the actual freezing point, 10·36°, of the self-dissociated acid in equilibrium, is as shown :

$[H_3SO_4]^+ = [HSO_4^-] = 0{\cdot}013$ molal. Total 0·026 molal. Depression 0·16°.
$[H_3O^+] = [HS_2O_7^-] = 0{\cdot}0083$ molal. Total 0·017 molal. Depression 0·10°.
All products of self-dissociation . . . 0·043 molal. Depression 0·26°.

From these data, we can calculate the following values for the autoprotolysis constant and the ionic self-dissociation constant, at the freezing point of pure sulphuric acid, 10·36° :

$$K_{ap} = 0{\cdot}00017 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$
$$K_{id} = 0{\cdot}00007 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

The present experiments were designed independently to confirm these conclusions concerning the self-dissociation. Although the phenomena which provide the basis for the analysis to be described are observed in combination with effects arising from the formation and ionisation of higher polysulphuric acids, the desired confirmation has been secured. (We shall find it convenient, for the purpose of illustrating computing procedures, to utilise the above estimates of the autoprotolysis and ionic self-dehydration constants, even though we shall later derive the same values for these two quantities in an independent way.)

(1.2) *The Species present in Dilute Oleum.*—The known phase-diagram for the system $H_2O$–$SO_3$ indicates the existence of only one solid phase having a composition intermediate between that of sulphuric acid and that of sulphur trioxide, *viz.*, disulphuric acid, $H_2S_2O_7$. On this account it has usually been assumed that sulphur trioxide in solution in sulphuric acid is largely converted into disulphuric acid.

As to dilute solutions of sulphur trioxide in sulphuric acid, this is undoubtedly true. In Part II it was found that a provisional first ionisation constant of disulphuric acid could be calculated if it were assumed that, at concentrations of the order of 0·1 molal, sulphur trioxide is converted almost entirely into disulphuric acid, and that, at such concentrations, only the first ionisation constant of this acid is of importance.

However, it will here be shown that this description provides only an approximate account of the behaviour of such solutions. Certainly, solutions in sulphuric acid of sulphur trioxide in concentrations of the order of 0·1 molal or somewhat stronger contain mainly disulphuric acid in its molecular and ionic forms; but such solutions also contain appreciable proportions of higher polysulphuric acids, notably trisulphuric acid, $H_2S_3O_{10}$, and tetrasulphuric acid, $H_2S_4O_{13}$. These acids belong to the series $H_2O(SO_3)_n$, concerning which little information has hitherto been available, except in relation to the first two members, sulphuric and disulphuric acids.

With regard to its first ionisation, disulphuric acid is an acid of moderate strength in solvent sulphuric acid (cf. Part II). Still with reference to first ionisations, we must, on general electrostatic grounds, expect the higher polysulphuric acids to be rather stronger acids than disulphuric acid. In Part II it was shown that disulphuric acid, at concentrations of the order of 0·1 molal in sulphuric acid, is considerably ionised with respect to its first stage of ionisation. It is established in this paper that the higher polysulphuric acids, which are present in such solutions, are ionised quite largely with respect to their first stages of ionisation, and are even further ionised as noted below.

On general electrostatic grounds, we must expect that, as the chain $\cdot[SO_2\cdot O]_n\cdot$ lengthens in a higher polysulphuric acid, *i.e.*, as $n$ increases, the second ionisation constant of the acid will rapidly become more nearly comparable to the first. The second ionisation constant of disulphuric acid is undoubtedly much smaller than the first; for we have no evidence that any appreciable proportion of the normal disulphate ion can coexist with molecular disulphuric acid. On the other hand, it will be shown that at least some of the polysulphuric acids which are present in dilute oleum, notably trisulphuric acid and tetrasulphuric acid, are considerably ionised with respect to both their stages of acidic ionisation.

### (2) *Freezing Point of Solutions of Ammonium Sulphate in Dilute Oleum. Solvolysis of the Hydrogen Disulphate Ion. Formation and Ionisation of Polysulphuric Acids.*

(2.1) *The ν-Factors of Ammonium Hydrogen Disulphate.*—In the experiments now to be described, the freezing point was measured as successive portions of ammonium sulphate were added to dilute oleums of various initial strengths. Ammonium sulphate is completely ionised (cf. Part I, *J.*, 1950, 2473) in sulphuric acid, according to the following equation :

$$(NH_4)_2SO_4 + H_2SO_4 = 2NH_4^+ + 2HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

As an initial simplification, we assume that the sulphur trioxide, which with sulphuric acid composes the oleum, is present entirely as disulphuric acid, which is ionising as an acid according to the following balanced reaction :

$$H_2S_2O_7 + H_2SO_4 = HS_2O_7^- + H_3SO_4^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Then the first effect of the added salt must be to destroy the sulphuric acidium ion $H_3SO_4^+$ by combination with hydrogen sulphate ion (cf. equation 1), and thus to replace the former ion by its equivalent of ammonium ion. When 0·5 mol. of ammonium sulphate has been added for every original mol. of disulphuric acid, then stoicheiometrically sufficient hydrogen sulphate ions will have been produced to secure the conversion of the whole of the disulphuric acid into ammonium hydrogen disulphate. The reaction may be formulated as a simple acid-to-base proton-transfer :

$$H_2S_2O_7 + HSO_4^- = HS_2O_7^- + H_2SO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

The solution now has the analytical composition of a solution of ammonium hydrogen disulphate in sulphuric acid, whether reaction (6) goes to completion or not. If reaction (6) were to proceed to completion, then the solution would contain two ions, the ammonium ion and the hydrogen disulphate ion, for every stoicheiometric molecule of ammonium hydrogen disulphate, *i.e.*, it would contain two ions for every original stoicheiometric molecule of disulphuric acid, or of sulphur trioxide.

Our interest at present is in the lack of completeness of reaction (6). Any such lack of completeness constitutes a partial solvolysis of the hydrogen disulphate ion—its acceptance of a proton from the solvent. The effect of the solvolysis on the total solutes is to replace a hydrogen disulphate ion by a disulphuric acid molecule and a hydrogen sulphate ion, *i.e.*, to replace one solute particle by two. Hence the effect is to create in the solution a total of more than two solute particles for every original stoicheiometric molecule of disulphuric acid. A quantitative solvolysis would produce a total of three solute particles for each molecule of disulphuric acid.

TABLE I.

*Freezing point of solutions of ammonium sulphate in dilute oleum.*

| Weight (g.). | | | | | Molality. | | F. p. (° c.). |
|---|---|---|---|---|---|---|---|
| Solution. | $Am_2SO_4$. | $H_2SO_4$. | $H_2S_2O_7$. | $AmHS_2O_7$. | $H_2S_2O_7$. | $AmHS_2O_7$. | |
| *Expt.* 10 * : | | | | | | | |
| — | — | 109·13 | 4·273 | — | 0·2200 | — | 8·860 |
| 0·410 | 0·0789 | 109·50 | 4·077 | 0·2334 | 0·2092 | 0·0108 | 8·858 |
| 0·558 | 0·1864 | 110·02 | 3·805 | 0·5506 | 0·1943 | 0·0257 | 8·849 |
| 0·815 | 0·3432 | 110·47 | 3·397 | 1·104 | 0·1728 | 0·0452 | 8·805 |
| 0·715 | 0·4879 | 111·08 | 3·028 | 1·435 | 0·1531 | 0·0669 | 8·755 |
| 1·030 | 0·6861 | 112·40 | 2·546 | 2·027 | 0·1273 | 0·0927 | 8·677 |
| 0·994 | 0·8758 | 113·41 | 2·072 | 2·587 | 0·1027 | 0·1173 | 8·572 |
| 1·079 | 1·083 | 114·30 | 1·547 | 3·200 | 0·0755 | 0·1445 | 8·451 |
| 0·958 | 1·267 | 115·18 | 1·083 | 3·743 | 0·0526 | 0·1674 | 8·307 |
| 1·065 | 1·473 | 116·37 | 0·576 | 4·352 | 0·0277 | 0·1923 | 8·159 |
| 1·065 | 1·678 | 117·13 | 0·047 | 4·958 | 0·0032 | 0·2178 | 7·983 |
| | | | | $AmHSO_4$. | | $AmHSO_4$. | |
| 1·050 | 1·880 | 117·95 | 0·000 | 0·322 | 0·0000 | 0·0283 | 7·795 |
| 1·637 | 2·190 | 119·04 | 0·000 | 0·862 | 0·0000 | 0·0630 | 7·478 |
| 1·654 | 2·504 | 120·14 | 0·000 | 1·409 | 0·0000 | 0·1020 | 7·153 |
| *Expt.* 11 † : | | | | | | | |
| | | | | $AmHS_2O_7$. | | $AmHS_2O_7$. | |
| — | — | 103·81 | 7·354 | — | 0·3980 | — | 7·660 |
| 0·750 | 0·1443 | 104·49 | 6·908 | 0·4265 | 0·3713 | 0·0267 | 7·678 |
| 1·626 | 0·4572 | 105·84 | 6·250 | 1·351 | 0·3318 | 0·0662 | 7·679 |
| 2·978 | 1·030 | 108·60 | 4·862 | 3·044 | 0·2514 | 0·1466 | 7·539 |
| 2·306 | 1·474 | 110·68 | 3·790 | 4·355 | 0·1924 | 0·2056 | 7·351 |
| 4·269 | 2·295 | 114·50 | 1·798 | 6·783 | 0·0809 | 0·3090 | 6·844 |
| 3·464 | 2·962 | 117·60 | 0·188 | 8·751 | 0·0090 | 0·3890 | 6·541 |
| $H_2O$ added. | | | $H_2O$. | | $H_2O$. | | |
| 0·682 | ,, | 118·15 | 0·063 | — | 0·0295 | — | 6·429 |
| 0·088 | ,, | 118·63 | 0·151 | — | 0·0767 | — | 6·498 |
| 0·243 | ,, | 119·95 | 0·394 | — | 0·1824 | — | 6·520 |
| 0·298 | ,, | 121·58 | 0·692 | — | 0·3162 | — | 6·311 |
| 0·166 | ,, | 122·48 | 0·858 | — | 0·3893 | — | 5·891 |
| *Expt.* 12 ‡ : | | | | | | | |
| Soln. added. | | | $H_2S_2O_7$. | | $H_2S_2O_7$. | | |
| — | — | 104·56 | 4·281 | — | 0·2300 | — | 8·800 |
| 2·867 | 0·6249 | 107·00 | 2·682 | 1·866 | 0·1408 | 0·0892 | 8·618 |
| 3·874 | 1·469 | 110·43 | 0·527 | 4·341 | 0·0281 | 0·2019 | 8·027 |
| $H_2O$ added. | | | $H_2O$. | | $H_2O$. | | |
| 0·066 | ,, | 111·01 | 0·0027 | — | 0·0014 | — | 8·125 |
| 0·056 | ,, | 111·33 | 0·0587 | — | 0·0293 | — | 8·200 |
| 0·106 | ,, | 111·91 | 0·165 | — | 0·0819 | — | 8·283 |
| 0·080 | ,, | 112·34 | 0·245 | — | 0·1212 | — | 8·303 |
| 0·108 | ,, | 112·93 | 0·353 | — | 0·1737 | — | 8·248 |
| 0·111 | ,, | 112·93 | 0·464 | — | 0·2283 | — | 7·877 |
| 0·112 | ,, | 112·93 | 0·576 | — | 0·2834 | — | 7·273 |

* Ammonium sulphate was added as a solution in the original oleum solvent. The weights in the first column are those of the added solution. The composition of the solution used for the first 11 additions was as follows: 22·735 g. of oleum; 5·420 g. of $Am_2SO_4$. The last 2 additions were made with a solution of the following composition: 30·887 g. of oleum; 7·231 g. of $Am_2SO_4$.

† The weights in col. 1 (first six entries) are those of an added solution of ammonium sulphate in the original oleum. The composition of this solution was as follows: 25·575 g. of oleum; 6·095 g. of $Am_2SO_4$.

‡ The added solution (col. 1) had the following composition: 25·235 g. of original oleum; 7·032 g. of $Am_2SO_4$.

TABLE I.—*continued.*

| Weight (g.). | | | | | Molality. | | |
|---|---|---|---|---|---|---|---|
| $Am_2SO_4$ added. | $Am_2SO_4$ total. | $H_2SO_4$. | $H_2S_2O_7$. | $AmHS_2O_7$. | $H_2S_2O_7$. | $AmHS_2O_7$. | F. p. (° c.). |
| *Expt.* 104 : | | | | | | | |
| — | — | 123·63 | 3·6784 | — | 0·1670 | — | 9·238 |
| 0·1394 | 0·1394 | 123·73 | 3·298 | 0·4120 | 0·1498 | 0·0272 | 9·203 |
| 0·1569 | 0·2963 | 123·85 | 2·875 | 0·8755 | 0·1304 | 0·0766 | 9·157 |
| 0·4341 | 0·7304 | 124·17 | 1·705 | 2·158 | 0·0771 | 0·0899 | 8·963 |
| 0·5144 | 1·2448 | 124·55 | 0·317 | 3·677 | 0·0143 | 0·1527 | 8·596 |
| | | | | $AmHSO_4$ | | $AmHSO_4$ | |
| 0·1696 | 1·3144 | 124·59 | 0·000 | 0·0906 | 0·0000 | 0·0063 | 8·443 |
| 0·1966 | 1·5210 | 124·45 | ,, | 0·4322 | ,, | 0·0303 | 8·242 |
| 0·2742 | 1·7952 | 124·24 | ,, | 0·7110 | ,, | 0·0638 | 7·949 |
| *Expt.* 105 : | | | | $AmHS_2O_7$. | | $AmHS_2O_7$. | |
| — | — | 117·84 | 3·316 | — | 0·1580 | — | 9·328 |
| 0·2695 | 0·2695 | 118·04 | 2·589 | 0·6962 | 0·1232 | 0·0348 | 9·258 |
| 0·7545 | 1·0240 | 118·60 | 0·555 | 3·024 | 0·0263 | 0·1317 | 8·787 |
| | | | | $AmHSO_4$. | | $AmHSO_4$. | |
| 0·3884 | 1·4124 | 118·61 | 0·000 | 0·3181 | 0·0000 | 0·0233 | 8·407 |
| 0·3290 | 1·7414 | 118·37 | ,, | 0·8912 | ,, | 0·0655 | 8·030 |
| 0·2719 | 2·0133 | 118·17 | ,, | 1·365 | ,, | 0·1004 | 7·697 |
| *Expt.* 106 : | | | | $AmHS_2O_7$. | | $AmHS_2O_7$. | |
| — | — | 126·84 | 3·230 | — | 0·1430 | — | 9·409 |
| 0·5971 | 0·0571 | 127·28 | 1·620 | 1·764 | 0·0715 | 0·0715 | 9·183 |
| 0·2315 | 0·8286 | 127·45 | 0·996 | 2·448 | 0·0439 | 0·0991 | 9·039 |
| 0·1291 | 0·9577 | 127·55 | 0·648 | 2·830 | 0·0285 | 0·1145 | 8·950 |
| $H_2O$ added. | | | | | | | |
| 0·0358 | 0·9577 | 127·94 | 0·294 | — | 0·0129 | — | 9·015 |
| | | | $H_2O$. | | $H_2O$. | | |
| 0·0683 | ,, | 128·47 | 0·0386 | — | 0·0166 | — | 9·115 |
| 0·0654 | ,, | 128·83 | 0·1040 | — | 0·0448 | — | 9·189 |
| 0·0659 | ,, | 129·19 | 0·1699 | — | 0·0731 | — | 9·230 |
| 0·0830 | ,, | 129·64 | 0·2529 | — | 0·1083 | — | 9·194 |
| 0·0824 | ,, | 130·08 | 0·3353 | — | 0·1432 | — | 8·933 |
| 0·1169 | ,, | 130·72 | 0·4522 | — | 0·1922 | — | 8·386 |

Before considering the experimental evidence on this matter, let us note that there is an alternative cause which could lead to the appearance of more than two solute particles for each original molecule of disulphuric acid. Such a result could arise, not only if the hydrogen disulphate ion received a proton from the solvent, but also if it donated a proton to the solvent :

$$HS_2O_7^- + H_2SO_4 = S_2O_7^{--} + H_3SO_4^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

However, it will be shown in Sections 2.3 and 3.1 that such an interpretation cannot be entertained. For a body of evidence exists to the effect that the hydrogen disulphate ion can transfer its proton only to a quite limited extent even to the hydrogen sulphate ion, which is the strongest base that can be supplied in any considerable concentration in solvent sulphuric acid. Therefore it is inconceivable that the hydrogen disulphate ion should transfer its proton to the sulphuric acid molecule to such an extent that the normal disulphate ion and the sulphuric acidium ion would have to co-exist each in appreciable concentration.

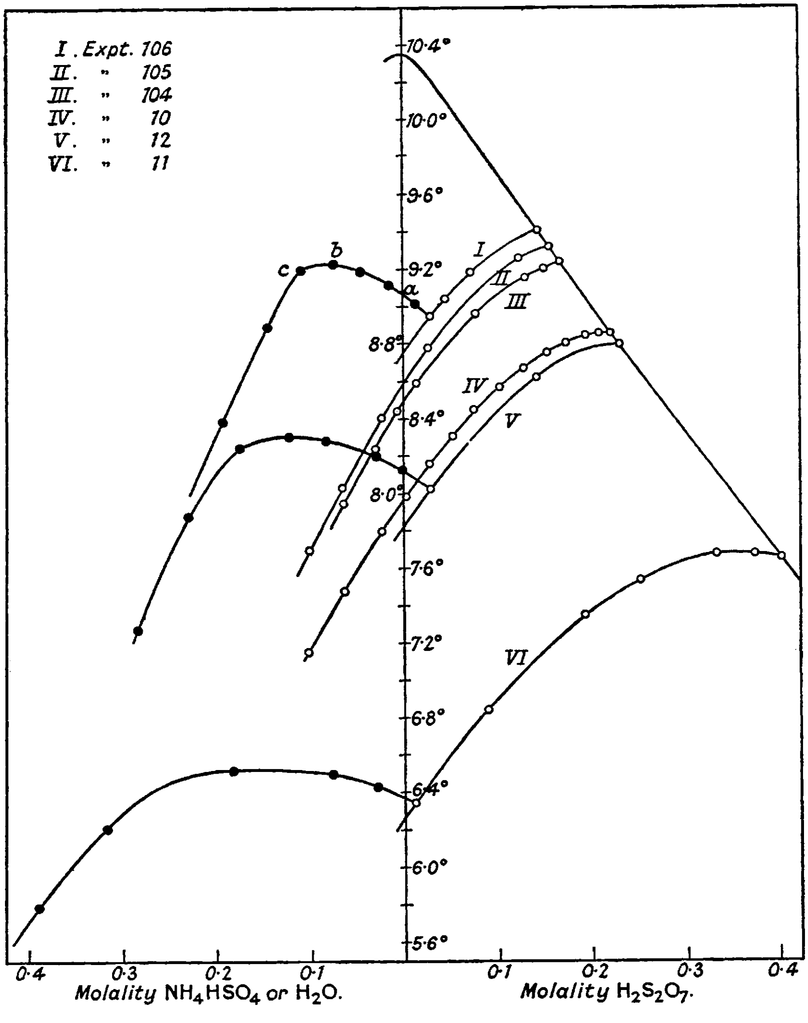
Table I contains the record of such cryoscopic observations as are required for the discussion given in Sections 2 and 3 of this paper.

These results are represented in Fig. 1. On the right-hand side (" acidic " side) of the central line, freezing points are plotted against the molality of disulphuric acid, calculated on the assumption that all the sulphur trioxide, which with sulphuric acid composes the oleum, is present in this form. The vertical line (" neutral " line) corresponds to the composition of the solvent sulphuric acid, or of solutions, in that solvent, whose compositions can be expressed entirely in terms of " neutral " salts, such as ammonium hydrogen disulphate. On the left-hand side (" basic " side) of the neutral line, the freezing points are plotted against the molality of hydrogen sulphate ion, calculated on the assumption that it is produced in a completed reaction between the solvent and either added ammonium sulphate or added water; and that it is destroyed in a completed reaction with any disulphuric acid originally present (cf. equation 6).

The freezing points of the original oleums, to which successive amounts of ammonium sulphate were added in the different experiments, are shown upon the nearly straight curve which slopes downward towards the right in Fig. 1 (cf. Fig. 1 of Part II, where the same curve is on the left of the diagram). The effect of the added ammonium sulphate on the freezing point is shown by the curves which, starting out from the nearly straight curve, slope generally downward towards the left, though with an initial bend-over, the significance of which will be considered in Section 2.2.

FIG. 1.

*Freezing points of solutions of ammonium sulphate in dilute oleums.*



● *Freezing points after the addition of* $H_2O$. ○ *Freezing points after the addition of* $(NH_4)_2SO_4$.

In some experiments, ammonium sulphate was added in quantity more than sufficient to react with all the original stoicheiometric disulphuric acid. In other experiments the ammonium sulphate was added in rather less than the amount necessary for this reaction, and then the excess of disulphuric acid was removed by adding water, and the addition of water was continued further. The water curves are those which, starting from points just to the right of the neutral line, slope upwards to the left, then pass through a maximum, and then descend; curves like these have previously been obtained by Poma (*J. Chim. physique*, 1912, **10**, 177).

We shall consider first the points at which the various curves cut the neutral line. At these points the solutions all have the analytical compositions of solutions of ammonium hydrogen disulphate. At the points at which the ammonium sulphate curves, produced if necessary, cut the neutral line, the molality of the ammonium hydrogen disulphate is equal to that of the stoicheiometric disulphuric acid in the initially employed oleum. At the points at which water curves cut the neutral line, the molality of the ammonium hydrogen disulphate is equal to that of such of the original disulphuric acid as was destroyed by the added ammonium sulphate. The molalities and freezing points of all these solutions of ammonium hydrogen disulphates are assembled in Table II.

TABLE II.

*Freezing points of solutions of ammonium hydrogen disulphate.*

| Expt. no. | F. p. (° c.). | Molality ($\Delta m$). | Depression ($\Delta\theta'$). | $\nu'$. | Depression ($\Delta\theta''$). | $\nu''$. |
|---|---|---|---|---|---|---|
| 106 | 9·06 | 0·115 | 1·56° | 2·27 | 1·48° | 2·14 |
| | 8·74 | 0·143 | 1·88 | 2·19 | 1·81 | 2·10 |
| 105 | 8·59 | 0·158 | 2·03 | 2·15 | 1·97 | 2·08 |
| 104 | 8·48 | 0·167 | 2·14 | 2·14 | 2·08 | 2·07 |
| 12 | 8·12 | 0·202 | 2·50 | 2·07 | 2·45 | 2·02 |
| | 7·83 | 0·230 | 2·79 | 2·03 | 2·74 | 1·99 |
| 10 | 7·97 | 0·240 | 2·65 | 2·02 | 2·60 | 1·98 |
| 11 | 6·37 | 0·389 | 4·25 | 1·84 | 4·21 | 1·82 |
| | 6·28 | 0·398 | 4·34 | 1·84 | 4·30 | 1·82 |

In this Table, a series of freezing-point depressions $\Delta\theta'$, are entered, which are computed with reference to the freezing point, 10·62°, which the pure solvent would have if it did not undergo self-dissociation (Part II, *J.*, 1950, 2493). However, the solvent actually suffers two forms of self-dissociation, one of which, the ionic self-dehydration, is easily shown to be almost competely suppressed by the amounts of hydrogen disulphate ions present in the solutions under consideration. The other is the autoprotolysis, and it will be shown that this is only partly repressed by the smaller amounts of hydrogen sulphate ions, which arise in the same solutions by solvolysis of the hydrogen disulphate ions. Part of the depression, $\Delta\theta'$, is due to the surviving autoprotolytic ions, and this must be calculated and deducted, in order to obtain the depression due to the added solute.

The calculation of this correction requires a knowledge of the solvolysis constant of the hydrogen disulphate ion, which is one of the data we wish to extract from the results, and also of the autoprotolysis constant of the solvent, which quantity we hope to derive with the help of the solvolysis constant. It is therefore necessary to start with rough estimates of these quantities and proceed by successive cycles of approximation. In illustration of the method we may take the following value of the solvolysis constant, *viz.*,

$$K_b(\mathrm{HS_2O_7^-}) = [\mathrm{H_2S_2O_7}][\mathrm{HSO_4^-}]/[\mathrm{HS_2O_7^-}] = 0{\cdot}008 \text{ g.-mol. kg.}^{-1}$$

and the already quoted estimate of the autoprotolysis constant, *viz.*,

$$K_{ap} = [\mathrm{H_3SO_4^+}][\mathrm{HSO_4^-}] = 0{\cdot}00017 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

From these values one can compute, for instance, that a 0·115 molal solution of ammonium hydrogen disulphate (cf. Table II, top line) is 0·030 molal with respect to hydrogen sulphate ion, and that, in consequence, the total concentration of surviving autoprotolytic ions is 0·012 molal, *i.e.*, enough to lower the freezing point by 0·07°. A further small correction of 0·01° has to be made in respect of the self-dehydration ions. The depression due to self-dissociation ions at the other investigated concentrations of ammonium hydrogen disulphate are similarly calculated, and, by subtracting the derived values from the depressions $\Delta\theta'$, the corrected depressions $\Delta\theta''$, listed in Table II, are obtained, which are attributable entirely to the added solute.

From the depressions $\Delta\theta'$ and $\Delta\theta''$, the $\nu$-factors for ammonium hydrogen disulphate, $\nu'$ and $\nu''$ respectively, have been calculated, using equation (4) of Part I (*J.*, 1950, 2473), with the values, $\nu_2 = 2$, $s_2 = 1$, and $m_3 = 0$, substituted in the nearly-unit correction factor. The substitution $s_2 = 1$ assumes the solvation number of ammonium hydrogen disulphate to be the same as that of ammonium hydrogen sulphate, namely, one (Part I, *loc. cit.*).

Both sets of $\nu$-factor are given in Table II, because the $\nu''$ values are, in principle at least, and probably in practice, over-corrected, though it is difficult to estimate the error. The reason for the error is that the solutions must contain, besides such hydrogen sulphate ion as is derived from the solvolysis of the hydrogen disulphate ion, some additional hydrogen sulphate ion arising from the formation and partial solvolysis of the anions of the higher polysulphuric acids, a matter which is next to be considered. This extra hydrogen sulphate ion will reduce the concentration of surviving autoprotolytic ions, thus rendering our correction too large.

At the lowest concentrations of ammonium hydrogen disulphate the ν-factors rise above 2, thus indicating a certain amount of solvolysis of the anion. At the higher concentrations, however, the ν-factors fall below 2, and we have to consider the significance of this effect. It cannot be due to electrostatic non-ideality, because such effects have been shown to be negligible by means of a comparison of non-electrolytic and electrolytic solutions (Part I, *J.*, 1950, 2473); and non-ideality effects due to solvation have already been taken into account. Therefore it must be concluded that the low ν-values are real, and that, in the more concentrated solutions, each molecule of ammonium hydrogen disulphate actually does produce an average of less than two solute particles. Since it is not conceivable that the ammonium ion undergoes any change, we have to accept the alternative that two or more hydrogen disulphate ions interact in some way to give a more complex multiple charged ion, perhaps together with a solvent molecule. The simplest possibility involves the transfer of a sulphur trioxide molecule from one hydrogen disulphate ion to another, followed by the transfer of a proton from the formed hydrogen trisulphate ion (which is expected to be an acid of considerable strength—cf. Section 1.2 to the basic hydrogen sulphate ion :

$$\left.\begin{aligned} 2HS_2O_7^- &= HS_3O_{10}^- + HSO_4^- \\ HS_3O_{10}^- + HSO_4^- &= S_3O_{10}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (8)$$

Any incompleteness in the second stage of this process constitutes a solvolysis of the trisulphate ion, with the formation of such extra hydrogen sulphate ion as that to which reference was made above in connexion with the probable over-correction of the freezing points for the suppression of solvent dissociation.

The next simplest possibility involves the formation of the ions of tetrasulphuric acid from three hydrogen disulphate ions :

$$\left.\begin{aligned} 3HS_2O_7^- &= HS_4O_{13}^- + 2HSO_4^- \\ HS_4O_{13}^- + HSO_4^- &= S_4O_{13}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (9)$$

Further condensations after this pattern are in principle possible. We cannot yet analyse the processes in detail, but we must, for reasons based on the mass law, expect all such equilibria to shift in the direction favouring anions of higher polysulphuric acids as the stoicheiometric concentration of ammonium hydrogen disulphate is increased. Furthermore, we must expect, not only on account of the mass law which alone would require the result, but also because higher polysulphuric acids should be stronger acids than lower, especially with respect to second stages of dissociation, that there will be a general shift towards doubly charged anions as the stoicheiometric concentration of the amonium salt is increased. This, then, is the qualitative interpretation of the observed fall in the ν-factors with increasing concentrations of the salt.

We can now proceed to the evaluation of the solvolysis constant of the hydrogen disulphate ion. From the above discussion it is clear that, if we could employ ν″ values for such low concentrations that trisulphates and higher polysulphate were completely absent, we could determine the solvolysis constant from the ordinary mass-law expression, which can thus be written in the form of a limit, as follows, $\Phi_0$ being simply an abbreviation for the explicit function on the right :

$$K_b(HS_2O_7^-) = \lim_{\Delta m \to 0} \{\Phi_0\} = \lim_{\Delta m \to 0} \{(\nu'' - 2)^2 \Delta m/(3 - \nu'')\}$$

In this formula ν″ is a function of $\Delta m$, the molality of the ammonium hydrogen disulphate; and it rises to 3 as $\Delta m$ approaches zero, independently of any effect due to higher polysulphuric acids. Thus ν″ is not a suitable quantity for extrapolation to low concentrations on the basis of the data of Table II. Even the expression $\Phi_0$ is not convenient for extrapolation, owing to the strong variation in this function, which is caused by the disturbance due to the higher acids. However, we can derive an expression more suitable for extrapolation by enquiring in what form the deviation of the function from constancy should first appear when, on proceeding from very dilute towards slightly more concentrated solutions, the ions of the higher polysulphuric acids begin to be formed.

The first disturbance to ν″, which should arise from the formation of the higher acids, has reference to the equilibrium

$$2HS_2O_7^- = S_3O_{10}^{--} + H_2SO_4$$

the constant of which, $[S_3O_{10}^{--}]/[HS_2O_7^-]^2$, we will call $\alpha$. Supposing the conversion to be small, the fraction of ammonium hydrogen disulphate converted into the doubly charged ion will be $2\alpha\Delta m$, and this will be equal to twice that lowering of $\nu''$ which results from the establishment of the equilibrium. Hence the initial deviation of $\Phi_0$ is to be corrected by simply adding $\alpha\Delta m$ to $\nu''$. Accordingly, we may set up the following more general expression for the solvolysis constant

$$K_b(HS_2O_7^-) = \lim_{\Delta m \to 0} \{\Phi_a\} = \lim_{\Delta m \to 0} \{(\nu'' + a\Delta m - 2)^2 \Delta m/(3 - \nu'' - a\Delta m)\}$$

With a correct choice of $\alpha$, the genalised function $\Phi_a$ should remain constant up to concentrations at which either the conversion into the trisulphate ion is no longer small, or the formation of the tetrasulphate ion is beginning to become important. All choices of $\alpha$ should lead to the same limit, provided that the function varies slowly enough at low concentrations to be extrapolated. In Table III values of $\Phi_a$ are given which are calculated from the data of Table II for three different choices of $\alpha$. All three functions, despite their strong divergence at the higher concentrations, extrapolate to the same low-concentration limit of $10^3 K_b = 8 \cdot 0$ g.-mol. kg.$^{-1}$.

TABLE III..

*Values of $\Phi_a$ leading to the solvolysis constant of the hydrogen disulphate ion.*

| $\Delta m$. | $\nu''$. | $10^3\Phi_{0\cdot6}$. | $10^3\Phi_{0\cdot8}$. | $10^3\Phi_{1\cdot0}$. | $\Delta m$. | $\nu''$. | $10^3\Phi_{0\cdot6}$. | $10^3\Phi_{0\cdot8}$. | $10^3\Phi_{1\cdot0}$. |
|---|---|---|---|---|---|---|---|---|---|
| 0·115 | 2·14 | 6·4 | 7·9 | 9·7 | 0·230 | 1·99 | 4·5 | 8·0 | 14·2 |
| 0·144 | 2·10 | 5·8 | 8·0 | 11·0 | 0·220 | 1·98 | 3·0 | 5·7 | 11·0 |
| 0·158 | 2·08 | 6·3 | 8·9 | 12·1 | 0·389 | 1·82 | 1·0 | 5·2 | 21·2 |
| 0·168 | 2·07 | 6·8 | 9·5 | 12·5 | 0·398 | 1·82 | 1·2 | 5·4 | 21·4 |
| 0·202 | 2·02 | 4·7 | 8·1 | 12·4 | | | | | |

Obviously the equilibrium constant $\alpha$ is in the neighbourhood of 0·8 g.-mol.$^{-1}$ kg. This means that, in a 0·1 molal solution of ammonium hydrogen disulphate, about 14% of the salt is converted into 7 mols. % of ammonium trisulphate.

(2.2) *Initial Effect of Ammonium Sulphate on the Freezing Point of Oleum.*—The presence of higher polysulphate ions in solutions of ammonium hydrogen disulphate implies the presence, along with disulphuric acid, of higher polysulphuric acids in oleum; for the production, by the addition of ammonium sulphate to oleum, of the various anions represented in equations (8) and (9), can evidently be represented as a progressive removal of protons, by the basic hydrogen sulphate ion, from molecules of the appropriate polysulphuric acids, *e.g.*,

$$\left.\begin{aligned} H_2S_3O_{10} + HSO_4^- &= HS_3O_{10}^- + H_2SO_4 \\ HS_3O_{10}^- + HSO_4^- &= S_3O_{10}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The anions being present, these equilibria must be set up, and hence the acids must be present, ionised or otherwise; for the question of the extent to which the anions are solvolysed is just that of the extent to which the acids are ionised.

These higher polysulphuric acids must participate in equilibria such as the following:

$$\left.\begin{aligned} 2H_2S_2O_7 &= H_2S_3O_{10} + H_2SO_4 \\ 3H_2S_2O_7 &= H_2S_4O_{13} + 2H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

On account of the mass law, such equilibria must shift in the direction favouring higher polysulphuric acids in stronger oleums.

It is possible on these ground to understand the peculiar effect of small amounts of added ammonium sulphate on the freezing points of oleums of different strengths. Reference to Fig. 1 (p. 2521) shows that all the ammonium sulphate curves start towards the left with a smaller downward slope than that which they acquire after a considerable quantity of ammonium sulphate has been added; and also that this reduced initial downward slope becomes still smaller as the strength of the original oleum becomes greater, even changing sign in the example of the strongest of the oleums, the ammonium sulphate curve for which rises initially.

The interpretation is as follows. We assume it to be a sufficient description of the limiting situation in very dilute oleum that only disulphuric acid and its ions are present. In this case the first effect of added ammonium sulphate will be to destroy the cation of the ionised acid, and thus to replace it by ammonium ion; and then, in order to restore the ionic equilibrium, some more molecular disulphuric acid will become ionised, a process which will increase the number of solute particles. In more concentrated oleum, a certain amount of trisulphuric acid will be present; and, as this is expected to be a stronger acid than disulphuric acid, it will tend to be destroyed first by the basic hydrogen sulphate ion. The effect of added ammonium sulphate on trisulphuric acid and its ions will be exactly as described for disulphuric acid, except that the loss of molecular trisulphuric acid by the ionisation, which it undergoes in order to replace its destroyed cation, will be restored from the pool of disulphuric acid, in accordance with the first of equations (11). This last step involves a disappearance of solute particles, and all the steps together lead to a reduced increase, up to the limit of no net change in the total number of solute particles. Thus, if the first-added ammonium sulphate should act only on the trisulphuric acid, the freezing-point curve would start horizontally, acquiring its normal downward slope at a later stage, when the trisulphuric acid had been " neutralised " and only disulphuric acid remained in a free condition. In this way we can qualitatively account for all the mentioned effects, except the initial rise of the freezing-point curve which is observed in the case of the strongest of the oleums. An actual rise in the curve cannot be explained by any of the possible reactions of trisulphuric acid.

However, we may suppose that the most concentrated of the oleums will contain appreciable amounts of tetrasulphuric acid; and that this, as the strongest acid present, will tend to be destroyed first by added ammonium sulphate. The mechanism of its destruction will be just as for trisulphuric acid, except that, since the last step is the restoration of molecular tetrasulphuric acid according to the second of equations (11) the loss of solute particles in this step will be twice as great as before. The over-all effect of the neutralisation of tetrasulphuric acid can therefore be to reduce the number of solute particles, and thus to produce an initially rising freezing-point curve. Tetrasulphuric acid is the lowest polysulphuric acid that can produce this effect, the observation of which provides clear evidence of the existence of the acid.

The presence of these higher acids in oleum makes it necessary to reconsider the provisional estimate given in Part II (*J.*, 1950, 2493) of the acidity constant $K_a$ of disulphuric acid. The estimation was based on the measured $\nu$-factors of the acid, the excess of $\nu$ over unity being ascribed to the first stage of ionisation of the acid. However, the formation and ionisation of the higher polysulphuric acids must disturb both the factors $\nu$ and the derived constant $K_a$. The observed increase of $K_a$ with increase of concentration (cf. Part II, Table V) indicates that the effect of the higher polysulphuric acids is to increase $\nu$, and therefore to increase the apparent $K_a$ of disulphuric acid. This seems very reasonable; for the higher polysulphuric acids are likely to be stronger acids than disulphuric acid in both stages of ionisation, but especially in the second stage; and therefore the higher acids might be almost completely ionised as to the first stage, and largely ionised with respect to the second, when disulphuric acid is still only partly ionised with respect to the first stage. One way of eliminating the disturbing effect of the higher acids would be to extrapolate the apparent $K_a$ of disulphuric acid to the limit of low oleum concentrations, *i.e.*, to the limit of low proportions of the higher poly-acids among the total poly-acids. The mean " apparent " $K_a$, called $K_a'$, was given in Part II as 0·028 g.-mol. kg.$^{-1}$. It is possible to make an extrapolation of the kind suggested on the basis of the data of which a sample is recorded in Part II. The result is to show that the true $K_a$ of disulphuric acid is in the neighbourhood of 0·020 g.-mol. kg.$^{-1}$. Confirmation of this value will be offered in Section 4.1.

(2.3) *Effect of Ammonium Sulphate on the Freezing Point of Solutions of Ammonium Hydrogen Disulphate.*—We proceed now to the discussion of the slopes at the other ends of the freezing-point curves for added ammonium sulphate. Three of these curves (Expts. No. 10, 104, and 105) have been carried over to the basic side of the neutral line (cf. Fig. 1, p. 2521). On the neutral line the composition is that of a solution of ammonium hydrogen disulphate in sulphuric acid. At points to the left the composition may be expressed in terms of the concentration of the basic solute, ammonium hydrogen sulphate, which has been introduced into the solution of the " neutral " salt.

The freezing points of the most basic solutions measured in these experiments, together with the derived freezing-point depressions, and $\nu$-factors, are given in Table IV. The depressions, $\theta'$, are calculated with reference to the freezing point, 10·62°, which pure sulphuric acid would have if it were not self-dissociated. The correction of these depressions to allow for residual solvent dissociation was made as is described in connexion with Table II. The corrected values are called $\Delta\theta''$. The $\nu$-factors are calculated by means of equation (4) of Part I (*J.*, 1950, 2473), with the insertion $s_2 = 1$, $\nu_2 = 2$, and $m_3 = 0$, in the correction factor, the first of these substitutions taking account of the solvation of the ammonium salts (cf. Part I). These $\nu$-factors, called $\nu''$ in the Table, refer to total solutes, ammonium hydrogen disulphate and ammonium hydrogen sulphate. For comparison, Table IV contains the values of $\nu$ for ammonium hydrogen disulphate alone, as measured in solutions which are the same except for the absence of the excess of ammonium hydrogen sulphate (cf. Table II).

TABLE IV.

*Freezing points of solutions of mixtures of ammonium hydrogen disulphate and ammonium hydrogen sulphate.*

| Expt. no. | F. p. (° c.). | Depression. $\Delta\theta'$. | $\Delta\theta''$. | Molalities. $AmHS_2O_7$. | $AmHSO_4$. | Total. | Overall $\nu''$. | $\nu$ ($AmHS_2O_7$). |
|---|---|---|---|---|---|---|---|---|
| 104 | 7·949 | 2·67° | 2·64° | 0·167 | 0·064 | 0·231 | 1·90 | 2·07 |
| 105 | 7·697 | 2·92 | 2·90 | 0·158 | 0·100 | 0·258 | 1·86 | 2·08 |
| 10 | 7·153 | 3·47 | 3·45 | 0·220 | 0·102 | 0·322 | 1·78 | 1·98 |

In Section 2.1 it was shown that the ν-factor for ammonium hydrogen disulphate arises partly from its ionisation, which alone would give the value 2, partly from the accompanying solvolysis of the hydrogen disulphate ion, which tends to raise the value, and partly from the simultaneous conversion into higher polysulphate ions, which tends to reduce the figure. Table IV shows that the addition of ammonium hydrogen sulphate considerably reduces the over-all ν-value; and this must mean that the hydrogen sulphate ion combines with the hydrogen disulphate ion, or with its conversion products, in some way which reduces the total number of solute particles. The possibilities are all of one type, *viz.*

$$\left.\begin{aligned} HSO_4^- + HS_2O_7^- &= S_2O_7^{--} + H_2SO_4 \\ HSO_4^- + HS_3O_{10}^- &= S_3O_{10}^{--} + H_2SO_4 \\ HSO_4^- + HS_4O_{13}^- &= S_4O_{13}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (12)$$

A further indication of the extent to which such processes take place may be obtained by computing the ν-factors for the last increment of ammonium hydrogen sulphate, employing for the purpose the observations on the two most basic solutions used in each experiment. The results of these calculations are in Table V. The correction for the decrease of residual self-dissociation is here only approximate, and hence ν is given to two figures only.

TABLE V.

*Values of the ν-factor for ammonium hydrogen sulphate in solutions of this salt and of ammonium hydrogen disulphate in sulphuric acid.*

| Expt. no. | F. p. (° c.). | $\Delta\theta$ (corr.). | Molalities. $AmHS_2O_7$. | $AmHSO_4$. | $\Delta m$ ($AmHSO_4$). | $\nu$ ($AmHSO_4$). |
|---|---|---|---|---|---|---|
| 105 | 8·030<br>7·697 | 0·35° | 0·158 | 0·0655<br>0·1004 | 0·0349 | 1·7 |
| 104 | 8·242<br>7·949 | 0·32 | 0·167 | 0·0303<br>0·0638 | 0·0335 | 1·6 |
| 10 | 7·478<br>7·153 | 0·35 | 0·220 | 0·0630<br>0·1020 | 0·0390 | 1·5 |

It is immediately apparent that a large proportion, *e.g.*, one-half, of the increment of hydrogen sulphate ions becomes consumed in the reactions represented by equations (12). The most interesting point, however, is that not nearly the whole of the hydrogen sulphate ion is thus consumed. We expect theoretically (Section 1.2) that the hydrogen trisulphate and higher hydrogen polysulphate ions are rather strong acids, and we have experimental indications (Section 2) that this is so. It is therefore likely that these ions, $HS_3O_{10}^-$, $HS_4O_{13}^-$, etc., would yield up their protons rather completely to the basic hydrogen sulphate ion in the reactions indicated by equations (12). Indeed, it seems probable that they will have largely done so, before the introduction of the particular increment of hydrogen sulphate ion under consideration. Therefore the fact that this increment is only partly destroyed must mean that the next acid from which it could obtain protons, *viz.*, the hydrogen disulphate ion, $HS_2O_7^-$, which will still be present in substantial quantity, is a very weak acid.

This conclusion is confirmed in Section 3.1; and it agrees with the assumption, made at the outset of Section 2.1, that, since the hydrogen disulphate ion transfers protons only in a limited way to the basic hydrogen sulphate ion, it will be unable to transfer them to sulphuric acid molecules to any extent of which count need be taken in relation to the totality of proton transfers occurring on the acid side of the neutral line of Fig. 1. This conclusion is otherwise expressed by the statement that the second dissociation constant of disulphuric acid is much smaller than the first—in contrast to the situation apparently obtaining in the higher polysulphuric acids (cf. Section 1.2).

### (3) *Effect of Water on the Freezing Points of Solutions of Ammonium Sulphate in Oleums. Reactions involved in the Titration of Oleum Solutions with Water.*

(3.1) *Effect of Water on the Freezing Points of Solutions of Ammonium Sulphate in Oleums.*— When successive amounts of water are added to a solution having the composition of a solution of ammonium hydrogen disulphate in sulphuric acid, the freezing point at first rises, then passes through a maximum, and then descends. Let us first consider the initial rise in the freezing point, *e.g.*, the section *a*—*b* of the curve of Expt. No. 106, shown in Fig. 1.

At *a*, on the neutral line, the solute has the composition of ammonium hydrogen disulphate. We should expect the added water to replace the hydrogen disulphate ion by the hydrogen sulphate ion, a process which should not change the freezing point :

$$HS_2O_7^- + H_2O = HSO_4^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

However, at *a*, as we have seen, the $\nu$-factor rises above 2·00, essentially owing to solvolysis of the hydrogen disulphate ion :

$$HS_2O_7^- + H_2SO_4 = H_2S_2O_7 + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Nevertheless, the precise value of $\nu$ is affected by two disturbances, one due to incomplete repression of the autoprotolysis of the solvent, and the other due to the formation of some trisulphate, or other higher polysulphate, anions. The water added, and the hydrogen sulphate ion formed from it, should diminish both disturbances; and, what is more important, it should considerably repress the main reaction (14). Essentially on this last account the $\nu$-factor should fall, and the freezing point should rise.

At the freezing-point maximum *b*, it may be assumed that the solvolytic reaction (14) has been completely repressed, and that disulphuric acid molecules are absent. Since the only solutes should now be ammonium hydrogen disulphate and ammonium hydrogen sulphate, the $\nu$-factor should have fallen to 2·00. Actually the freezing point rises higher than would be calculated on this basis, the $\nu$-factor having fallen to 1·95; and still smaller $\nu$-factors are obtained from the measurements on the more concentrated solutions used in the other experiments on the effect of added water. This is indicated in Table VI, the $\nu$-factors in which are calculated from freezing-point depressions reckoned with reference to the theoretical freezing point of non-dissociated sulphuric acid, 10·62°, and then corrected as usual for residual self-dissociation.

TABLE VI.

*Values of the $\nu$-factor at the maximum freezing point obtained by adding water to solutions of ammonium sulphate in oleums.*

| Expt. | F. p. (° c.). | $\Delta\theta$ (corr.). | Molality.* | $\nu$-Factors. |
|---|---|---|---|---|
| 106 | 9·23 | 1·34° | 0·115 | 1·95 |
| 12 | 8·20 | 2·29 | 0·202 | 1·89 |
| 11 | 6·52 | 4·09 | 0·389 | 1·75 |

* Molality of ammonium ion, or *equivalent*-molality of total singly and doubly charged anions.

These reductions in the $\nu$-factors must mean that ammonium hydrogen disulphate and ammonium hydrogen sulphate are not the only solutes at the freezing-point maximum; and, indeed, that these substances have interacted, to produce a net loss of solute particles, as was discussed in Section 2.3 :

$$HS_2O_7^- + HSO_4^- = S_2O_7^{--} + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Since the hydrogen sulphate ion is the strongest base that can occur in quantity in solvent sulphuric acid, the circumstance that, in the presence of approximately equivalent amounts of the two ions, reaction (15) does not go nearly to completion is a clear indication of the weakness of the hydrogen disulphate ion as an acid in this solvent.

The decrease of the $\nu$-factor from 1·95 to 1·75 with increasing concentration is too great to be attributed solely to a mass-action effect on equilibrium (15), and it must therefore indicate the presence of higher polysulphate ions in these solutions. It has been shown that, at the neutral line, the more concentrated solutions contain considerable amounts of singly and doubly charged higher polysulphate ions : added water will desulphate these according to reactions, such as (16), which do not change the freezing point :

$$\left.\begin{aligned} \mathrm{HS_3O_{10}^-} + \mathrm{H_2O} &= \mathrm{HS_2O_7^-} + \mathrm{H_2SO_4} \\ \mathrm{S_3O_{10}^{--}} + \mathrm{H_2O} &= \mathrm{S_2O_7^{--}} + \mathrm{H_2SO_4} \\ \mathrm{HS_4O_{13}^-} + \mathrm{H_2O} &= \mathrm{HS_3O_{10}^-} + \mathrm{H_2SO_4} \\ \mathrm{S_4O_{13}^{--}} + \mathrm{H_2O} &= \mathrm{S_3O_{10}^{--}} + \mathrm{H_2SO_4} \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (16)$$

Reference to Fig. 1 will show that the rise in freezing point from the neutral line to the maximum, on adding water, is relatively small in the most concentrated solution ; and this indicates that the reactions occurring on the addition of water are, in fact, mainly (13) and (16). However, the large fall of ν-factor with increasing concentration indicates that reactions (16) are not complete at the maximum, and that these solutions contain, therefore, in addition to the hydrogen disulphate and normal disulphate ions, a certain quantity of doubly charged higher polysulphate ions.

If one continues to add water, passing beyond the freezing-point maximum until a point is reached, such as *c* in Fig. 1, at which the total amount of added water is stoicheiometrically sufficient to complete reaction (13), then disulphuric acid and both its anions should have been destroyed, as well as all higher polysulphuric acids and their anions. Thus the only surviving solute should be ammonium hydrogen sulphate ; and now the ν-factor really should be 2·00.

The result of this test is given in Table VII. The freezing-point depressions $\Delta\theta'$ are calculated with reference to the theoretical freezing point, 10·62°, of the non-dissociated solvent. The depressions $\Delta\theta''$ are corrected as usual for the repression of solvent dissociation. The resulting ν-values are labelled $\nu''$. They are equivalent to a confirmation of the value, 10·52°, deduced in Part I (*J.*, 1950, 2473) for the freezing point of self-dehydrated, but not autoprotolysed sulphuric acid. In these solutions, and especially in the more concentrated ones, the solvent is very approximately in this condition. If we calculate that solvent freezing point from which depressions should be reckoned in order that they shall give a value of exactly 2·00 to the ν-factor of ammonium hydrogen sulphate, the results are 10·53°, 10·51°, and 10·52° for Expts. No. 106, 12, and 11, respectively (mean 10·52°).

TABLE VII.

*Freezing points and ν-factors of solutions of ammonium hydrogen sulphate.*

| | | | Depression. | | |
|---|---|---|---|---|---|
| Expt. no. | F. p. (° c.). | Molality. | $\Delta\theta'$. | $\Delta\theta''$. | $\nu''$. |
| 106 | 9·16 | 0·115 | 1·46° | 1·34° | 1·95 |
| 12 | 8·09 | 0·202 | 2·53 | 2·42 | 2·01 |
| 11 | 5·89 | 0·389 | 4·73 | 4·63 | 2·00 |

If one still continues to add water, thus passing beyond points such as *c*, for which the solute is ammonium hydrogen sulphate, the freezing-point curves descend rapidly. This is because the extra water becomes ionised according to the equation

$$\mathrm{H_2O} + \mathrm{H_2SO_4} = \mathrm{H_3O^+} + \mathrm{HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

As is established in Part II (*J.*, 1950, 2493) reaction (17) is not quite complete, being governed by a definite equilibrium constant.

In two experiments the measurements were made by which ν-factors can be calculated for an increment of added water over a part of the freezing-point curve lying wholly beyond the point for which the solute is ammonium hydrogen sulphate. Even in these solutions ionic self-dehydration and autoprotolysis of the solvent are not fully repressed, and a correction for the further repression effected by the increments of water is applied in reckoning the freezing-point depressions due to the water. The derived ν-factors for the increments of water are given in the penultimate column of Table VIII. They ought to be equal to those ν-factors for water in the presence of hydrogen sulphate ions, which can be calculated from the basicity constant for water, as determined in Part II, by the methods (if they are still accurate at the highest of the concentrations now employed) already illustrated in other connexions in Part III (*J.*, 1950, 2504). The ν-factors thus computed are entered in the last column of Table VIII.

(3.2) *Reactions involved in the Titration of Oleum Solutions with Water.*—Brand (*J.*, 1946, 585, 880) has developed a method for the estimation of the stoicheiometric concentration of sulphur trioxide in solvent sulphuric acid by titration with water until, under specified conditions

TABLE VIII.

*Values of the ν-factor for water in the presence of ammonium hydrogen sulphate.*

| | | | Molalities. | | | ν ($H_2O$). | |
|---|---|---|---|---|---|---|---|
| Expt. no. | F. p. (° c.). | Δθ (corr.). | $AmHSO_4$. | $H_2O$. | Δ*m* ($H_2O$). | Found. | Calc. |
| 106 | 8·933<br>8·386 | 0·550° | 0·1145 | 0·0287<br>0·0777 | 0·0490 | 1·82 | 1·81 |
| 12 | 7·877<br>7·273 | 0·605 | 0·202 | 0·0263<br>0·0814 | 0·0551 | 1·80 | 1·74 |

and at a stated temperature, fuming ceases to be visible; and he has applied this technique in order to determine the extent to which certain substances, when dissolved in oleum, reduce the amount of sulphur trioxide which can be titrated in this way. Potassium hydrogen sulphate was found to reduce the titratable sulphur trioxide by 0·5 mol. per mol. of added salt; and other solutes were found to reduce the sulphur trioxide by amounts, which accorded with their known modes of ionisation, if the assumption was made that each mol. of formed hydrogen sulphate ion always removed 0·5 mol. of sulphur trioxide. Brand pointed out that fuming must indicate the presence of non-ionised disulphuric acid; and he offered a hypothesis which attributes stoicheiometric significance to the factor 0·5, the suggestion being that molecular disulphuric acid is not wholly destroyed until the second stage of its ionic dissociation, as well as the first, is substantially complete, two hydrogen sulphate ions being required for each molecule of disulphuric acid thus converted :

$$H_2S_2O_7 + 2HSO_4^- = S_2O_7^{--} + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The hypothesis would imply that the acidity of the hydrogen disulphate ion is not much less than that of the disulphuric acid molecule, contrary to conclusions reached in Sections 2.3 and 3.1.

Let us consider what happens when, say, potassium hydrogen sulphate is added to an oleum, and the excess of sulphur trioxide is titrated with water. For simplicity in a preliminary description, we shall ignore the formation of any polysulphates more complex than disulphates. The potassium hydrogen sulphate can be regarded as being first converted into potassium hydrogen disulphate; and, if the stoicheiometric excess of sulphur trioxide is removed by the addition of water, the total solute will then have the composition of potassium hydrogen disulphate. However, the solution will still contain a substantial proportion of molecular disulphuric acid, and therefore will still fume, because of the incompleteness of the first stage of ionisation of disulphuric acid, or, in other words, because of the proved solvolysis (Section 2.1) of the hydrogen disulphate ion in the following balanced reaction :

$$H_2S_2O_7 + HSO_4^- = HS_2O_7^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Therefore more water must be added to stop fuming; and, since we have the relation $[H_2S_2O_7] = K_b[HS_2O_7^-]/[HSO_4^-]$, with $K_b = 0{\cdot}008$ molal, an upper limit can be set to the amount of extra water needed. It cannot be as much as would convert all the hydrogen disulphate ion into hydrogen sulphate ion, and thus reduce the ratio $[HS_2O_7^-]/[HSO_4^-]$ to zero; for that would imply a titration technique of infinite sensitivity. Brand's results mean that fuming ceases to be visible, under his conditions, when enough extra water has been added to convert about one-half of the hydrogen disulphate ion into hydrogen sulphate ion, thus reducing the ratio $[HS_2O_7^-]/[HSO_4^-]$ to about unity, and therefore the concentration of molecular disulphuric acid to about 0·008 mol.

It will be noted that the above description does not assume that the hydrogen disulphate and hydrogen sulphate ions must necessarily be produced in equal amounts because in order to stop fuming they have to undergo the completed reaction

$$HS_2O_7^- + HSO_4^- = S_2O_7^{--} + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

a process which, with (19), constitutes Brand's reaction (18). The interpretation based on the solvolysis of the hydrogen disulphate ion makes the factor 0·5 a chance result, dependent on the magnitude of the solvolysis constant in relation to the sensitivity of the titration method under the conditions (particularly the temperature) chosen for its operation. This does not imply that reaction (20) does not proceed at all : it was shown in Section 3.1 that it does take place to a limited extent. But the occurrence of any substantial solvolysis according to equation (19)—and it was shown in Section 2.1 that such solvolysis is substantial—is enough to destroy the stoicheiometric significance of the factor 0·5.

A very slight extension of the discussion already given of Expts. No. 11, 12, and 106 establishes these conclusions. At point *a* in Fig. 1, some molecular disulphuric acid is present, and this is why the point lies as low as it does; but towards *b* the disulphuric acid becomes consumed by the increasing concentration of hydrogen sulphate ions, and so the freezing point rises. At the freezing-point maximum *b*, the molecular disulphuric acid should have been destroyed; and at this point the composition corresponds approximately (but not exactly) to equivalent proportions of ammonium hydrogen sulphate and ammonium hydrogen disulphate, and therefore to the end-point of the water titration. The datum which shows quite clearly that, at and near the freezing-point maximum *b*, and therefore at the end-point of the water titration, the solute is not normal ammonium disulphate, formed in a completed reaction (20), is that the $\nu$-factor is not 1·5. It is 1·95; and the defect below 2·00 measures the degree of incursion of reaction (20).

The neglect of the higher polysulphates in this discussion is probably justified for dilute solutions, such as apply to Expt. 106, but not for the more concentrated solutions, *e.g.*, of Expt. 11. The relatively small rise in the freezing point that occurs on the addition of water to more concentrated solutions of ammonium hydrogen disulphate has been explained in Section 3.1 as being due to the occurrence of reactions (13) and (16). It was also pointed out that the higher polysulphate ions, originally present at the neutral line, are not completely destroyed by the addition of an amount of water sufficient to reach the freezing-point maximum (or the end-point of the water titration). Again, therefore, we find a fortuitous situation, inasmuch as the values of the various equilibrium constants, determining the relative amounts of polysulphate ions and non-ionised disulphuric acid, are such that the amount of non-ionised disulphuric acid is reduced to a quantity less than can be detected by the fuming property (*i.e.*, less than 0·008 molal) in a solution containing approximately equal concentrations of hydrogen sulphate and hydrogen disulphate ions.

## (4) *Further Comments on the Species present in Sulphuric Acid and in Dilute Oleum.*

(4.1) *The Self-dissociation Equilibria of Sulphuric Acid.*—The present analysis of the dissociation equilibria of sulphuric acid is dependent on our being able to estimate three quantities, *viz.*, the total concentration of the dissociation products, the solvolysis constant of the hydrogen disulphate ion, and the acidity constant of disulphuric acid. These quantities have to be combined in the following way. Since the product of the acidity constant of any acid and the solvolysis constant of the corresponding anion in any solvent, will always give the autoprotolysis constant of the solvent, the acidity constant of disulphuric acid, and the solvolysis constant of the hydrogen disulphate ion, in sulphuric acid, will allow us to compute the autoprotolysis constant of sulphuric acid. Thus one can obtain the concentrations of each of the autoprotolytic ions; and, in so far as it may be found that these concentrations are not great enough to make up the estimated concentration of total dissociation products, a balance will remain which can be assigned to the products of the ionic self-dehydration.

The total concentration of dissociation products is the best known of the three required quantities. It was determined in Part II to be 0·043 molal, *i.e.*, enough to lower the freezing point of the solvent by 0·26°.

In consequence of the work described in Section 2.1, the value of the solvolysis constant of the hydrogen disulphate ion is taken to be as follows :

$$K_b(\text{HS}_2\text{O}_7^-) = [\text{H}_2\text{S}_2\text{O}_7][\text{HSO}_4^-]/[\text{HS}_2\text{O}_7^-] = 0{\cdot}0080 \text{ g.-mol. kg.}^{-1}$$

From this value of $K_b$, and the acidity constant of disulphuric acid, as deduced in Section 2.2 of this paper, on the basis of work reported in Part II, *viz.*,

$$K_a[\text{H}_2\text{S}_2\text{O}_7] = [\text{H}_3\text{SO}_4^+][\text{HS}_2\text{O}_7^-]/[\text{H}_2\text{S}_2\text{O}_7] = 0{\cdot}020 \text{ g.-mol. kg.}^{-1},$$

the ionic product for autoprotolysis may be calculated. From this, and the total concentration of dissociation products, one may compute the ionic product for self-dehydration. The results are as follows :

$$K_{\text{ap}} = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 0{\cdot}00016 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$
$$K_{\text{id}} = [\text{H}_3\text{O}^+][\text{HS}_2\text{O}_7^-] = 0{\cdot}00008 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

These values agree closely with those, noted in Section 1.1 of this paper, which were derived from data given in Parts I and II.

(4.2) *Collateral Evidence of the Existence of Higher Polysulphuric Acids.*—In this paper the existence has been indicated of a number of polysulphuric acids higher than disulphuric acid;

and specific evidence has been presented that at least trisulphuric acid and tetrasulphuric acid are present in appreciable quantities in dilute, or moderately dilute, oleum. Further support for these conclusions is afforded by Raman spectroscopic evidence, as is described by Millen in an accompanying paper (*J.*, 1950, paper no. 507). It therefore seems natural to consider whether any collateral evidence of the existence of these higher acids can be obtained, either from the isolation of salts or derivatives, or from the proved existence of analogously constituted acids.

When alkali-metal sulphates are heated with sulphur trioxide at temperatures between 100° and 300°, and the excess of sulphur trioxide is distilled off, a stable solid remains, which is invariably found to be the disulphate, $M_2S_2O_7$. This might mean only that the metallic trisulphates and tetrasulphates are unstable to heat, and not that they cannot exist at any temperature.

On the other hand, it is certain that both nitrosonium and nitronium salts, not only of disulphuric acid, but also of some of the higher polysulphuric acids, can be prepared. Nitrosonium disulphate, $(NO)_2S_2O_7$, is well known. When heated, it begins to decompose at about 100°, giving off oxides of nitrogen; and near 300° the material boils, and a white solid collects on the cooler surfaces. There has been some dispute about the composition of this solid. According to Jones, Price, and Webb (*J.*, 1929, 312) it has the composition $2N_2O_3,5SO_3$ : as a molecular formula this seems unlikely; but it might indicate a mixture of the original disulphate with the trisulphate, $(NO)_2S_3O_{10}$. However, according to Manchot and Schmidt (*Ber.*, 1929, **62**, 126), the white solid has the composition of nitrosonium tetrasulphate, $(NO)_2S_4O_{13}$. What seems clear is that the material possesses a higher sulphur-to-nitrogen ratio than does the original disulphate, and that therefore it probably contains a higher polysulphate. The evidence concerning nitronium salts is more definite. In an accompanying paper, Goddard, Hughes, and Ingold describe both of the nitronium disulphates, $(NO_2)HS_2O_7$ and $(NO_2)_2S_2O_7$. They also describe nitronium trisulphate, $(NO_2)_2S_3O_{10}$, which they found to be stable up to temperatures above 100°. They attempted, but failed, to prepare nitronium tetrasulphate.

Next, by arguments of analogy, the thesis may be developed that the tendency to the formation of higher poly-acids $H_2O(XO_3)_n$, which is so marked a feature of the chemistry of molybdenum and tungsten, is already developed to some extent in that of sulphur, and that the phenomenon can be traced back through the chemistry of the intermediate elements, selenium and chromium, as well as, in the other direction, to that of uranium.

Diselenic acid, $H_2Se_2O_7$, has never been prepared, presumably because selenium trioxide is very difficult to prepare, and has never been obtained in a state of purity. However, Goddard, Hughes, and Ingold showed (*loc. cit.*) that nitronium salts of diselenic acid exist, $(NO_2)HSe_2O_7$, or $(NO_2)_2Se_2O_7$, or both, although, here again, they were not able to obtain a pure individual. Meyer and Stateczny (*Z. anorg. Chem.*, 1922, **121**, 1) studied the phase diagram of the system $H_2SeO_4$–$SO_3$, and observed the formation of two stable solid compounds, selenatosulphuric acid, $H_2SSeO_7$, and selenatodisulphuric acid, $H_2S_2SeO_{10}$. The latter is clearly an analogue of trisulphuric acid. Although the authors do not mention the point, their freezing-point curve suggests the existence of a third compound, probably selenatotrisulphuric acid, $H_2S_3SeO_{13}$, the analogue of tetrasulphuric acid. Selenatosulphuric acid melts at 6·6°, and selenatodisulphuric acid at 20°; both compounds fume in air. Salts of selenatosulphuric acid have been prepared, but not salts of selenatodisulphuric acid.

Neither dichromic acid, $H_2Cr_2O_7$, nor any of the higher polychromic acids, have yet been prepared in the pure condition, owing to their tendency towards self-dehydration. But the salts, $M_2Cr_2O_7$, of dichromic acid are familiar substances, and a number of metallic trichromates and tetrachromates, $M_2Cr_3O_{10}$ and $M_2Cr_4O_{13}$, are known. On the other hand, two hetero-di-acids containing chromium have been obtained, not only as salts, but also in the free state. They are chromatosulphuric acid, and chromatoselenic acid, $H_2SCrO_7$ and $H_2SeCrO_7$ (Gilbert, Buckley, and Masson, *J.*, 1922, **121**, 1934; Meyer and Statezcny, *loc. cit.*).

It would thus appear that the present work extends to sulphur a property which is somewhat general in the chemistry of Group VI elements.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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