THE SULFURIC ACID SOLVENT SYSTEM

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I. Introduction

Interest in sulfuric acid-water mixtures and anhydrous sulfuric acid as solvents has considerably intensified in recent years following the pioneer work of Hantzsch (*53, 54*), mainly in the period 1907-1911, and the work of Hammett (*55, 56, 57, 84*) in the 1930's. It is perhaps surprising that the chemical and physical properties of anhydrous sulfuric acid have been comparatively little investigated until recent years considering that sulfuric acid is probably the most widely used of inorganic chemicals and is available in an excellent state of purity.

This review is concerned in particular with recent developments in the chemistry of solutions in anhydrous sulfuric acid. As a solvent it is of interest from a number of points of view. It has long been used as a medium for certain reactions such as, for example, aromatic nitration, although its role in this particular reaction has only recently been understood (*36*). It is a good solvent for a wide variety of organic compounds, very many of which give stable solutions from which they may be recovered unchanged simply by dilution with water. It is a highly acidic medium and as such has been used for the study of the basicity of very weak bases such as ketones and nitro-compounds. Although it is an extremely weakly basic solvent a few substances have nevertheless been found which show acidic behavior. In general our knowledge of acids and bases has been considerably widened as a result of the study of sulfuric acid solutions. Our understanding of the behavior and relationships of a wide variety of sulfates, sulfato complexes, and mixed oxy- and hydroxysulfates can be considerably increased by considering them in terms of the sulfuric acid solvent system just as Franklin did so successfully for nitrogen compounds in the liquid ammonia solvent system (*27*). Sulfuric acid resembles water as a solvent in many ways despite its much higher acidity; and a comparison of such properties as the conductivities, viscosities, densities, and activities of electrolyte solutions in sulfuric acid with those of aqueous electrolyte solutions is proving valuable in aiding our understanding of these solutions and of electrolyte solutions in general.

A. Some Physical Properties of Sulfuric Acid

Sulfuric acid of 100% composition may be prepared (*37*) by adding aqueous acid to oleum until it has the maximum freezing point of 10.371°C. It is a very viscous liquid with a conveniently wide liquid range. It has a dielectric constant higher than that of water and a conductivity greater than that of most other pure liquids. A minimum in the conductivity of the H_2O-SO_3 system occurs very nearly, but not exactly, at the composition H_2SO_4; in fact at a molal concentration of 0.002 excess water at 25° (*49*). Its high viscosity and boiling point show that it is a highly associated liquid in which there are presumably strong hydrogen bonds between the molecules. It has been shown that the solid has a layer-type structure in which each sulfuric acid molecule is hydrogen-bonded to four others (*78*). The structure of the liquid may well resemble that of the solid, just as that of water is in some important ways similar to that of ice. The existence of hydrogen bonds, of length 2.85 Å, between sulfuric acid molecules has been deduced from X-ray diffraction data on 97% aqueous sulfuric acid (*19, 20*). Values of some of the physical constants of sulfuric acid are given in Table I.

TABLE I

Some Physical Constants of Sulfuric Acid

Property	Value	Temperature (°C)	References
Freezing point	10.371°		*69*
Boiling point	290–317°		*87*
Viscosity	24.54 centipoise	25	*44*
Density, d_4^{25}	1.8269	25	*44*
Dielectric constant	100	25	*8, 34, 46*
	120	10	*8, 34, 46*
Specific conductance	1.0439×10^{-2} ohm^{-1}cm^{-1}	25	*49*
Heat capacity	0.338 cal/deg/gm	25	*68*
Heat of fusion	2560 cal/mole	10.37	*67*

B. The Self-Dissociation Reactions of Sulfuric Acid

Despite its extremely high acidity sulfuric acid belongs to the large class of solvents known as amphiprotic or amphoteric solvents which have both acidic and basic properties. In all solvents of this type proton transfer between solvent molecules, or autoprotolysis, occurs in which one molecule acts as an acid and the other as a base. Thus in water we have the familiar reaction,

$$2H_2O = H_3O^+ + OH^- \tag{1}$$

in liquid ammonia the reaction

$$2NH_3 = NH_4^+ + NH_2^- \tag{2}$$

and in sulfuric acid

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-. \tag{3}$$

The extent of the autoprotolysis is a measure of both the acidic and basic strengths of the solvent and is given by the *autoprotolysis constant* or *ionic product;* for example, for water $K_{ap} = [H_3O^+]\ [OH^-] = 10^{-14}$ (25°) and for sulfuric acid $K_{ap} = [H_3SO_4^+]\ [HSO_4^-] = 1.7 \times 10^{-4}$ (10°). The autoprotolysis constant of sulfuric acid is greater than that for any other solvent that has been studied. Such a large value implies that, in spite of its very high acidity, sulfuric acid must also be appreciably basic.

There are, however, some additional self-dissociation processes in sulfuric acid which must also be considered. The primary self-dissociation reaction may be considered to be

$$2H_2SO_4 = H_2O + H_2S_2O_7. \tag{4}$$

Both of these products are further ionized (*28*); water extensively according to the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \tag{5}$$

and disulfuric acid partially, according to the equation

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-. \tag{6}$$

Since the ions $H_3SO_4^+$ and HSO_4^- are in equilibrium as a consequence of the autoprotolysis reaction [Eq. (3)] it follows that the ions H_3O^+ and $HS_2O_7^-$ must also be in equilibrium

$$2H_2SO_4 = H_3O^+ + HS_2O_7^-. \tag{7}$$

This has been called the ionic self-dehydration reaction (*29*). Only four of the five equilibria, Eqs. (3) to (7) are independent and it has been found convenient to discuss the self-dissociation in terms of Eqs. (3), (5), (6), and (7). Values for the corresponding equilibrium constants are given in Table II. The values at 10° were obtained from a detailed study (*4, 5*) of the freezing points of solutions of metal hydrogen sulfates, water, and disulfuric acid, each of which represses the self-dissociation equilibria in a different way. Table III gives the concentration of each of the products of the self-dissociation. The total molal concentration of 0.0424 at 10° corresponds to a freezing point of 10.625°

TABLE II

EQUILIBRIUM CONSTANTS FOR THE SELF-DISSOCIATION REACTIONS OF SULFURIC ACID

Reaction	10°	25°
$K_{ap} = [H_3SO_4^+][HSO_4^-]$	1.7×10^{-4}	2.4×10^{-4}
$K_{id} = [H_3O^+][HS_2O_7^-]$	3.5×10^{-5}	4.0×10^{-5}
$K_a = [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7]$	1.4×10^{-2}	1.4×10^{-2}
$K_b = [H_3O^+][HSO_4^-]/[H_2O]$	1	1

for the hypothetical undissociated acid. The values of the self-dissociation constants at 25° were obtained (*26*) from the values at 10° and the electrical conductivities at 10° and 25° of solutions of metal hydrogen sulfates, water, and disulfuric acid. The values given in Tables II and III are more accurate than those that have been given previously (*28*, *29*, *62*) as certain simplifying assumptions which are not entirely justified were made in earlier work.

TABLE III

CONCENTRATIONS (m) OF THE SELF-DISSOCIATION SPECIES IN SULFURIC ACID

Species	10°	25°
HSO_4^-	0.0150	0.0178
$H_3SO_4^+$	0.0113	0.0135
H_3O^+	0.0080	0.0088
$HS_2O_7^-$	0.0044	0.0045
$H_2S_2O_7$	0.0036	0.0043
H_2O	0.0001	0.0001
Total	0.0424	0.0490

The ions that are formed by the autoprotolysis of any solvent are of particular importance in the chemistry of solutions in that solvent. The anion is formed by the ionization of any base and is the strongest possible base that can exist in that solvent. The cation is formed by any acid and is the strongest acid in the solvent. Thus in sulfuric acid the strongest possible base is the hydrogen sulfate ion and all intrinsically stronger bases are fully ionized to give the hydrogen sulfate ion

$$B + H_2SO_4 = BH^+ + HSO_4^-. \tag{8}$$

Acids give rise to the $H_3SO_4^+$ ion

$$HA + H_2SO_4 = H_3SO_4^+ + A^-. \tag{9}$$

C. Experimental Methods

The two main methods by which sulfuric acid solutions have been investigated are cryoscopic and electrical conductivity measurements. Some use has also been made of Raman, infrared, and ultraviolet absorption spectra.

1. Cryoscopic Measurements

The cryoscopic method was used in Hantzsch's original work (*53, 54*) and was later developed by Hammett and Deyrup (*56*) and by Gillespie *et al.* (*48*). Sulfuric acid freezes at 10.371°C and has a relatively large molal freezing-point depression or cryoscopic constant $k = 6.12$ (*32*). It is thus a convenient solvent for cryoscopic measurements provided that adequate precautions are taken to prevent absorption of water from the atmosphere. From freezing-point measurements the number, ν, of moles of particles (ions and molecules) produced by one mole of any solute may be obtained. Some examples are given in Table IV.

TABLE IV

Examples of Values of ν and γ for Various Solutes

System	ν	γ
$CH_3CO_2H + H_2SO_4 = CH_3CO_2H_2^+ + HSO_4^-$	2	1
$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_3O^+ + HSO_4^-$	3	1
$C_6H_4(NH_2)_2 + 2H_2SO_4 = C_6H_4(NH_3)_2^{++} + 2HSO_4^-$	3	2
$(CH_3)_3SiOSi(CH_3)_3 + 3H_2SO_4 = 2(CH_3)_3Si \cdot SO_4H + H_3O^+ + HSO_4^-$	4	1
$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$	4	2
$B_2O_3 + 9H_2SO_4 = 3H_3O^+ + 2B(HSO_4)_4^- + HSO_4^-$	6	1
$H_3BO_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^-$	6	2
$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$	6	3

A good deal of confusion and much controversy between early workers (*54, 55, 77*) resulted from a lack of understanding of the nature and extent of the self-dissociation of sulfuric acid, which is repressed by most solutes and thus affects the freezing-point depressions that they produce. Following Hammett and Deyrup (*56*) it became common practice to carry out cryoscopic measurements in sulfuric acid containing sufficient water to depress the freezing point to approximately 10.0° in order to repress largely the solvent self-dissociation. This is not, however, an entirely satisfactory procedure. The self-dissociation is not completely repressed (*5*), and allowance for it should still in principle be made. Moreover water has been found, in the case of nonelectrolytes and weak electrolytes at least, to have an effect on the depression produced by the solute (*10, 39, 42*). This has been attributed by Brayford and Wyatt (*10*) to "salting-out" and "salting-in" effects of the hydroxonium hydrogen sulfate produced by the water. These effects have led, in at least two cases, to erroneous or inaccurate interpretations of freezing-point measurements, carried out in the presence of small amounts of water (*7, 10, 39, 42*). Since the repression of the self-dissociation equilibria by the added electrolyte can be allowed for by making use of the constants given in Table II (*5*), it would seem preferable, except perhaps when only very approximate results are required, to use 100% sulfuric acid, rather than slightly aqueous acid, as a solvent for cryoscopic measurements, as has in fact been done in recent work (see e.g. *24, 39*).

For freezing-point measurements made in 100% sulphuric acid ν is given by the expression

$$\nu = \theta(1 + 0.002\theta)/6.12\phi m - m_d/m$$

where θ is the freezing-point depression calculated from the freezing-point (10.625°) of hypothetical undissociated sulphuric acid, ϕ is the osmotic coefficient, m is the stoichiometric concentration of the solute allowing for any solvent used up in its ionization and m_d is the total concentration of the self-dissociation species (*5, 32*). Since ϕ is in general not known it must be assumed to have the value of unity and an approximate value of ν, denoted here by ν', may then be calculated from the expression

$$\nu' = \theta(1 + 0.002\theta)/6.12m - m_d/m.$$

Some workers who have used slightly aqueous sulphuric acid as solvent have expressed their results in terms of the van't Hoff i-factor

$$i = \theta/6.12\mathrm{m}$$

Thus i is a further approximation to ν.

2. Conductimetric Measurements

A few measurements of the conductivities of solutions in sulfuric acid were made by the early workers (*6, 53, 61, 63*) but there were considerable differences between their results and conclusions, again partly because of a lack of understanding of the solvent self-dissociation and the contribution that it made to the conductivities of the solutions studied. A comprehensive investigation of the conductivities of solutions in sulfuric acid was first made by Gillespie and Wasif (*45*) and this showed that such measurements were of considerable value in the study of the ionizations of solutes in sulfuric acid.

For a pure liquid, sulfuric acid has a high electrical conductivity (*49*)—0.01044 ohm^{-1}cm^{-1} at 25°. This is due primarily to its extensive autoprotolysis and also to the fact that both the ions thus formed, $H_3SO_4^+$ and HSO_4^-, have relatively high mobilities. The mobilities of these ions are in fact much greater than those of any other ions in sulfuric acid. This is shown, for example, by the values given in Table V for the cation transport numbers, t_+, of various metal hydrogen sulfates (*43*). The mobilities of these metal ions are extremely small in sulfuric acid because of its very high viscosity—24.5 centipoise at 25°—which is approximately 25 times that of water. The hydrogen sulfate ion and the hydrogen ion ($H_3SO_4^+$) are however unaffected by this high viscosity because they conduct almost entirely by a proton-transfer mechanism (*43*) quite analogous to that generally accepted to explain the abnormally high mobilities of H_3O^+ and of OH^- in water (*80*). The mechanism is illustrated very diagrammatically for $H_3SO_4^+$ in Fig. 1. Successive transfer of protons along hydrogen bonds result in an effective movement of $H_3SO_4^+$ ions through the solution without the need for the actual diffusion of individual ions. Values of the mobilities of $H_3SO_4^+$,

TABLE V

CATION TRANSPORT NUMBERS FOR SOME ELECTROLYTES (*43*)

Electrolyte	m	t_+
$AgHSO_4$	0.249	0.026
$KHSO_4$	0.624	0.030
$NaHSO_4$	0.792	0.021
$LiHSO_4$	0.556	0.013
$Ba(HSO_4)_2$	0.174	0.009
$Sr(HSO_4)_2$	0.211	0.007

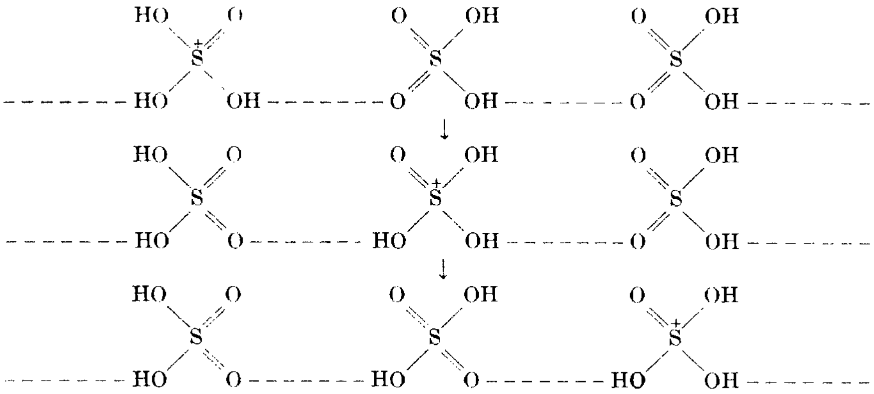

FIG. 1. Proton-transfer conduction of the $H_3SO_4^+$ ion in sulfuric acid.

TABLE VI

IONIC MOBILITIES IN 100% SULFURIC ACID AND WATER AT INFINITE DILUTION (25°)

Ion	$\lambda^0(H_2SO_4)$	$\lambda^0(H_2O)$
$H_3SO_4^+$	242	—
HSO_4^-	171	—
H_3O^+	~5	349.8
OH^-	—	198.6
Na^+	~3	50.1
K^+	~5	73.5
Ba^{++}	~2	63.6
	(*26*)	(*80*)

HSO_4^-, and other ions in 100% H_2SO_4 are given in Table VI together with the values for some ions in water at infinite dilution. The mobilities of the $H_3SO_4^+$ and HSO_4^- ions in sulphuric acid are quite comparable with those of the H_3O^+ and OH^- ions in water. However, the mobilities of other ions in sulphuric acid are much smaller than the mobilities of the corresponding ions in water because of the very high viscosity of sulphuric acid.

The conductivities of solutions of acids and bases in sulfuric acid are thus determined almost entirely by the concentration of $H_3SO_4^+$ or HSO_4^- respectively. All simple bases ionizing according to Eq. (8), that is, mono (hydrogensulfates), have very similar molar conductances and all bases which give rise to two hydrogen sulfate ions, that is, di(hydrogensulfates) such as nitric acid

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (10)$$

have molar conductances approximately twice those of a mono(hydrogensulfate) at the same hydrogen sulfate ion concentration (*45*). Molar conductances of a number of typical electrolytes are given in Table VII. Electrical conductivity measurements thus provide a means of determining the number, γ, of moles of hydrogen sulfate ions or hydrogen ions produced by one mole of any solute. Some typical examples are given in Table IV. The value of γ from conductivity measurements taken together with that of ν from freezing-point measurements often enables the mode of ionization of a solute to be determined unambiguously.

3. Spectroscopic Measurements

Differences in the visible and ultraviolet absorption spectra of bases and their conjugate acids have been utilized in determining their degrees of ionization in sulfuric acid-water mixtures (*21, 22, 55*) and, in

TABLE VII

MOLAR CONDUCTANCES OF SOME ELECTROLYTES (*45*)

Mono(hydrogensulfates)

M	NH_4HSO_4	$(CH_3)_2CO$	H_2O	C_2H_5OH	CH_3CO_2H
0.1	157	153	150	156	152
0.2	118	116	114	117	116
0.3	104	104	100	103	99.3
0.4	94.4	95.0	90.5	93.1	89.5
0.6	82.2	80.1	78.3	79.8	77.1
0.8	73.7	72.4	69.6	70.1	67.9
1.0	66.3	63.9	63.2	62.2	59.8

Di(hydrogensulfates)

M	HNO_3	o-$C_6H_4(NH_2)_2$	$Ba(HSO_4)_2$
0.05	304	306	304
0.10	228	236	221
0.15	201	201	179
0.20	177	187	150
0.30	155	153	132
0.40	138	130	110

the case of very weak bases such as nitro compounds, in oleums (*7*).

Raman spectra have been used to identify and to measure approximately the concentration of various species in sulfuric acid solutions. Thus the nitronium ion NO_2^+ was identified (*17, 58, 75*) and its linear structure proved by the observation of its single sharp and intense Raman line at 1400 cm^{-1}, and the hydrogen sulfate ion may be recognized and its concentration estimated by a characteristic strong Raman line at 1050 cm^{-1} (*58, 75*).

II. Solutions in Sulfuric Acid

A. NONELECTROLYTES

Sulfuric acid is a poor solvent for nonelectrolytes. The hydrogen-bonding interactions between the sulfuric acid molecules are so strong that unless a solute is strongly solvated, either because it is ionic or because it can strongly hydrogen bond with sulfuric acid, it is unlikely to be able to disrupt sufficiently the structure of the sulfuric acid to enable it to dissolve. Yet if a molecule is sufficiently basic to form strong hydrogen bonds with sulfuric acid it is likely that some proton transfer along the hydrogen bonds will occur, resulting in at least a small degree of ionization. Thus in order to behave as a nonelectrolyte a solute must have sufficient basic characteristics to form strong hydrogen bonds with the solvent but must be insufficiently basic to protonate. The only nonelectrolytes that are known at present are sulfuryl chloride (*48*), picric acid (*10*), and a few other polynitroaromatic compounds (*7, 10, 42*). Trichloracetic acid and chlorosulfonic acid may also be nonelectrolytes although the evidence is not conclusive (*45, 48*). Dimethylsulfate and phosphorus oxychloride, which early workers believed to be nonelectrolytes, have been shown to react with the solvent (*48*).

It is interesting to note that the conductivities of solutions of nonelectrolytes in sulfuric acid are lower than that of the solvent itself, presumably because the nonelectrolyte decreases the mobilities and perhaps also the concentrations of the highly conducting $H_3SO_4^+$ and HSO_4^- ions (*42, 45*). The effect of nonelectrolytes on the mobilities of these ions has been attributed to the strong hydrogen-bonding interactions between the solute and the solvent molecules. This decreases the effectiveness of the latter in the proton-transfer conduction process (*45*).

B. ELECTROLYTES

Sulfuric acid is a good solvent for electrolytes, as is consistent with its high dielectric constant and the polar nature of its molecules. Many of the soluble electrolytes are rather unfamiliar and cannot be obtained at all in aqueous solution, whereas many of the electrolytes that are encountered in aqueous solution are not stable in sulfuric acid.

1. Strong Bases

a. Metal Hydrogen Sulfates. The alkali metal and some other metal hydrogen sulfates dissolve in sulfuric acid as fully ionized binary electrolytes and are strong bases analogous to the hydroxides in water

$$KHSO_4 = K^+ + HSO_4^- \tag{11}$$

$$KOH = K^+ + OH^-. \tag{12}$$

The corresponding normal sulfates are completely converted to the hydrogen sulfates and formally they are analogous to the metal oxides in water (*37*).

$$K_2SO_4 + H_2SO_4 = 2K^+ + 2HSO_4^- \tag{13}$$

$$K_2O + H_2O = 2K^+ + 2OH^-. \tag{14}$$

The solubilities of a number of metal sulfates are given in Table VIII. The sulfates of Al, Fe(III), Ni(II), Be, and Cd(II) have also been investigated and found to have solubilities less than 0.1 mole % (*23*). It is interesting to note that the solubilities of the hydrogen sulfates in sulfuric acid closely parallel those of the hydroxides in water and

TABLE VIII

SOLUBILITIES OF METAL SULFATES IN SULFURIC ACID AT 25°

Sulfate	Solubility (mole %)	Solid phase	Reference
Li_2SO_4	14.28	$2LiHSO_4 \cdot H_2SO_4$	*60*
K_2SO_4	9.28	$KHSO_4 \cdot H_2SO_4$	*60*
Ag_2SO_4	9.11	$2AgHSO_4 \cdot H_2SO_4$	*59*
$BaSO_4$	8.85	$Ba(HSO_4)_2 \cdot 2H_2SO_4$	*59*
Na_2SO_4	5.28	$4NaHSO_4 \cdot 7H_2SO_4$	*60*
$CaSO_4$	5.16	$Ca(HSO_4)_2 \cdot 2H_2SO_4$	*59*
$SrSO_4$	Soluble > 2	—	*23*
Rb_2SO_4	Soluble > 2	—	*23*
Cs_2SO_4	Soluble > 2	—	*23*
Tl_2SO_4	Soluble > 2	—	*23*
$(NH_4)_2SO_4$	Soluble > 2	—	*23*
$PbSO_4$	1.2	$PbSO_4$	*23*
Hg_2SO_4	0.78	$Hg_2(HSO_4)_2$	*59*
$MgSO_4$	0.18	$Mg(HSO_4)_2 \cdot 2H_2SO_4$	*59*
$ZnSO_4$	0.17	—	*59*
$FeSO_4$	0.17	—	*59*
$CuSO_4$	0.08	$CuSO_4$	*59*
$HgSO_4$	0.02	$HgSO_4$	*59*

the acetates in anhydrous acetic acid. As is indicated in Table VIII the solid phase in equilibrium with the saturated solution is in the case of the more soluble sulfates a solvate of the hydrogen sulfate, while, for the less soluble it is the unsolvated hydrogen sulfate or the normal sulfate. The formation of solvates is some indication that these electrolytes are solvated in solution. Additional evidence of this solvation has been obtained from freezing-point (*37*), density (*44*), viscosity (*33, 44*), conductivity (*45*), and transport-number (*43*) measurements on their solutions. The extent of solvation decreases from Li^+ to Cs^+ for the alkali metals and the divalent Ba^{++} and Sr^{++} are more highly solvated than any of the alkali metal cations.

Salts of other inorganic acids are almost without exception either insoluble, for example, AgCl, $CuBr_2$, $AlCl_3$, and $AlPO_4$, or undergo complete solvolysis as is illustrated by the following examples:

$$NaCl + H_2SO_4 = Na^+ + HSO_4^- + HCl \tag{15}$$

$$NH_4ClO_4 + H_2SO_4 = NH_4^+ + HSO_4^- + HClO_4 \tag{16}$$

$$Na_3PO_4 + 3H_2SO_4 = 3Na^+ + 3HSO_4^- + H_3PO_4 \tag{17}$$

$$KNO_3 + H_2SO_4 = K^+ + HSO_4^- + HNO_3. \tag{18}$$

Sometimes the free acid that is formed undergoes further reaction as is the case with nitric and phosphoric acids (see *b* and *c*). All such soluble salts thus give strongly basic solutions as a result of solvolysis. Solvolysis occurs partly because of the rather high concentration of hydrogen sulfate ions in sulfuric acid but mainly because the acids from which these salts are derived are exceedingly weak acids or do not behave as acids at all in solution in sulfuric acid. Of the acids mentioned above HCl is un-ionized and sparingly soluble, and probably reacts to some extent to give chlorosulfonic acid; perchloric acid is exceedingly weak, and both phosphoric and nitric acids behave as bases (see Section *3*).

b. Simple Conjugate Acid Formation. Most organic compounds, with the exception of aliphatic hydrocarbons, some aromatic hydrocarbons, and their halogen derivatives, are soluble in sulfuric acid. This is because they contain atoms such as O, N, S, or P with one or more unshared pairs of electrons which almost always exhibit basic properties in sulfuric acid. Thus a large number of organic compounds behave as strong bases, being completely converted into their conjugate acids. Sulfuric acid may be said to exert a considerable leveling effect on the strengths of bases. Examples include ketones,

$$CH_3CO \cdot C_6H_5 + H_2SO_4 = CH_3COH^+ \cdot C_6H_5 + HSO_4^- \tag{19}$$

amines,

$$C_6H_5NH_2 + H_2SO_4 = C_6H_5 \cdot NH_3^+ + HSO_4^- \tag{20}$$

carboxylic acids,

$$CH_3COOH + H_2SO_4 = CH_3COOH_2^+ + HSO_4^- \tag{21}$$

esters,

$$C_6H_5COOC_2H_5 + H_2SO_4 = C_6H_5COOH^+ \cdot C_2H_5 + HSO_4^- \tag{22}$$

and amides

$$C_6H_5CONH_2 + H_2SO_4 = C_6H_5CONH_3^+ + HSO_4^-. \tag{23}$$

Many of these solutions are quite stable and the organic compound can be recovered unchanged simply by diluting the sulfuric acid solution with water. In other cases subsequent reactions ensue, such as hydrolysis, in the case of some esters (*35, 70*) and amides (*14*), for example,

$$CH_3OC_6H_4COOCH_3 + 2H_2SO_4 = CH_3OC_6H_4COOH_2^+ + CH_3SO_4H + HSO_4^- \tag{24}$$

$$C_6H_5CONH_2 + H_2SO_4 = C_6H_5CO_2H^+ + NH_4^+ + HSO_4^- + HS_2O_7^-. \tag{25}$$

A detailed review of the behavior of organic compounds in sulfuric acid has been given by Gillespie and Leisten (*35*).

Phosphoric acid provides an example of an inorganic substance that behaves as a simple base [Eq. (43)].

c. Conversion of Oxy and Hydroxy Compounds into Their Sulfato Derivatives. A number of other types of basic behavior, in addition to simple protonation, are also known. Thus many oxy and hydroxy compounds are converted to sulfato derivatives with the elimination of water, which ionizes as a base according to Eq. (5). The sulfato compound that is formed may be a nonelectrolyte, or it may itself exhibit basic properties either by protonating or by ionizing off a hydrogen sulfate ion, or it may even behave as an acid. The simplest examples of this type of behavior are given by a number of substances of the general formula XOH which are converted to the hydrogen sulfate XSO_4H

$$XOH + 2H_2SO_4 = XSO_4H + H_3O^+ + HSO_4^- \qquad (26)$$

and thus behave as bases. In addition the hydrogen sulfate itself sometimes acts as a base either forming its conjugate acid

$$XSO_4H + H_2SO_4 = XSO_4H_2^+ + HSO_4^- \qquad (27)$$

or ionizing into X^+ and SO_4H^- just like a metal hydrogen sulfate. Ethyl alcohol is a base of this type being converted to ethylhydrogen sulfate (*30, 48*).

$$C_2H_5OH + 2H_2SO_4 = C_2H_5SO_4H + H_3O^+ + HSO_4^-. \qquad (28)$$

There is some evidence (*30*), although it is not very conclusive that ethyl hydrogen sulfate is itself a rather weak base ionizing slightly according to the equation

$$C_2H_5SO_4H + H_2SO_4 = C_2H_5SO_4H_2^+ + HSO_4^-. \qquad (29)$$

Nitric acid (*36*), triphenylcarbinol (*35*), and mesitoic acid (*35*) all provide examples of the formation of a hydrogen sulfate XSO_4H that is fully ionized to X^+ and HSO_4^- so that the over-all ionizations of these compounds are as follows:[1]

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (30)$$

$$Ph_3COH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^- \qquad (31)$$

$$Me_3C_6H_2CO_2H + 2HSO_4 = Me_3C_6H_2 \cdot CO^+ + H_3O^+ + 2HSO_4^-. \qquad (32)$$

Such positive ions formed by the ionization of hydrogen sulfates in sulfuric acid are all very strongly electrophilic and can only exist in a very weakly basic solvent such as sulfuric acid or in a suitable nonprotonic solvent. Their formation in sulfuric acid is due not only to its high acidity but also to the very low activity of water when in dilute

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[1] Bases of the type exemplified by nitric acid and triphenylcarbinol have been called "secondary bases" but as there are a number of other similar, but nevertheless different, and equally important types of basic behavior it does not seem necessary to single out this particular one for a special name.

solution in sulfuric acid. This low water activity results because the water is largely converted to H_3O^+ and the remaining unionized water is strongly hydrogen bonded to the solvent. One advantage of sulfuric acid as a solvent for such ions is that it is a good solvent for electrolytes whereas nonprotonic solvents are often poor solvents for electrolytes. Thus in sulfuric acid relatively concentrated solutions of these reactive ions can be obtained. This is of considerable importance, particularly in those cases where such species have been postulated as unstable reaction intermediates in other solvents. The nitronium ion is, of course, the reactive intermediate in aromatic nitration under many conditions (*36*).

Anhydrides X_2O can similarly be converted to a hydrogen sulfate and thus act as bases

$$X_2O + 3H_2SO_4 = 2XSO_4H + H_3O^+ + HSO_4^-. \qquad (33)$$

Hexamethyldisiloxane behaves in this way (Section III, C, *1*, *a*)

$$(CH_3)_3SiOSi(CH_3)_3 + 3H_2SO_4 = 2(CH_3)_3SiSO_4H + H_3O^+ + HSO_4^- \qquad (34)$$

and the trimethylsilicon hydrogen sulfate that is formed appears to be a nonelectrolyte. Dinitrogen pentoxide forms the fully ionized nitronium hydrogen sulfate (Section III, D, *1*)

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^-. \qquad (35)$$

Other more complicated examples of the formation of sulfato-derivatives are given in Section III. Only one more example of particular interest will be mentioned here, namely, that in which the sulfate formed is an acid. Thus boric acid is converted to boron tri(hydrogensulfate) (Section III, B),

$$B(OH)_3 + 6H_2SO_4 = 3B(SO_4H)_3 + 3H_3O^+ + 3HSO_4^-. \qquad (36)$$

But boron tri(hydrogensulfate) is an acid and reacts with the hydrogen sulfate ion,

$$B(SO_4H)_3 + HSO_4^- = B(SO_4H)_4^-. \qquad (37)$$

However, only one-third of the hydrogen sulfate formed is neutralized so that the over-all reaction of boric acid is still that of a base,

$$B(OH)_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^-. \qquad (38)$$

d. Anhydride Formation. Still another type of basic behavior is provided by a number of hydroxy compounds that are converted to their anhydrides as, for example, is the case with a number of weak inorganic acids,

$$2HOCl + H_2SO_4 = Cl_2O + H_3O^+ + HSO_4^- \qquad (39)$$

$$H_2SO_3 + H_2SO_4 = SO_2 + H_3O^+ + HSO_4^-. \qquad (40)$$

2. Weak Bases

Some substances with very weakly basic properties are only partially ionized in sulfuric acid and it is possible to measure their degree of ionization and hence obtain their basicity constants by means of cryoscopic, conductimetric, and spectroscopic measurements. A number of nitro-compounds have been carefully studied by several different methods. It may be seen in Table IX that the results obtained by the different methods are in excellent agreement. The conductivities of solutions of a number of nitro compounds are shown in Fig. 2 together with those for a fully ionized binary electrolyte ($C_6H_5CO_2H_2^+ \cdot HSO_4^-$) for comparison. Other weak bases include sulfones, sulfonic acids, and nitriles. Their basic dissociation constants are also given in Table IX. Some nitriles have also been found (*71*) to undergo hydrolysis according to the equation

TABLE IX

DISSOCIATION CONSTANTS OF SOME WEAK BASES

	K_b				
	Conductimetric (*42, 71*)	Cyroscopic (*31, 39, 42*)	Spectroscopic (*7*)	Titration† (*41*)	
Base				$H_2S_2O_7$	$HB(HSO_4)_4$
p-tert-Butylnitrobenzene	—	0.10	0.10	—	—
p-Nitrotoluene	0.095	0.094	0.077	—	0.097
o-Nitrotoluene	0.067	0.062	—	—	0.069
m-Nitrotoluene	0.023	0.020	0.024	0.024	0.017
Nitrobenzene	0.010	0.011	0.009	0.013	0.009
p-Chloronitrobenzene	0.004	0.003	0.0046	—	—
Nitromethane	0.0025	0.004*	—	—	—
Acetonitrile	0.16	—	—	—	—
Benzonitrile	0.07	—	—	—	—
p-Toluenesulfonic acid	—	0.026*	—	—	—
Benzenesulfonic acid	—	0.011*	—	—	—
Diphenylsulfone	—	0.016*	—	—	—

* These values are probably rather high as the measurements were made in slightly aqueous rather than 100% sulfuric acid (see ref. *39*).

† Calculated from the position of minimum conductivity in the titrations of these acids (Section II, B, *4*).

$$CH_3CN + 2H_2SO_4 = CH_3CONH_3^+ + HS_2O_7^-. \tag{41}$$

3. Acids

The majority of substances that are normally regarded as acids, that is from the standpoint of aqueous solution chemistry, no longer behave

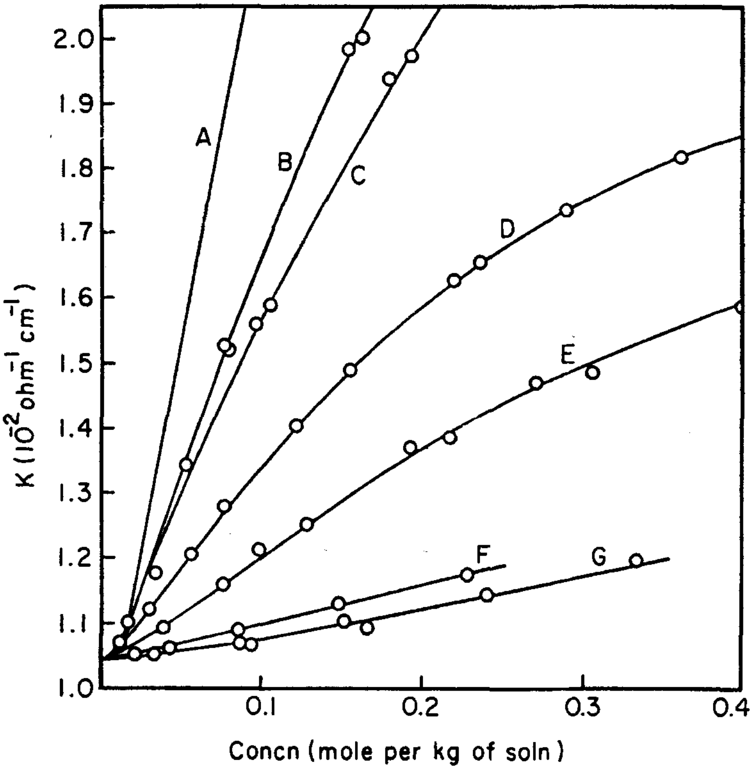

FIG. 2. Conductivities of solutions of some nitro compounds. KEY: *A*, $C_6H_5CO_2H$; *B*, *p*-$C_6H_4Me \cdot NO_2$; *C*, *o*-$C_6H_4Me \cdot NO_2$; *D*, *m*-$C_6H_4Me \cdot NO_2$; *E*, $PhNO_2$; *F*, *p*-$C_6H_4Cl \cdot NO_2$; *G*, $MeNO_2$. Reproduced from ref. *42*.

as acids at all in solution in sulfuric acid, but as bases of various types as is shown by the following examples:

$$CH_3CO_2H + H_2SO_4 = CH_3CO_2H_2^+ + HSO_4^- \qquad (42)$$

$$H_3PO_4 + H_2SO_4 = H_4PO_4^+ + HSO_4^- \qquad (43)$$

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (44)$$

$$H_3BO_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^- \qquad (45)$$

$$H_2SO_3 + H_2SO_4 = SO_2 + H_3O^+ + HSO_4^-. \qquad (46)$$

Hydrofluoric acid reacts to form fluorsulfonic acid

$$HF + H_2SO_4 = HSO_3F + H_3O^+ + HSO_4^-. \qquad (47)$$

Hydrogen chloride is not very soluble in sulfuric acid but probably reacts to some extent to give chlorsulfonic acid. Hydrogen bromide and iodide are oxidized to their respective elements. Even perchloric acid, which is often regarded as the strongest known acid, shows little or no acid properties in solution in sulfuric acid, as is implied, for example, by the virtually complete solvolysis of metal perchlorates (Section II, B, *1*, *a*). Perchloric acid must be a very weak acid whose ionization according to the equation

$$HClO_4 + H_2SO_4 = H_3SO_4^+ + ClO_4^- \tag{48}$$

is very slight. It appears that fluorsulfonic acid is slightly stronger than perchloric acid. It causes a small but definite increase in the conductivity when dissolved in sulfuric acid, and it can be "titrated" with suitable bases (*3*) (Section II, B, *4*). From such measurements the equilibrium constant for its dissociation according to the equation

$$HSO_3F + H_2SO_4 = H_3SO_4^+ + SO_3F^- \tag{49}$$

has been estimated and is given in Table X. The conductivity of its solutions is shown together with that of other acids and the nonelectrolyte sulfuryl chloride in Fig. 3.

TABLE X

DISSOCIATION CONSTANTS OF SOME ACIDS

Acid	K_a	Reference
H_2SO_4*	1.7×10^{-5} (10°)	*5*
$HClO_4$	Very weak	*30*
$HAs(HSO_4)_4$	Very weak	*41*
$HPb(HSO_4)_6^-$	1.8×10^{-3} (10°)	*40*
HSO_3F	3×10^{-3} (25°)	*3*
$H_2Pb(HSO_4)_6$	1.1×10^{-2} (10°)	*40*
$H_2S_2O_7$	1.4×10^{-2} (10°)	*5*
$H_2S_3O_{10}$ etc.	Moderately strong	*29*
$HB(HSO_4)_4$	Strong	*24*

* $K_a(H_2SO_4) = K_{ap}/10.2$.

The first acids of the sulfuric acid system to be recognized (*29*) were disulfuric acid, $H_2S_2O_7$, and the higher polysulfuric acids, $H_2S_3O_{10}$ etc., which are present in oleum. Dilute oleum contains mainly disulfuric acid, $H_2S_2O_7$, and from cryoscopic measurements on such solutions the first dissociation constant of disulfuric acid has been found to be 1.4×10^{-2} (*5*). It is approximately 30% ionized in a 0.1 *m* solution;

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-. \tag{50}$$

The conductivities of its solutions, which are shown in Fig. 3, are also consistent with this value for its acid-dissociation constant. The higher polysulfuric acids are present in increasing amount in more concentrated oleums and they appear to be somewhat stronger acids than disulfuric

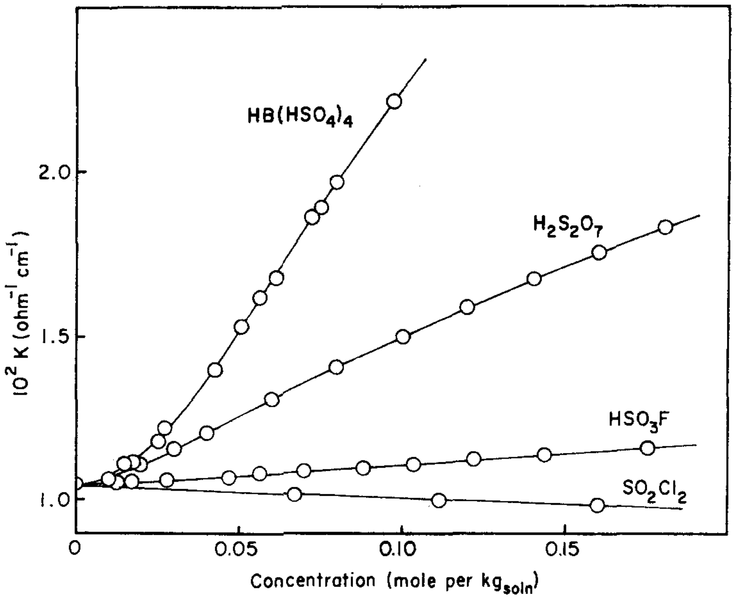

FIG. 3. Conductivities of solutions of some acids.

acid but it has not been possible to measure their dissociation constants because several of them are always present together in any oleum.

Recently evidence has been obtained for the existence of several complex hydrogensulfato acids, namely tetra(hydrogensulfato)boric acid $HB(HSO_4)_4$ which is a strong acid, hexa(hydrogensulfato)plumbic acid $H_2Pb(HSO_4)_6$ whose first dissociation constant is comparable with that of disulfuric acid, tetra(hydrogensulfato) arsenious acid $HAs(HSO_4)_4$ which is very weak, and hexa(hydrogensulfato)stannic acid $H_2Sn(HSO_4)_6$ whose strength has not yet been accurately measured although it is probably somewhat stronger than the corresponding plumbic acid. These acids are fully discussed in Section III.

4. Acid-Base Reactions

Acid-base neutralization reactions can be carried out in sulfuric acid as in any other amphoteric solvent. In sulfuric acid the neutralization reaction is essentially

$$H_3SO_4^+ + HSO_4^- = 2H_2SO_4. \qquad (51)$$

Compare

$$H_3O^+ + OH^- = 2H_2O \qquad (52)$$

in water. Since the ions $H_3SO_4^+$ and HSO_4^- have much higher conductivities than any other ions in sulfuric acid such neutralization reactions are very conveniently followed by measuring the electrical conductivity of the solution which decreases as base is added to acid or *vice versa,* passes through a minimum and then increases again (Fig. 4). The position of this minimum conductivity depends on the strength of the acid and the base. If the autoprotolysis were the only self-dissociation process of the solvent and if the conductivity of $H_3SO_4^+$ were equal to that of HSO_4^- then the minimum conductivity in the reaction of a strong base

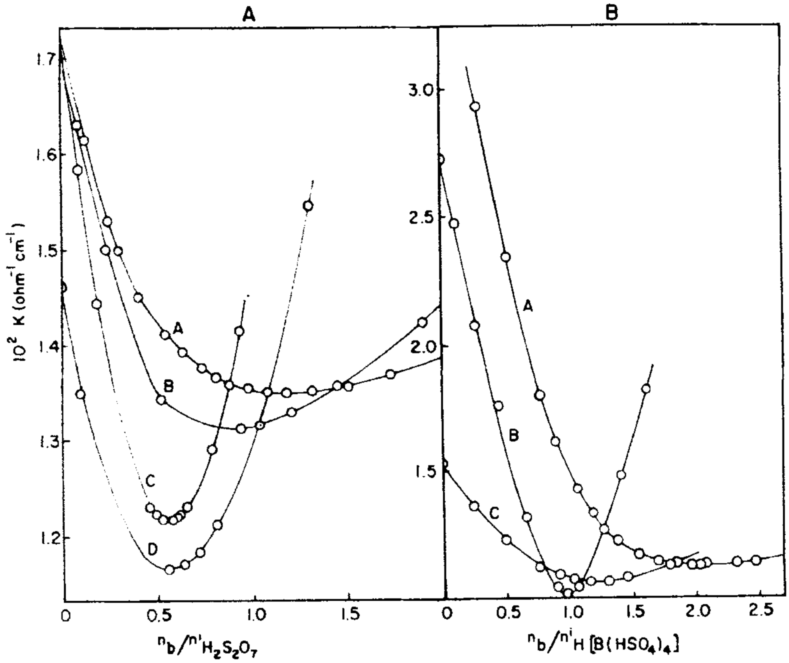

FIG. 4. Acid-base conductimetric titrations.

KEY: (4A): *A*, Nitrobenzene; *B*, *m*-Nitrotoluene; *C* and *D*, Benzoic acid; (4B); *A*, *m*-Nitrotoluene; *B*, Potassium hydrogensulfate; *C*, *o*-Nitrotoluene.

with a strong acid would come exactly at the ratio of added base to moles of initial acid $n_b/n_a^i = 1.0$, that is, at the true end-point of the reaction. If allowance is made for the difference in the mobilities of $H_3SO_4^+$ and HSO_4^- and also for the other self-dissociation processes of sulfuric acid then it may be shown (*26*) that the minimum conductivity would be expected at the mole ratio $n_b/n_a^i = 0.98$. It is evident that when a weak acid is titrated with a strong base the minimum conductivity will occur at $n_b/n_a^i < 1.0$ and when a strong acid is titrated with a weak base it will occur at $n_b/n_a^i > 1.0$. It may be shown (*26*) that in general for an acid with a dissociation constant K_a and a base with a dissociation constant K_b the minimum conductivity at 25° occurs at

$$n_b/n_a^i = 0.98(1 + 0.017/K_b)/(1 + 0.014/K_a).*$$

Thus if the position of minimum conductivity is determined experimentally a value of either K_a or K_b may be obtained if the other is known. Some examples of titrations involving the strong acid $HB(HSO_4)_4$ and the weak acid $H_2S_2O_7$ and several strong and weak bases are shown in Fig. 4. Values of the basic dissociation constants of several nitro compounds calculated from the position of the minimum conductivity in titrations of both $H_2S_2O_7$ and $HB(HSO_4)_4$ are in good agreement with values obtained by other methods (Table IX).

III. The Behavior of Some Inorganic Compounds in Sulfuric Acid

A. SULFATO AND HYDROGENSULFATO COMPOUNDS

The inorganic chemistry of the sulfuric acid solvent system has not yet been as extensively studied as that of some other solvents such as liquid ammonia, but a sufficient variety of certain classes of compounds has now been investigated for it to be possible to give a reasonably systematic account of their behavior.

Because only a very few anions are known at present that do not undergo extensive, if not complete, solvolysis in sulfuric acid, investigations have been mainly confined to the behavior of sulfates and hydrogen sulfates, which are the analogues of the oxides and hydroxides in water. It must not be concluded, however, that the chemistry of solutions in sulfuric acid is therefore without any great interest, because a great variety of different cations are known, many of which cannot exist in aqueous solutions. When an oxide or hydroxide is dissolved in sulfuric acid there is in general a tendency for it to be converted to a sulfate or hydrogen sulfate with the elimination of water (Section II, B, *1*, *c*), although the extent to which this occurs varies widely from one element to another. Thus, for example, the oxides and hydroxides of the more electropositive metals are completely converted into the corresponding hydrogen sulfates, while phosphoric acid, for example, is merely protonated and undergoes no conversion into a sulfato derivative. In general a wide variety of compounds intermediate between the oxides and hydroxides of the aqueous system and the sulfates and hydrogen sulfates of the sulfuric acid system may be formed. Some of the possible compounds and the relations between them are illustrated in Fig. 5 for the

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* Except for H_2O and H_2SO_7 for which slightly different equations are needed.

	X_2O_3	$XO(OH)$	$X_2O(OH)_4$	$X(OH)_3$
	$X_2O_2(SO_4)$	$X_2O_2(OH)(HSO_4)$	$X_2O(OH)_3(HSO_4)$	
$SO_3 \downarrow$	$X_2O(SO_4)_2$	$XO(HSO_4)$	$X_2O(OH)_2(HSO_4)_2$	$X(OH)_2(HSO_4)$
	$X_2(SO_4)_3$	$X_2O(SO_4)(HSO_4)_2$	$X_2O(OH)(HSO_4)_3$	
		$XSO_4(HSO_4)$	$X_2O(HSO_4)_4$	$X(OH)(HSO_4)_2$
			$X_2SO_4(HSO_4)_4$	
				$X(HSO_4)_3$

$$\xrightarrow{\qquad\qquad H_2O \qquad\qquad}$$

	YO_2	$YO(OH)_2$	$Y(OH)_4$
$SO_3 \downarrow$	$YO(SO_4)$	$YO(OH)(HSO_4)$	$Y(OH)_3(HSO_4)$
	$Y(SO_4)_2$	$YO(HSO_4)_2$	$Y(OH)_2(HSO_4)_2$
		$YSO_4(HSO_4)_2$	$Y(OH)(HSO_4)_3$
			$Y(HSO_4)_4$

$$\xrightarrow{\qquad\qquad H_2O \qquad\qquad}$$

FIG. 5. Oxy-, hydroxy-, sulfato-, and hydrogen sulfato-derivatives of a trivalent element X and a tetravalent element Y.

cases of a trivalent atom or group X and a tetravalent atom or group Y. Moving from left to right across the diagram corresponds to the addition of water, from top to bottom to the addition of sulfur trioxide, and diagonally from upper left to lower right to the addition of sulfuric acid. The compounds in the top row belong entirely to the water solvent system while those in the bottom diagonal belong entirely to the sulfuric acid solvent system. It appears that one of the important factors determining the extent of sulfation is the electronegativity of the group X (or Y), the extent of sulfation increasing with decreasing electronegativity. The formulae given in Fig. 5 are empirical only, and are not intended to represent the actual molecular constitution of the compounds. Thus they may in fact be polymeric, for example, Sb_2O_3 and $RSiO \cdot HSO_4$ (Section III, C, *1*, *c*), or they may be ionized either completely or partially as bases, for example,

$$NO \cdot HSO_4 = NO^+ + HSO_4^- \tag{53}$$

$$CH_3 \cdot Sn(HSO_4)_3 = CH_3 \cdot Sn(HSO_4)_2^+ + HSO_4^- \tag{54}$$

or in a few cases as acids, for example,

$$B(HSO_4)_3 \rightarrow HB(HSO_4)_4 \rightarrow H_3SO_4^+ + B(HSO_4)_4^- \tag{55}$$

$$Pb(HSO_4)_4 \rightarrow H_2Pb(HSO_4)_6 \rightarrow 2H_3SO_4^+ + Pb(HSO_4)_6^= \tag{56}$$

in exactly the same way as oxides and hydroxides may behave as either acids or bases, or both.

We are now in a position to discuss the behavior of the compounds of some of the elements of Groups III, IV, V, and VI, that have so far been studied. Apart from the fact that compounds of the alkali and alkaline earth metals are generally converted to ionic hydrogen sulfates and that compounds of a number of other metals generally give insoluble sulfates (Section II, B, *1, a*) practically nothing is known of the behavior of the compounds of elements other than those discussed below.

B. Group III: Boron

Boric acid and boric oxide and probably many other boron compounds are converted in sulfuric acid to boron tri(hydrogensulfate), $B(HSO_4)_3$, which behaves as a strong acid, $HB(HSO_4)_4$. The evidence for the formation of this acid and its salts provides an interesting example of the application of the cryoscopic and conductimetric methods for determining modes of ionization (*24*).

1. Boric Acid and Boric Oxide

It has been known for a long time that boric acid is very soluble in sulfuric acid, and various compounds of boric acid and boric oxide with sulfuric acid have been reported. One of these compounds has the composition $H_3BO_3 \cdot 3SO_3$, and may be regarded as boron tri(hydrogensulfate), $B(HSO_4)_3$ (*12*). Hantzsch (*53*) suggested that this compound is formed when boric oxide is dissolved in sulfuric acid. Freezing-point measurements (*24*) showed that $\nu = 6$ for both H_3BO_3 and B_2O_3. The formation of $B(HSO_4)_3$ would give $\nu = 7$ and $\nu = 8$ for boric acid and boric oxide respectively

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^- \tag{57}$$

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^- \tag{58}$$

which is not in agreement with the experimental observations. Conductivity measurements, Fig. 6, showed that for boric acid $\gamma = 2$ and for

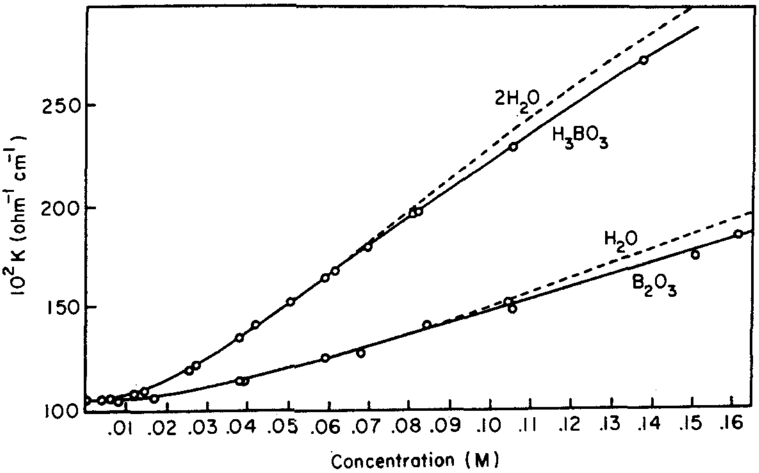


Fig. 6. Conductivities of solutions of boric acid and boric oxide. Reproduced from ref. *24*.

boric oxide $\gamma = 1$, which is again not in agreement with Eqs. (57) and (58), which require $\gamma = 3$ in both cases. If, however, we assume that boron tri(hydrogensulfate) combines with hydrogen sulfate ion to form the boron tetra(hydrogensulfate) ion

$$B(HSO_4)_3 + HSO_4^- = B(HSO_4)_4^- \tag{59}$$

by analogy with

$$BF_3 + F^- = BF_4^-$$

and (*15*)

$$B(OH)_3 + OH^- = B(OH)_4^-$$

Eqs. (57) and (58) can be rewritten as follows

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^- \tag{60}$$

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^-. \tag{61}$$

It may be seen that now $\nu = 6$ and $\gamma = 2$ for boric acid and $\nu = 6$ and $\gamma = 1$ for boric oxide in agreement with the experimental results.

2. Tetra(hydrogensulfato)boric Acid

The conclusion that the boron tetra(hydrogensulfate) ion is formed in these solutions is of great interest since, as it apparently does not undergo solvolysis, the corresponding acid $HB(HSO_4)_4$ must be a strong acid in the sulfuric acid solvent system, and must be extensively ionized according to Eq. (55) above. The solutions formed by dissolving boric oxide or boric acid in sulfuric acid contain a mixture of hydroxonium boron tetra(hydrogensulfate) and hydroxonium hydrogensulfate. Solutions of the free acid can be prepared by removing the hydroxonium ion by means of the reaction

$$H_3O^+ + SO_3 = H_3SO_4^+ \tag{62}$$

by dissolving the boric acid or oxide in oleum instead of sulfuric acid. Equations (60) and (61) then become

$$H_3BO_3 + 3H_2S_2O_7 = H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4 \tag{63}$$

$$B_2O_3 + 3H_2S_2O_7 + 4H_2SO_4 = 2H_3SO_4^+ + 2B(HSO_4)_4^-. \tag{64}$$

Cryoscopic and conductimetric measurements (*24*) confirm these reactions and therefore that the acid $HB(HSO_4)_4$ is very extensively, if not completely, ionized. Such a solution of $HB(HSO_4)_4$ can be titrated with a strong base such as $KHSO_4$ and the titration can be followed conductimetrically (Fig. 4):

$$\underset{\text{base}}{KHSO_4} + \underset{\text{acid}}{HB(HSO_4)_4} = \underset{\text{salt}}{KB(HSO_4)_4} + \underset{\text{solvent}}{H_2SO_4}. \tag{65}$$

The conductivity falls rapidly as $KHSO_4$ is added to a solution of $HB(HSO_4)_4$

and the highly conducting $H_3SO_4^+$ ion is replaced by the poorly conducting K^+ ion. It passes through a minimum at the mole ratio $n_{KHSO_4}/n^i_{HB(HSO_4)_4} = 0.98$, where n_{KHSO_4} is the number of moles of $KHSO_4$ added and $n^i_{HB(HSO_4)_4}$ is the initial number of moles of $HB(HSO_4)_4$, and then rises again because of the HSO_4^- arising from the excess $KHSO_4$. At the minimum the solution contains the fully ionized but relatively poorly conducting salt potassium boron tetra(hydrogensulfate), $K^+ \cdot B(HSO_4)_4^-$. In agreement with this interpretation of the conductivity results is the fact that up to the composition $n_{KHSO_4}/n^i_{HB(HSO_4)_4} = 1.0$ the freezing point hardly changes (Fig. 7). This is because $H_3SO_4^+$ is being replaced by K^+, and $B(HSO_4)_4^-$ remains unchanged in the solution; hence the total number of solute particles remains unchanged. After this composition the freezing point decreases as a consequence of the extra ions due to the excess $KHSO_4$ (*24*).

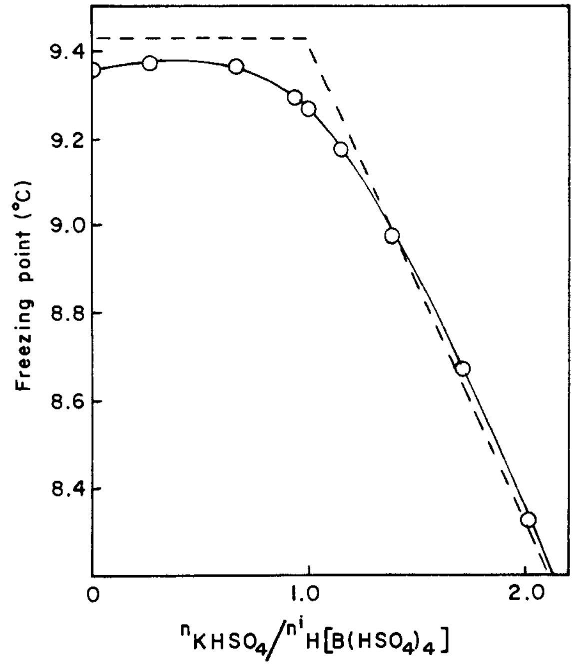
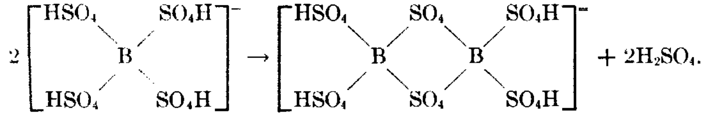


FIG. 7. Freezing points of $H[B(HSO_4)_4]$-$KHSO_4$ solutions. KEY: —o—, experimental curve; – – –, calculated "ideal" curve.

Attempts to obtain simple salts, for example, $KB(HSO_4)_4$, from such solutions have not so far been successful (*41*). In order to get a solid to crystallize out it was found necessary to prepare considerably more concentrated solutions than those used in the physical measurements, and under these conditions the solid sodium, potassium, ammonium, and strontium salts that were obtained had a ratio of sulfate to boron of less than four. They appear to contain polymeric anions formed from the boron tetra(hydrogensulfate) anion by the elimination of sulfuric acid. One of the simplest of such anions that can be envisaged is the dimeric ion containing bridging sulfate groups



(66)

There are many more complex possibilities for anions derived from compounds intermediate in composition between $B(HSO_4)_3$ and $B_2(SO_4)_3$. This is analogous to the behavior of the borate ion, which, in dilute aqueous solution has the formula $B(OH)_4^-$ (*15*) although many solid borates contain complex anions such as $B_4O_7^{=}$ and $B_6O_{11}^{4-}$.

C. GROUP IV

1. *Silicon*

A number of organosilicon compounds have been investigated by several groups of workers (*26, 76, 79, 83*). The results of some recent conductivity measurements (*26*) are shown in Fig. 8.

a. Trialkylsilanols, R_3SiOH, and Their Derivatives. The experimental values (*26, 76, 79*) of $\nu = 4.1$ and $\gamma = 1.0$ for hexamethyldisiloxane indicate that it ionizes according to the equation

$$[(CH_3)_3Si]_2O + 3H_2SO_4 = 2(CH_3)_3SiSO_4H + H_3O^+ + HSO_4^-. \qquad (67)$$

Price (*79*) suggested that trimethylsilicon hydrogen sulfate ionizes further to give the trimethylsiliconium ion,

$$(CH_3)_3SiSO_4H = (CH_3)_3Si^+ + HSO_4^- \qquad (68)$$

but there is no evidence from the cryoscopic or conductimetric measurements that this occurs to any appreciable extent (*26*). The results of measurements on solutions of trimethylethoxysilane (*26*), triethylethoxysilane (*76*), and triethylsilanol (*76*) show that they also react to give the corresponding trialkylsilicon hydrogensulfates

$$R_3SiOEt + 3H_2SO_4 = R_3SiSO_4H + EtSO_4H + H_3O^+ + HSO_4^- \qquad (69)$$

$$R_3SiOH + 2H_2SO_4 = R_3SiSO_4H + H_3O^+ + HSO_4^-. \qquad (70)$$

b. Dialkylsilanols, $R_2Si(OH)_2$, and Their Derivatives. The experimental values of $\nu = 7.2$ and $\gamma = 2.0$ obtained for dimethyldiethoxysilane (*26*) are in agreement with the formation of the corresponding di(hydrogensulfate)

$$(CH_3)_2Si(OEt)_2 + 6H_2SO_4 = (CH_3)_2Si(SO_4H)_2 + 2EtSO_4H + 2H_3O^+ + 2HSO_4^-. \qquad (71)$$

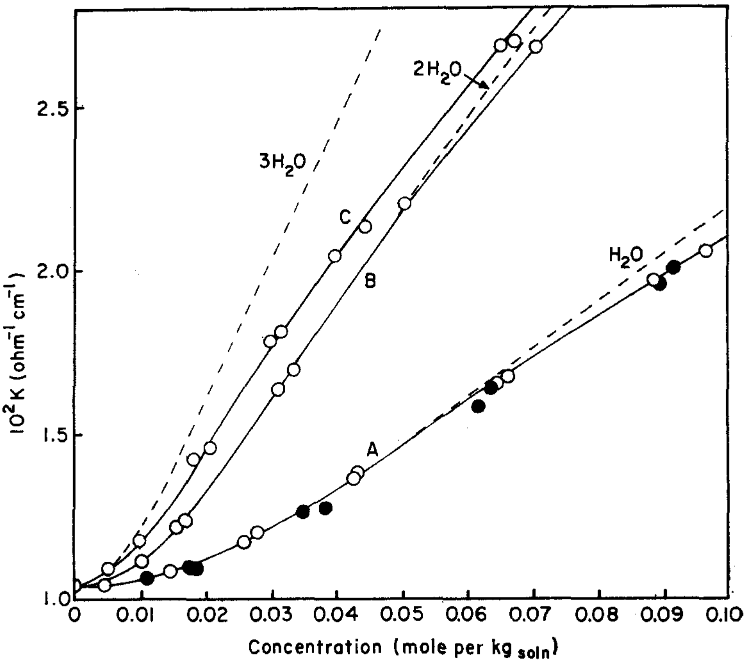


FIG. 8. Conductivities of solutions of some silicon compounds. KEY: *A*, ○ Hexamethyldisiloxane, ● Trimethylethoxysilane; *B*, Dimethyldiethoxysilane; *C*, Methyltriethoxysilane.

The value of $i = 12.6$ obtained by Price (*79*) for the compound $[(CH_3)_2SiO]_4$ is also consistent with the formation of dimethylsilicon di(hydrogensulfate)

$$[(CH_3)_2SiO]_4 + 12H_2SO_4 = 4(CH_3)_2Si(SO_4H)_2 + 4H_3O^+ + 4HSO_4^-. \qquad (72)$$

The rather high values of ν and i given by these compounds can be attributed mainly to nonideality of the solutions as has been discussed in detail by Flowers *et al.* (*26*).

c. Monoalkylsilanols, RSi(OH)$_3$, and Their Derivatives. If methyltriethoxysilane formed methylsilicon tri(hydrogensulfate) values of $\nu = 10$ and $\gamma = 3$ would be expected:

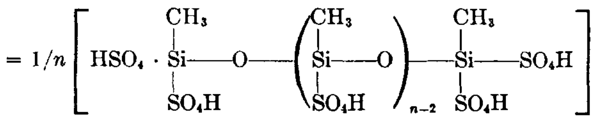
$$CH_3Si(OEt)_3 + 9H_2SO_4 = CH_3Si(SO_4H)_3 + 3EtHSO_4 + 3H_3O^+ + 3HSO_4^-.$$

The actual experimental values obtained (*26*) were $\nu = 8.0\text{-}7.7$ and $\gamma = 2.6\text{-}2.2$ over the concentration range 0.015-0.055 *m*. It appears therefore that in this case conversion to the corresponding sulfato derivatives is not complete. Thus if the oxide $(SO_4H)_2CH_3SiOSiCH_3(SO_4H)_2$ were formed $\nu = 8.5$ and $\gamma = 2.5$ would be expected

$$2CH_3Si(OEt)_3 + 15H_2SO_4 = (SO_4H)_2CH_3 \cdot SiOSi \cdot CH_3(SO_4H)_2 \\ + 6EtSO_4H + 5H_3O^+ + 5HSO_4^-. \quad (73)$$

The smaller values of ν and γ actually obtained indicate that higher polymers are in fact formed. In general one can write

$$CH_3Si(OEt)_3 + (6 + 3/n)H_2SO_4$$



$$= 1/n\left[\mathrm{HSO_4 \cdot \underset{SO_4H}{\overset{CH_3}{Si}}-O-\left(\underset{SO_4H}{\overset{CH_3}{Si}}-O\right)_{n-2}-\underset{SO_4H}{\overset{CH_3}{Si}}-SO_4H}\right]$$

$$+ 3EtHSO_4 + (2 + 1/n)H_3O^+ + (2 + 1/n)HSO_4^-. \quad (74)$$

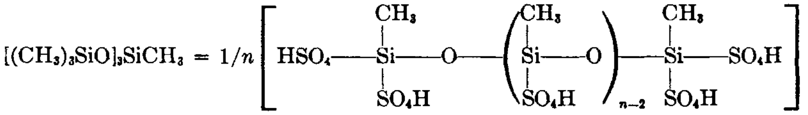
	n	ν	γ
Dimer	2	8.5	2.5
Trimer	3	8.0	2.3
Tetramer	4	7.75	2.25

The formation of a mixture of these polymers would account satisfactorily for the experimental observations. The formation of cyclic polymers as suggested by Price (*79*) would give $\nu = 7.5\text{-}7.0$ and $\gamma = 2.0$

$$CH_3Si(OEt)_3 \rightarrow 1/n[CH_3Si(SO_4H)O]_n + 3EtSO_4H + 2H_3O^+ + 2HSO_4^- \quad (75)$$

and is not therefore in good agreement with the experimental results.

The values of i between 8.5 and 8.0 obtained (*79*) for the compound $[(CH_3)_3SiO]_3SiCH_3$ are consistent with the formation of the dimers and trimers described above



$$[(CH_3)_3SiO]_3SiCH_3 = 1/n\left[\mathrm{HSO_4-\underset{SO_4H}{\overset{CH_3}{Si}}-O-\left(\underset{SO_4H}{\overset{CH_3}{Si}}-O\right)_{n-2}-\underset{SO_4H}{\overset{CH_3}{Si}}-SO_4H}\right]$$

$$+ 3(CH_3)_3SiSO_4H + (2 + 1/n)H_3O^+ + (2 + 1/n)HSO_4^- \quad (76)$$

$$\nu = 7 + 3/n$$

d. Silicic Acid Derivatives. The compounds $Si(OEt)_4$, Ph_3SiOH, $Ph_2Si(OH)_2$, $Si(OAc)_4$, and $(naphthyl)_3SiOH$ appear to be insoluble in sulfuric acid (*26*). They probably react to form insoluble polymers. Some cryoscopic and conductimetric measurements have been made on solutions of $SiPh_4$ which dissolves to some extent with the formation of only a relatively small amount of insoluble polymer. The interpretation of the results is not very certain but they appear to indicate that benzene sulfonic acid and a three-dimensional oxy(hydrogensulfato) polymer are formed (*26*).

$$SiPh_4 \rightarrow 4PhSO_3H + 1/2n[Si_2O_3(HSO_4)_2]_{n/2} + 2.5H_3O^+ + 2.5HSO_4^-. \quad (77)$$

The compound $Si[OSi(CH_3)_3]_4$ appears to give a similar polymer (*79*).

$$Si[OSi(CH_3)_3]_4 \rightarrow 4(CH_3)_3SiSO_4H + 1/2n[Si_2O_3(HSO_4)_2]_{n/2} + 2.5H_3O^+ + 2.5HSO_4^-. \qquad (78)$$

It may be noted that in solution in sulfuric acid no more than two hydrogen sulfate groups become attached to a silicon atom. In cases where a tri- or tetra(hydrogensulfate) could in principle be formed oxysulfato compounds are in fact obtained.

2. Tin

a. Hexa(hydrogensulfato)stannic Acid. Stannic acid and stannic sulfate appear to be almost insoluble in sulfuric acid, but a number of salts of sulfato-stannic acid, $H_2Sn(SO_4)_3$, have been prepared by evaporating mixtures of stannic oxide, a metal sulfate, and sulfuric acid (*13, 85, 86*), for example, $Rb_2Sn(SO_4)_3$, $K_2Sn(SO_4)_3$, $Ag_2Sn(SO_4)_3 \cdot 3H_2O$, $CaSn(SO_4)_3 \cdot 3H_2O$, $PbSn(SO_4)_3 \cdot 3H_2O$. All the hydrated salts contain three molecules of water, and they may perhaps be formulated as salts of tri(hydrogensulfato)stannic acid, $H_2Sn(OH)_3(HSO_4)_3$, for example, $Ag_2Sn(OH)_3(HSO_4)_3$. Evidence for the existence of hexa(hydrogensulfato)stannic acid, $H_2Sn(HSO_4)_6$, in solution in sulfuric acid has been obtained from the study of the freezing points and conductivities of solutions of tetraphenyltin, triphenyl tin hydroxide, and tin tetraacetate in sulfuric acid (*41*). The results of these measurements are consistent with the following modes of ionization for these compounds, and are not in agreement with other modes of ionization that may be formulated.

$$Ph_4Sn + 14H_2SO_4 = H_2Sn(HSO_4)_6 + 4PhSO_3H + 4H_3O^+ + 4HSO_4^- \qquad (79)$$

$$Ph_3SnOH + 13H_2SO_4 = H_2Sn(HSO_4)_6 + 3PhSO_3H + 4H_3O^+ + 4HSO_4^- \qquad (80)$$

$$Sn(OAc)_4 + 10H_2SO_4 = H_2Sn(HSO_4)_6 + 4AcOH_2^+ + 4HSO_4^- \qquad (81)$$

The values of ν and γ decrease with increasing concentration in each case and this can be attributed to the equilibrium between the free acid, its anions, and hydrogen sulfate ion,

$$H_2Sn(HSO_4)_6 + 2HSO_4^- = HSn(HSO_4)_6^- + HSO_4^- + H_2SO_4 = Sn(HSO_4)_6^{=} + 2H_2SO_4. \qquad (82)$$

In the case of the phenyl compounds, the phenyl groups are rapidly and quantitatively removed to form benzene sulfonic acid and water, as is also the case for phenyl boron and silicon compounds.

b. Tetramethyltin. When tetramethyltin is dissolved in sulfuric acid at room temperature there is a rapid evolution of methane as a result of the reaction

$$(CH_3)_4Sn + H_2SO_4 = (CH_3)_3Sn \cdot SO_4H + CH_4. \qquad (83)$$

A similar reaction is known to occur with the halogen hydracids. When this reaction was allowed to proceed to completion, cryoscopic and conductimetric measurements (*41*) on the resulting solution showed that $\nu = 2$ and $\gamma = 1$, indicating that trimethyltin hydrogen sulfate ionizes as a strong base according to the equation

$$(CH_3)_3Sn \cdot SO_4H = (CH_3)_3Sn^+ + HSO_4^-. \qquad (84)$$

This reaction can also be written in the form

$$(CH_3)_3Sn \cdot SO_4H + H_2SO_4 = (CH_3)_3Sn \cdot SO_4H_2^+ + HSO_4^- \qquad (85)$$

and it is not possible at present to distinguish between these two possibilities. In any similar cases we shall for simplicity write the reaction in the first of the forms given above.

c. Trimethyltin Sulfate. This behavior of trimethyltin hydrogensulfate is confirmed by that of trimethyltin sulfate, which was found (*41*) to give $\nu = 4$ and $\gamma = 2$, in accord with the ionization

$$[(CH_3)_3Sn]_2SO_4 = 2(CH_3)_3Sn^+ + 2HSO_4^-. \qquad (86)$$

Thus trimethyltin hydrogensulfate is a strong base in sulfuric acid. The corresponding hydroxide is, on the other hand, only a weak base in water (*11*).

*d. Di-*n*-Butyltin Diacetate.* Cryoscopic and conductimetric measurements (*41*) on di-*n*-butyltin diacetate indicate that it forms the di(hydrogensulfate) which behaves as a strong base

$$(n\text{-Bu})_2Sn(OAc)_2 + 4H_2SO_4 = (n\text{-Bu})_2SnSO_4H^+ + 2AcOH_2^+ + 3HSO_4^-. \qquad (87)$$

e. Methylstannonic Acid. Methylstannonic acid dissolves in sulfuric acid only very slowly even at 60°. However, solutions could be obtained sufficiently concentrated to enable cryoscopic and conductimetric measurements to be made (*41*). The results show that methyltin tri(hydrogensulfate) is formed

$$CH_3SnO(OH) + 5H_2SO_4 = CH_3Sn(HSO_4)_3 + 2H_3O^+ + 2HSO_4^- \qquad (88)$$

which then ionizes as a weak base.

In contrast to the behavior of silicon all the tin compounds investigated are completely converted to the corresponding sulfato compounds, which is consistent with the smaller electronegativity of tin. The basicity of the tin hydrogen sulfates decreases as the number of hydrogen sulfate groups on the tin atom increases, thus R_3SnSO_4H and $R_2Sn(HSO_4)_2$ are strong bases, while $RSn(HSO_4)_3$ is a weak base and $Sn(HSO_4)_4$ is an acid.

3. Lead [Hexa(hydrogensulfato)plumbic Acid]

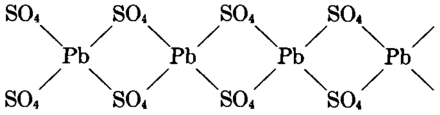
Plumbous salts are in general converted to plumbous di(hydrogensulfate) which is a fully ionized strong base (Section II, B, *1, a*). Lead dioxide is insoluble in sulfuric acid and the only soluble compound of Pb(IV) that has been investigated is lead tetraacetate, which, like tin tetraacetate, is fully converted to the tetra(hydrogensulfate). Since this behaves as an acid, it may be regarded as hexa(hydrogensulfato)plumbic acid, $H_2Pb(HSO_4)_6$ (*40*)

$$Pb(OAc)_4 + 10H_2SO_4 = H_2Pb(HSO_4)_6 + 4AcOH_2^+ + 4HSO_4^-. \qquad (89)$$

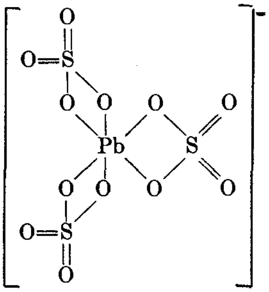
From the variation of the values of ν and γ with concentration it was possible to deduce values for the two dissociation constants of this acid, $K_1 = 1.1 \times 10^{-2}$ and $K_2 = 1.8 \times 10^{-3}$

$$H_2Pb(HSO_4)_6 \rightarrow H_3SO_4^+ + HPb(HSO_4)_6^- \rightarrow 2H_3SO_4^+ + Pb(HSO_4)_6^{=}. \qquad (90)$$

Solutions of hexa(hydrogensulfato)plumbic acid on warming deposit bright yellow plumbic sulfate $Pb(SO_4)_2$ which like $Sn(SO_4)_2$ is only slightly soluble in sulfuric acid. It seems reasonable to suppose that the insolubility of these sulfates results from their being polymeric. Their structures have not been determined. One possibility is illustrated in Formula (I). Salts of trisulfatoplumbic acid have been prepared (*16*), for example, $K_2Pb(SO_4)_3$ and these are also only slightly soluble in sulfuric acid, as are the corresponding sulfatostannates. The structures of these salts are not known; they could be imagined as containing discrete anions containing three chelated sulfate groups as in Formula (II),

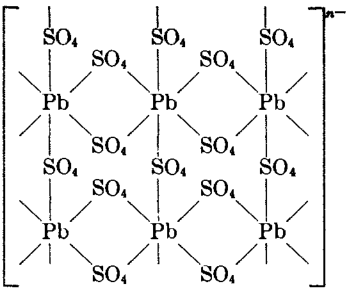


(I)



(II)

but their insolubility is more consistent with a structure containing a three-dimensional polymeric anion, such as that represented rather diagrammatically in Formula (III). Salts of the corresponding hydroxy acids are well-known, for example, $K_2Sn(OH)_6$ and $Na_2Pb(OH)_6$. It is note-



(III)

worthy that just as sulfatoplumbic acid readily loses sulfuric acid on warming to deposit insoluble plumbic sulfate, so hydroxyplumbic acid readily loses water and deposits insoluble PbO_2 on warming, while both hydroxy- and sulfatostannic acids appear to be rather more stable.

D. GROUP V

1. *Nitrogen*

Nitric acid, metallic nitrates, and dinitrogen pentoxide are converted to nitronium hydrogen sulfate, which is a fully ionized strong base (*36, 45, 47, 58, 75*):

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \quad (91)$$

$$KNO_3 + 3H_2SO_4 = K^+ + NO_2^+ + H_3O^+ + 3HSO_4^- \quad (92)$$

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^-. \quad (93)$$

Dinitrogen trioxide and nitrites react to give fully ionized nitrosonium hydrogen sulfate (*47, 75*)

$$N_2O_3 + 3H_2SO_4 = 2NO^+ + H_3O^+ + 3HSO_4^- \quad (94)$$

$$NaNO_2 + 3H_2SO_4 = Na^+ + NO^+ + H_3O^+ + 3HSO_4^- \quad (95)$$

and dinitrogen tetroxide gives a mixture of nitronium and nitrosonium hydrogen sulfates (*47, 75*)

$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-. \quad (96)$$

There is no doubt that nitronium and nitrosonium hydrogen sulfates are ionized as bases according to the equations

$$NO_2 \cdot HSO_4 = NO_2^+ + HSO_4^- \quad (97)$$

$$NO \cdot HSO_4 = NO^+ + HSO_4^- \quad (98)$$

and not, for example, according to the equation

$$NO_2 \cdot HSO_4 + H_2SO_4 = NO_2 \cdot SO_4H_2^+ + HSO_4^- \quad (99)$$

as both the nitronium and nitrosonium ions have been positively identified by means of their Raman spectra (*36, 58, 75*).

Ammonia and all the amines that have been investigated behave as strong bases in sulfuric acid. Even triphenylamine, which is generally regarded as an exceedingly weak base, incapable of forming salts, has been shown (*50*) by means of cryoscopic and conductimetric measurements to be a strong base in sulfuric acid, ionizing completely according to the equation

$$Ph_3N + H_2SO_4 = Ph_3NH^+ + HSO_4^-. \qquad (100)$$

2. Phosphorus

Phosphoric acid behaves as a strong base, as is shown, for example, by cryoscopic and conductimetric measurements (*41*) on KH_2PO_4. They show that $\nu = 4$ and $\gamma = 2$, in agreement with ionization according to the equation

$$KH_2PO_4 + 2H_2SO_4 = K^+ + H_4PO_4^+ + 2HSO_4^-. \qquad (101)$$

Like triphenylamine, triphenylphosphine is a strong base (*50*) being fully protonated according to the equation

$$Ph_3P + H_2SO_4 = Ph_3PH^+ + HSO_4^-. \qquad (102)$$

In addition it undergoes either rather slow sulfonation or oxidation, or both.

3. Arsenic

The pentoxide is insoluble in sulfuric acid at room temperature, and dissolves only slowly even at temperatures near the boiling point of the acid. Arsenious oxide, on the other hand, is moderately, if rather slowly, soluble in sulfuric acid. Cryoscopic and conductimetric measurements (*41*) have shown that it ionizes in an analogous manner to N_2O_3, forming $AsO \cdot HSO_4$,

$$As_2O_3 + 3H_2SO_4 = 2AsO \cdot HSO_4 + H_3O^+ + HSO_4^-. \qquad (103)$$

However, whereas the ionization of $NO \cdot HSO_4$ is complete, that of $AsO \cdot HSO_4$ is only approximately 50% complete in a 0.05 *M* solution of As_2O_3,

$$AsO \cdot HSO_4 = AsO^+ + HSO_4^-. \qquad (104)$$

Moreover the results indicate that at higher concentrations some polymeric cation is formed in increasing amounts. It has not so far been possible to determine the nature of this ion. The simplest polymeric ion that can be formulated would appear to be $As_3O_4^+$

$$AsO^+ + As_2O_3 = As_3O_4^+. \qquad (105)$$

Whereas the antimonyl ion SbO^+ and the bismuthyl ion BiO^+ are well-known, this appears to be the first definite evidence for the arsonyl ion AsO^+.

By dissolving arsenious oxide in oleum, it can be further sulfated and arsenic tri(hydrogensulfate) is obtained. This appears to behave as a very weak acid, and therefore it can probably be formulated as tetra (hydrogensulfato)arsenious acid, $HAs(HSO_4)_4$,

$$As_2O_3 + 3H_2S_2O_7 = 2As(HSO_4)_3 \tag{106}$$

$$As(HSO_4)_3 + H_2SO_4 = HAs(HSO_4)_4. \tag{107}$$

If further As_2O_3 is added to a solution of $As(HSO_4)_3$ freezing-point and conductivity measurements indicate that a polymeric species, which is probably $(SO_4H)_2AsOAs(SO_4H)_2$ is formed,

$$As_2O_3 + 4As(HSO_4)_3 = 3(SO_4H)_2AsOAs(SO_4H)_2. \tag{108}$$

Addition of still more As_2O_3 finally leads to the formation of $AsO \cdot HSO_4$,

$$As_2O_3 + As(HSO_4)_3 = 3AsO \cdot HSO_4. \tag{109}$$

A number of compounds of As_2O_3 with sulfur trioxide have been described, which may be formulated as oxysulfato derivatives with formulae such as have been given in Fig. 5. Thus, from solutions of As_2O_3 in aqueous sulfuric acid, the compound $As_2O_3 \cdot SO_3$ or $(AsO)_2SO_4$ has been crystallized (*1*). The same compound has also been obtained from the flues of pyrites burners (*72*). From 98% H_2SO_4 the compound $As_2O_3 \cdot 2SO_3$ has been obtained (*1*): this may be formulated as $As_2O(SO_4)_2$. From the reaction of As_2O_3 and sulfur trioxide the formation of the compounds $As_2O_3 \cdot 3SO_3$, $As_2O_3 \cdot 4SO_3$, $As_2O_3 \cdot 6SO_3$, and $As_2O_3 \cdot 8SO_3$ has been claimed (*1, 72, 81*). The first may be formulated as $As_2(SO_4)_3$, and the others may be polysulfates. Several complex sulfates of As(III) have been described (*66*), for example, $PbO \cdot As_2O_3 \cdot 2SO_3$ and $CaO \cdot As_2O_3 \cdot 3SO_3$. These may all be formulated as derivatives of oxysulfato acids intermediate between $HAsO_2$ and $HAs(SO_4)_2$. Thus the first may be written as $Pb[AsO(SO_4)]_2$, and the second as $Ca[As_2O(SO_4)_3]$. The relationships between the various compounds of arsenic (III) that appear to exist in sulfuric acid solutions is shown diagrammatically below (also see Fig. 5).

$$\begin{tikzcd}
H_3SO_4^+ + As(HSO_4)_4^- & HAs(HSO_4)_4 \arrow[l] & As(HSO_4)_3 \arrow[l] \arrow[d, shift right, "H_2O"'] \\
& & (HSO_4)_2AsOAs(HSO_4)_2 \arrow[u, shift right, "H_2S_2O_7"'] \arrow[d, shift right, "H_2O"'] \\
& & AsO \cdot HSO_4 \arrow[u, shift right, "H_2S_2O_7"'] \arrow[r] & AsO^+ + HSO_4^-
\end{tikzcd}$$

4. *Antimony*

The trioxide is insoluble in sulfuric acid at room temperature, but it dissolves on strong heating, and on cooling crystals of $Sb_2(SO_4)_3$ are deposited (*2*). From more aqueous sulfuric acid both $SbO \cdot SO_4H$ and $(SbO)_2SO_4$ have been obtained (*2*). A number of salts of the acid $HSb(SO_4)_2$ have been prepared (*52, 65*). They are insoluble in sulfuric acid at room temperature. It has been suggested that the salts contain the $Sb(SO_4)_2^-$ anion in which the two sulfate groups are chelated to the antimony (*82*). However, their insolubility in sulfuric acid makes it much more probable that they contain large polymeric anions in which the sulfate groups bridge from one antimony atom to another.

E. GROUP VI

1. *Selenium Dioxide*

It has been known for many years that selenium dioxide is soluble in sulfuric acid to give a bright yellow solution (*73*). It has been shown recently (*25*), by cryoscopic and conductimetric measurements, that in dilute solutions it behaves as a weak base ($K_b = 4.4 \times 10^{-2}$),

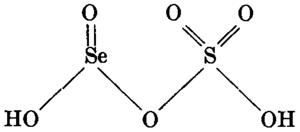
$$SeO_2 + H_2SO_4 = HSeO_2^+ + HSO_4^- \qquad (110)$$

forming the $SeO \cdot OH^+$ ion. It is probable that the un-ionized portion of the selenium dioxide is present as selenious hydrogensulfate, $SeO(OH)(SO_4H)$. The reaction of selenium dioxide with sulfuric acid would then be more correctly written

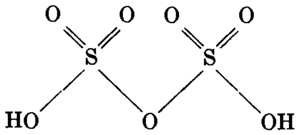
$$SeO_2 + H_2SO_4 = SeO(OH)(HSO_4) = SeO \cdot OH^+ + HSO_4^-. \qquad (111)$$

Selenious hydrogensulfate (Formula IV) could also be described as selenious-sulfuric acid, by analogy with disulfuric acid (Formula V) and selenic-sulfuric acid (Formula VI), although in sulfuric acid it behaves as a base rather than as an acid.

Small amounts of the ion $HSe_2O_4^+$ are also present in dilute solutions of SeO_2 in sulfuric acid, together with the un-ionized diselenious hydrogensulfate, $Se_2O_3(OH)(HSO_4)$ (Formula VII). Relatively greater



(IV)



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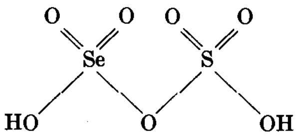

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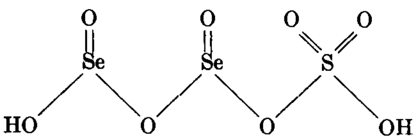

(VII)

amounts of this dimeric ion and probably higher polymeric ions are formed with increasing concentration of selenium dioxide.

When selenium dioxide is added to an oleum the conductivity decreases and passes through a minimum when one mole of SeO_2 has been added for each mole of disulfuric acid originally present in the oleum. The simplest interpretation of this result is that a largely un-ionized complex $SeO_2 \cdot H_2S_2O_7$ is formed. This may be formulated either as $SeO(HSO_4)_2$ or $SeO(OH)(HS_2O_7)$. Confirmation of such an un-ionized species is obtained from freezing-point measurements which show that at the composition of minimum conductivity $\nu = 1.3$. There is also some evidence for the existence of the corresponding derivatives of diselenious acid, that is, $Se_2O_3(HSO_4)_2$ or $Se_2O_3(OH)(HS_2O_7)$. It is not possible on the basis of available experimental data to distinguish between these alternative formulations, although the first is perhaps the most probable in each case and is also consistent with the general scheme of oxysulfato derivatives given in Fig. 5. The relationships between the sulfato compounds of selenium(IV) for which evidence has been obtained and the corresponding hydroxides and oxides are shown below.

SeO_2	$Se_2O_3(OH)_2$	$SeO(OH)_2$
	$Se_2O_3(OH)(SO_4H)$	$SeO(OH)(SO_4H)$
	$Se_2O_3(SO_4H)_2$	$SeO(SO_4H)_2$

2. *Tellurium Dioxide*

It is, perhaps, at first sight surprising that tellurium dioxide is insoluble in sulfuric acid, particularly because a compound $2TeO_2 \cdot SO_3$ (*9*) has been described, and as TeO_2 is soluble in other strong acids, for example, HNO_3, $HClO_4$, and HSO_3F, from which compounds such as $2TeO_2 \cdot HNO_3$ (*64*) and $2TeO_2 \cdot HClO_4$ (*18*) have been isolated. All these compounds can be regarded as derivatives of ditellurous acid, for example, $Te_2O_3(OH)(NO_3)$, $Te_2O_3(OH)(ClO_4)$, and $Te_2O_3(SO_4)$. It seems possible that TeO_2 does form a sulfate when treated with sulfuric acid, but that being highly polymeric it is insoluble in sulfuric acid.

3. *Sulfur Dioxide*

Sulfur dioxide is moderately soluble in sulfuric acid (*51, 74*) and gives a solution that has an electrical conductivity which is very slightly greater than that of the solvent (*41*). This is probably caused by a rather slight ionization according to the equation

$$SO_2 + H_2SO_4 = HSO_2^+ + HSO_4^-. \qquad (112)$$

The solubility of sulfur dioxide is greater in oleum and increases rapidly with increasing oleum concentration, that is, with increasing acidity of the solvent (*74*). This suggests that the basicity of sulfur dioxide is essentially responsible for its solubility in sulfuric acid and oleum, presumably because of the formation of a hydrogen-bonded complex which precedes the actual proton transfer accompanying ionization;

$$H_2SO_4 + SO_2 \rightleftharpoons HSO_3OH \cdots O{=}S{=}O \rightleftharpoons HSO_4^- + HSO_2^+.$$

Evidence for the basicity of the S=O group is also given by the fact that a number of substituted diphenyl sulfoxides, $R_2S{=}O$, have been shown to behave as strong bases and the corresponding sulfones, R_2SO_2, as weak bases in solution in sulfuric acid (*38*);

$$R_2S{=}O + H_2SO_4 = R_2S{=}OH^+ + HSO_4^- \qquad (113)$$

$$R_2SO_2 + H_2SO_4 = R_2SO_2H^+ + HSO_4^-. \qquad (114)$$

References

1. Adie, R. H., *J. Chem. Soc.* **55,** 157 (1889).
2. Adie, R. H., *J. Chem. Soc.* **57,** 540 (1890).
3. Barr, J., and Gillespie, R. J., unpublished.
4. Bass, S. J., and Gillespie, R. J., *J. Chem. Soc.* to be published.
5. Bass, S. J., Gillespie, R. J., and Robinson, E. A., *J. Chem. Soc.* to be published.
6. Bergius, F., *Z. physik. Chem.* **72,** 338 (1910).
7. Brand, J. C. D., Horning, W. C., and Thornley, M. B., *J. Chem. Soc.* p. 1374 (1952).
8. Brand, J. C. D., James, J. C., and Rutherford, A., *J. Chem. Soc.* p. 2447 (1953).
9. Brauner, B., *J. Chem. Soc.* **55,** 382 (1889).
10. Brayford, J. R., and Wyatt, P. A. H., *J. Chem. Soc.* p. 3453 (1955).
11. Bredig, G., *Z. physik. Chem.* **13,** 303 (1894).
12. d'Arcy, F. R., *J. Chem. Soc.* **55,** 155 (1889).
13. Druce, J. G. F., *Chem. News* **128,** 33 (1924).
14. Duffy, J. A., and Leisten, J. A., *Nature* **178,** 242 (1956).
15. Edwards, J. O., Morrison, G. C., Ross, V. F., and Schultz, J. W., *J. Am. Chem. Soc.* **77,** 266 (1955).
16. Elbs, K., and Fischer, F., *Z. Elektrochem.* **7,** 243 (1901).
17. Fèneant, S., and Chedin, J., *Mém. serv. chim. état* (*Paris*) **40,** 292 (1955).
18. Fichter, F., and Schmid, M., *Z. anorg. Chem.* **98,** 141 (1916).
19. Finback, C., and Viervoll, H., *Tidsskr. Kjemi, Bergvesen Met.* **3,** 36 (1943).
20. Finback, C., Rønning, O., and Viervoll, H., *Tidsskr. Kjemi, Bergvesen Met.* **4,** 26 (1944).
21. Flexser, L. A., and Hammett, L. P., *J. Am. Chem. Soc.* **60,** 885 (1938).
22. Flexser, L. A., Hammett, L. P., and Dingwall, A. *J. Am. Chem. Soc.* **57,** 2103 (1935).
23. Flowers, R. H., and Gillespie, R. J., unpublished.
24. Flowers, R. H., Gillespie, R. J., and Oubridge, J. V., *J. Chem. Soc.* p. 1925 (1956).
25. Flowers, R. H., Gillespie, R. J., and Robinson, E. A., *J. Nuclear & Inorg. Chem.* In press. (1959).

26. Flowers, R. H., Gillespie, R. J., and Robinson, E. A., *J. Chem. Soc.*, to be published.
27. Franklin, E. C., "The Nitrogen System of Compounds," Rheinhold, New York, 1935.
28. Gillespie, R. J. *J. Chem. Soc.* p. 2493 (1950).
29. Gillespie, R. J., *J. Chem. Soc.* p. 2516 (1950).
30. Gillespie, R. J., *J. Chem. Soc.* p. 2537 (1950).
31. Gillespie, R. J., *J. Chem. Soc.* p. 2542 (1950).
32. Gillespie, R. J., *J. Chem. Soc.* p. 1951 (1954).
33. Gillespie, R. J., *Discussions Faraday Soc.* **24,** 230 (1957).
34. Gillespie, R. J., and Cole, R. H., *Trans. Faraday Soc.* **52,** 1325 (1956).
35. Gillespie, R. J., and Leisten, J. A., *Quart. Revs.* **8,** 40 (1954).
36. Gillespie, R. J., and Millen, D. J., *Quart. Revs.* **2,** 277 (1948).
37. Gillespie, R. J., and Oubridge, J. V., *J. Chem. Soc.* p. 80 (1956).
38. Gillespie, R. J., and Passerini, R. C., *J. Chem. Soc.* p. 3850 (1956).
39. Gillespie, R. J., and Robinson, E. A., *J. Chem. Soc.* p. 4233 (1957).
40. Gillespie, R. J., and Robinson, E. A., *Proc. Chem. Soc.* 145 (1957).
41. Gillespie, R. J., and Robinson, E. A., unpublished.
42. Gillespie, R. J., and Solomons, C., *J. Chem. Soc.* p. 1796 (1957).
43. Gillespie, R. J., and Wasif, S., *J. Chem. Soc.* p. 209 (1953).
44. Gillespie, R. J., and Wasif, S., *J. Chem. Soc.* p. 215 (1953).
45. Gillespie, R. J., and Wasif, S., *J. Chem. Soc.* p. 221 (1953).
46. Gillespie, R. J., and White, R. F. M., *Trans. Faraday Soc.*, **54,** 1846 (1958).
47. Gillespie, R. J., Graham, J., Hughes, E. D., Ingold, C. K., and Peeling, E. R. A., *J. Chem. Soc.* p. 2504 (1950).
48. Gillespie, R. J., Hughes, E. D., and Ingold, C. K., *J. Chem. Soc.* p. 2504 (1950).
49. Gillespie, R. J., Oubridge, J. V., and Solomons, C., *J. Chem. Soc.* p. 1804 (1957).
50. Gillespie, R. J., Oubridge, J. V., and Robinson, E. A., unpublished.
51. Gold, V., and Hawes, B. W. V., *J. Chem. Soc.* p. 2102 (1951).
52. Gutmann, A., *Arch. Pharm.* **236,** 477 (1898).
53. Hantzsch, A., *Z. physik. Chem.* **61,** 257 (1907).
54. Hantzsch, A., *Z. physik. Chem.* **62,** 626 (1908); **65,** 41 (1908); **68,** 204 (1909); *Gazz. chim. ital.* **39**(i), 120 (1908); **39**(ii), 512 (1908); **41**(i), 645 (1911).
55. Hammett, L. P., and Deyrup, A. J., *J. Am. Chem. Soc.* **54,** 2721 (1932).
56. Hammett, L. P., and Deyrup, A. J., *J. Am. Chem. Soc.* **56,** 827 (1933).
57. Hammett, L. P., and Paul, M. A., *J. Am. Chem. Soc.* **56,** 827 (1934).
58. Ingold, C. K., Millen, D. J., and Poole, H. G., *J. Chem. Soc.*, p. 2576 (1950).
59. Kendall, J., and Davidson, A. W., *J. Am. Chem. Soc.* **43,** 979 (1921).
60. Kendall, J., and Landon, M. L., *J. Am. Chem. Soc.* **42,** 2131 (1920).
61. Kendall, J., Adler, H., and Davidson, A. W., *J. Am. Chem. Soc.* **43,** 1846 (1921).
62. Kirkbride, B. J., and Wyatt, P. A. H., *Trans. Faraday Soc.* **54,** 483 (1958).
63. Kneitsch, R., *Ber.* **34,** 4069 (1901).
64. Köthner, D., *Ann.* **399,** 1 (1901).
65. Kühl, H., *Z. anorg. Chem.* **54,** 256 (1907).
66. Kühl, H., *Arch. Pharm.* **245,** 377 (1907).
67. Kunzler, J. E., and Giauque, W. F., *J. Am. Chem. Soc.* **74,** 804 (1952).
68. Kunzler, J. E., and Giauque, W. F., *J. Am. Chem. Soc.* **74,** 3472 (1952).
69. Kunzler, J. E., and Giauque, W. F., *J. Am. Chem. Soc.* **74,** 5271 (1952).
70. Leisten, J. A., *J. Chem. Soc.* p. 1572 (1956).
71. Liler, M., and Kosanovic, D., *J. Chem. Soc.* p. 1084 (1958).

72. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," p. 332. Longmans Green, New York, 1929.
73. Meyer, J., and Langner, M., *Ber.* **60**, 285 (1927).
74. Miles, F. D., and Carson, T., *J. Chem. Soc.* **1946**, 786.
75. Millen, D. J., *J. Chem. Soc.* **1950**, 2600.
76. Newman, M. S., Craig, R. A., and Garrett, A. B., *J. Am. Chem. Soc.* **71**, 869 (1949).
77. Oddo, G., and Scandola, E., *Z. physik. Chem.* **62**, 243 (1908); **66**, 138 (1908); *Gazz. chim. ital.* **38(i)**, 603 (1908); **39(i)**, 569 (1909); **39(ii)**, 1 (1908); **40(ii)**, 163 (1910).
78. Pascard, R., *Compt. rend.* **240**, 2162 (1955).
79. Price, F., *J. Am. Chem. Soc.* **70**, 871 (1948).
80. Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," p. 116. Butterworths, London, 1955.
81. Schultz-Sellac, C., *Ber.* **4**, 109 (1871).
82. Sidgwick, N. V., "The Chemical Elements and Their Compounds," p. 798. Oxford University Press, London and New York, 1950.
83. Szmant, H. H., Devlin, O. M., and Brost, G. A., *J. Am. Chem. Soc.* **73**, 3059 (1951).
84. Treffers, H. P., and Hammett, L. P., *J. Am. Chem. Soc.* **59**, 1708 (1937).
85. Weinland, R. F., and Kühl, H., *Ber.* **39**, 2951 (1906).
86. Weinland, R. F., and Kühl, H., *Z. anorg. Chem.* **54**, 244 (1907).
87. Yost, D. M., and Russell, H., "Systematic Inorganic Chemistry," Prentice-Hall, New York, 1944.