TABLE II

THE STOICHIOMETRY OF THE MATERIALS INVOLVED IN THE REACTION BETWEEN WOLFRAM DIOXIDE AND DICHLORODIFLUOROMETHANE; ALL RUNS AT 525°

| Run | 9 | 10 | 11 | 12 | 13 | 14 | 16 |
|---|---|---|---|---|---|---|---|
| W reacted, gram-atoms | 0.0742 | 0.0666 | 0.1067 | 0.0663 | 0.0474 | 0.0709 | 0.0067 |
| $CCl_2F_2$ reacted, moles | 0.132 | ..... | ...... | ...... | 0.0561 | 0.0991 | 0.0198 |
| Time reactor at 525°, hours | 3.8 | 4.0 | 5.0 | 3.3 | 3.0 | 2.8 | 2.0 |
| Rate of $CCl_2F_2$ addition, g./hr. | 11.2 | 27.2 | 24.0 | 11.4 | 6.3 | 6.9 | 5.3 |
| Products obtained C, gram atoms | 0.0106 | 0.0149 | 0.0162 | 0.0109 | .... | 0.0127 | 0.00087 |
| CO, moles | ..... | ..... | .1051 | .0665 | .0423 | .0683 | .0030 |
| $CO_2$, moles | ..... | ..... | .0046 | .0031 | .0031 | .00066 | .00069 |
| $COF_2$, moles | ..... | .0013 | .0022 | .0011 | .0023 | .0014 | .0024 |
| $COCl_2$, moles | ..... | ..... | .00082 | .00024 | .0016 | .0166 | .00050 |
| Totals in reactor wash and samples | | | | | | | |
| $W^{6+}$, g.-atoms | ..... | .0475 | .1019 | .0622 | .0456 | .0649 | .0052 |
| $F^-$, g.-atoms | ..... | .1131 | .2302 | .1473 | .1321 | .1580 | .0185 |
| $Cl^-$, g.-atoms | ..... | .0931 | .1712 | .1187 | .1251 | .1670 | .0333 |
| Mole ratios | | | | | | | |
| $X^-/W$ | ..... | 4.34 | 3.95 | 4.27 | 5.64 | 5.01 | 10.06 |
| W/C | 7.01 | 4.47 | 6.58 | 6.08 | .... | 5.61 | 6.58 |
| $CF_2Cl_2/W$ | 1.78 | ..... | ...... | ...... | 1.19 | 1.40 | 3.48 |
| W/CO | ..... | ..... | 1.02 | 0.99 | 1.12 | 1.05 | 1.90 |

and carbonyl fluoride could interact with the corresponding wolfram oxytetrahalides to give the wolfram hexahalides and carbon dioxide.

## Summary

By passing dichlorodifluoromethane over wolfram dioxide at a temperature of 525° in a nickel metal reactor with removable product collector units in a temperature gradient zone it was found that the main wolfram-containing products were solid solutions of crystal form and color similar to those of wolfram oxytetrachloride. The product compositions could be represented as wolfram oxytetrachloride in which from 14.4 to 49.9 mole per cent. of the chloride was replaced by fluoride. Very small amounts of wolfram hexafluoride and wolfram hexachloride were also found. The wolfram was in the plus six oxidation state in all of the products.

In addition to the wolfram-containing products, carbon, carbon monoxide, carbon dioxide, carbonyl chloride, and carbonyl fluoride were found.

Consideration of the amounts of the various products obtained indicated that the main reaction may be represented by the equation $2WO_2 + 2CCl_2F_2 = WOF_4 + WOCl_4 + 2CO$. The other products likely resulted from interaction of these substances with the nickel metal reactor walls and with the nickel halide films thereon.

DAVIS, CALIFORNIA RECEIVED JANUARY 10, 1950

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

# The Electrical Conductivities of Solutions of Potassium Bisulfate in Concentrated and Fuming Sulfuric Acid[1]

BY RICHARD A. REINHARDT[2]

The present work was carried out to study further the solvolytic equilibria of water and sulfur trioxide dissolved in sulfuric acid by observing the effect on the conductivity produced by adding potassium bisulfate to concentrated and fuming sulfuric acids. In addition, in view of the discrepancies between the results of previous workers,[3] the conductivities of fuming sulfuric acid, without added salt, have been redetermined.

## Experimental

The experiments were carried out in a dry box through which passed a continuous stream of dried air and which fitted over an oil-bath maintained at 25 ± 0.02°. Pressure from the dried-air system was used to transfer liquids.

Solutions were prepared by mixing together weighed portions of two previously standardized stock solutions, one containing slightly less, the other slightly more than

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[1] Taken from the dissertation of R. A. Reinhardt presented to the Graduate School of the University of California in September, 1947, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Allied Chemical and Dye Corporation Fellow, 1946-1947. Present address: Department of Chemistry, Cornell University, Ithaca, New York.

[3] (a) W. Kohlrausch, *Ann. physik. Chem.*, **253**, 69 (1882) (b) R. Knietsch, *Ber.*, **34**, 4109 (1901); (c) A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); (d) F. Bergius, *ibid.*, **72**, 351 (1910).

100% sulfuric acid, and then adding weighed increments of potassium bisulfate.

The resistance of the conductivity cell was measured on the usual Kohlrausch-type bridge, with an oscilloscope as the null-point instrument. The precision of the measurements was about 0.1%.

The stock solutions were analyzed by titration with aqueous sodium hydroxide from a weight buret. Sulfuric acid of minimum conductivity (considered pure $H_2SO_4$[4]) was used as the primary standard. Precision of the analyses was from 0.01 to 0.02% sulfuric acid.

**Presentation of Data.**—The data are given in Tables I and II at rounded concentrations of potassium bisulfate. For those cases where potassium bisulfate was added, the concentration of water or of sulfur trioxide is given on a solid-free basis. All concentrations, $C$, are given in moles per liter, conductivities in ohm$^{-1}$ cm.$^{-1}$ × $10^3$. Molarities were calculated from density measurements by the author[5] which have not been included in this paper.

TABLE I

CONDUCTIVITIES OF $KHSO_4$–$H_2O$ MIXTURES × $10^3$

| $C_{H_2O}$ | $C_{KHSO_4}$ → | 0.05 | 0.10 | 0.20 | 0.40 |
|---|---|---|---|---|---|
| 0.11 | Obs. | 21.50 | 25.5 | 32.8 | |
| | Theor. | 20.8 | 24.8 | 31.9 | |
| .21 | Obs. | 28.37 | 32.02 | 37.05 | |
| | Theor. | 28.3 | 31.9 | 38.0 | |
| 1.24 | Obs. | 73.1 | 75.2 | 79.9 | 84.2 |
| | Theor. | 72.6 | 74.1 | 77.2 | 82.4 |

TABLE II

CONDUCTIVITIES OF $KHSO_4$–$SO_3$ MIXTURES × $10^3$

| $C_{SO_3}$ | $C_{KHSO_4}$ → 0.00 | 0.05 | 0.10 | 0.15 | 0.25 | 0.35 | 0.50 |
|---|---|---|---|---|---|---|---|
| 0.06 | 13.31 | 11.97 | 13.88 | 17.24 | 25.66 | | |
| .16 | 19.52 | 16.42 | 14.42 | 13.52 | 15.63 | 20.11 | |
| .21 | 20.26 | 16.77 | 14.86 | 13.83 | 15.07 | 19.5 | |
| .29 | 20.65 | 17.70 | 16.44 | | | | |
| .40 | 22.68 | 19.64 | 17.39 | 15.85 | 14.89 | 16.67 | |
| .55 | 25.40 | 22.71 | 20.33 | 18.48 | 16.36 | 16.09 | 19.03 |
| .60 | 26.39 | 23.13 | 20.89 | 18.85 | | | |
| .67 | 28.00 | | | | | | |
| .97 | 31.32 | 29.14 | 27.23 | 25.67 | 23.48 | 22.09 | 20.73 |
| 1.17 | 32.36 | | | | | | |
| 1.47 | 34.52 | | | | | | |
| 1.72 | 36.24 | 34.42 | 32.83 | 31.42 | 29.04 | 27.21 | 25.13 |
| 1.95 | 36.70 | | | | | | |
| 2.38 | 37.81 | | | | | | |
| 2.66 | 37.98 | | | | | | |
| 3.35 | 37.62 | | | | | | |

## Discussion of Results

At the beginning of the present work the possibility of a slow reaction between the molecules present in sulfur trioxide and water solutions was considered as a conceivable explanation for the variation in the results of previous workers[3] for the conductivity of fuming sulfuric acid. At no time during the measurements, however, was any change in conductivity observed after such solutions had been mixed and brought to thermal equilibrium. The results of this paper (in Table II) agree most nearly with those of W. Kohlrausch.[3a]

If bisulfate ion contributes virtually completely to the conductivity in solutions of water in sulfuric acid,[6] and if water is indeed completely ionized into hydronium and bisulfate ions,[7] then a mixture of water and potassium bisulfate dissolved in sulfuric acid should have the same conductivity as water at the same total concentration. The results of such measurements are shown in Table I. The lines headed "Theor" represent the conductivities of water alone, taken from the data of Lichty,[4] in which the water concentration equals the sum of the concentration of water and potassium bisulfate. In general, the agreement is satisfactory, and it seems doubtful that differences, where observed, are of significance.

Table II shows the results on sulfur trioxide-potassium bisulfate mixtures. The addition of bisulfate to fuming acid causes at first a decrease in conductivity; but before an amount of bisulfate equimolar to the original sulfur trioxide content has been added, the conductivity passes through a minimum and then increases.

**The Autoprotolysis of Pure Sulfuric Acid.**—The flattening of the maximum of the freezing-point curve for the vicinity of pure sulfuric acid[7,8] has been attributed by Hammett and Deyrup[7] to the autoprotolysis of the solvent

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

and, in addition, some dissociation involving sulfur trioxide, as

$$3H_2SO_4 = H_3O^+ + H_2S_2O_7 + HSO_4^-$$

If it is assumed that only the first of these equations is of importance at 25°, several estimates are available for the autoprotolysis constant. Hammett and Deyrup[9] calculated the concentration of bisulfate ion in 100% sulfuric acid from their values of the acidity function in this region. From their result, 0.027 mole/kg., the autoprotolysis constant, $K_s$ = 0.024 mole$^2$ liter$^{-2}$. The author has performed similar calculations from the $H_0$ values at 0.01, 0.03 and 0.05% water, obtaining values of $K_s$ ranging from 0.003 to 0.005.

From the conductivity of pure sulfuric acid (0.01) and accepted values for the ionic conductance of barium ion in water and the viscosities of water and sulfuric acid,[10] and assuming that the transference number of barium ion for barium bisulfate in sulfuric acid is 0.01,[6] that the conductance–viscosity product for barium ion is the same in sulfuric acid as in water, and that the conductances of bisulfate and sulfonium (*i. e.*, $H_3SO_4^+$) are equal, $K_s$ is computed to be 0.0006.

If the straight portions of the freezing point curve for the vicinity of pure sulfuric acid[7] are extended, they must meet at a point corresponding to the hypothetical undissociated solvent. This point is found to be 0.13° above the actual freezing point of the pure acid; and, using the molal

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[4] D. M. Lichty, THIS JOURNAL, **30**, 1845 (1908).

[5] R. A. Reinhardt, Thesis, University of California, 1947.

[6] L. P. Hammett and F. A. Loewenheim, THIS JOURNAL, **56**, 2620 (1934).

[7] L. P. Hammett and A. J. Deyrup, *ibid.*, **55**, 1900 (1933).

[8] Brand, *J. Chem. Soc.*, 585 (1946).

[9] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2731 (1932).

[10] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Vol. V, p. 10; Vol. VI, p. 230; Dunstan, *Proc. Chem. Soc.*, **30**, 104 (1914).

freezing point depression as 5.9 deg. mole$^{-1}$ kg.,[7] $K_s$ is computed to be 0.0004.

The general agreement between these three methods, within a factor of ten, seems to indicate that the dissociation to sulfur trioxide and its reaction products is not of significance. Lewis and Bigeleisen[11] attributed the steep rise in $-H_0$ in the region 95–100% acid as due to the presence of sulfur trioxide, postulating that the curve for the "activity of hydrogen ion" lay well below the acidity function curve. But if free sulfur trioxide (or pyrosulfuric acid) were present in pure sulfuric acid $-H_0$ would be larger than if only proton acids were present; and thus a smaller value of $-H_0$ would have to be used by Hammett and Deyrup[9] in their calculation, giving rise to a higher concentration of bisulfate ion than actually computed.

Proceeding on the assumption of Hammett and Deyrup that

$$H_0 = \log K + \log (HSO_4^-)/(H_2SO_4)$$

values of log $K$ can be computed from $H_0$, assuming complete ionization of water. Thus calculated, log $K$ is found to be about $-8.0$ (using $H_0$ values in ref. 9) and is effectively constant from 90 to 99.9% acid. Thus the shape of the acidity function curve is entirely consistent with the idea that water is highly ionized and that the concentration of sulfur trioxide in concentrated sulfuric acid need not be reckoned with.

**Sulfur Trioxide–Potassium Bisulfate Mixtures.**—Since evidence from Raman spectra shows pyrosulfuric acid to be the principal solute species in fuming sulfuric acid,[12] and since the increase in conductivity on addition of sulfur trioxide indicates some ionization of pyrosulfuric acid, it may be presumed that fuming sulfuric acid contains sulfonium ion, bipyrosulfate ion and un-ionized pyrosulfuric acid. Thus it seems reasonable that added bisulfate could neutralize both the sulfonium ion (the reversal of autoprotolysis) and the pyrosulfuric acid. Assuming the first ionization constant of pyrosulfuric acid to be greater than the second (though they may well be close together, as for the first two constants of pyrophosphoric acid), reaction with bipyrosulfate ion cannot be expected in the presence of excess free pyrosulfuric acid. Two net equations may be written

$$H_3SO_4^+ + HSO_4^- = 2H_2SO_4\text{, and}$$
$$HSO_4^- + H_2S_2O_7 = H_2SO_4 + HS_2O_7^-$$

As potassium bisulfate is added to fuming sulfuric acid, the number of ions increases. In the initial stages, at least, the concentration of bisulfate ion remains low, that of sulfonium decreases, and thus that of bipyrosulfate increases rather rapidly. Since the conductivity decreases, it follows that the molar conductance of bipyrosulfate ion must be appreciably lower than that of sulfonium ion. The existence of a minimum can be interpreted as showing that the concentration of bisulfate is beginning to become significant, and that its conductance is also greater than that of bipyrosulfate. Since the minimum occurs before all of the pyrosulfuric acid has been neutralized, this neutralization is a reaction which does not proceed to completion, except in the presence of excess pyrosulfuric acid or bisulfate ion. Therefore, since the reaction between sulfonium and bisulfate ions is surely nearly complete, pyrosulfuric acid must behave as a weak acid in the solvent sulfuric acid. Quantitatively, this is borne out by fact that sulfur trioxide causes a slower rise in conductivity, when added to pure sulfuric acid, than does water.

Brand[13] noted that if water was added to fuming sulfuric acid containing potassium bisulfate, the fuming disappeared when the ratio of the stoichiometric concentration of bisulfate to that of sulfur trioxide, corrected for the reaction with water, was about two. This indicates that if bisulfate were added to fuming sulfuric acid, the concentration of pyrosulfuric acid would remain appreciable until about two moles of the bisulfate had been added for each mole of pyrosulfuric acid originally present. Such a conclusion is in substantial agreement with those arrived at in the present paper.

If potassium bisulfate is added to fuming sulfuric acid, a point will be reached where the concentration of bisulfate and sulfonium ions will be equal to one another, and thus equal to their values in pure sulfuric acid. This point probably lies between the minimum in conductivity and the equivalence point. If at such point the conductivity of pure sulfuric acid (0.0108) is subtracted from the observed conductivity, and the result divided by the concentration of added potassium ion (which must here equal the bipyrosulfate concentration), the molar conductance of bipyrosulfate ion is obtained (ignoring the small contribution due to potassium ion). An idea of the value of this can be obtained by comparing the results of such a calculation at the minimum and at the equivalence point. For example, in solutions originally 0.16 $M$ in sulfur trioxide, the minimum occurs at 0.135 $M$ potassium ion, where the conductivity is 0.0130; and at 0.16 $M$ potassium ion, the conductivity is 0.0137. The values of the molar conductance of bipyrosulfate, as computed from these data, are, respectively, 23 and 24. In general, the results are about the same, regardless of which points on a given curve are chosen. From one curve to another, the bipyrosulfate conductance falls off somewhat with increasing original sulfur trioxide content, from about 40 at 0.06 $M$ sulfur trioxide, to 25 at the higher concentrations. Note that at corresponding concentrations, the conductance of water (*i. e.*, of bisulfate ion) varies from 160 to 90.

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[11] G. N. Lewis and J. Bigeleisen, THIS JOURNAL, **65**, 1148 (1943).

[12] See T. F. Young and L. A. Blatz, *Chem. Rev.*, **44**, 98 (1949).

[13] Brand, *J. Chem. Soc.*, 880 (1946).

**The Freezing-point Curve for Sulfur Trioxide.**—The data of Hammett and Deyrup[7] and Brand[8] show that the molar freezing-point depression for sulfur trioxide in sulfuric acid is nearly constant; the slope of the line corresponds to about 1.3 moles of new substance for each mole of added sulfur trioxide. This slope is constant as far as the measurements were made—to about 0.5 *M*. If pyrosulfuric acid were formed but incompletely ionized, the curve should have a slope of nearly two in dilute solution and curve upwards, approaching a slope of one. The observed effect is not in accord with the ideas presented, and no explanation can as yet be offered.

**Acknowledgment.**—The author wishes to express his indebtedness to the later Professor W. C. Bray, under whose direction this research was begun, and to Professor W. M. Latimer, who undertook the direction of the work after Professor Bray's death in 1946.

## Summary

1. The conductivities of fuming sulfuric acid have been redetermined and the results compared with those of previous authors.

2. The effect of added potassium bisulfate on the conductivities of solutions of water and sulfur trioxide in sulfuric acid has been studied. The evidence from water solutions substantiates prior evidence that water is highly ionized in this solvent. The studies in fuming sulfuric acid can be interpreted qualitatively as showing that pyrosulfuric acid is a weak acid in sulfuric acid, and that its neutralization by bisulfate ion does not proceed to completion except in the presence of an excess of one of the reactants.

3. The autoprotolysis constant for pure sulfuric acid has been estimated by several methods. The agreement between these methods is cited as evidence that the dissociation of pure sulfuric acid is due chiefly to the autoprotolysis reaction.

ITHACA, N. Y. RECEIVED DECEMBER 6, 1949

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

# Solutions of Ammonium Chlorogallate in Diethyl Ether

BY HAROLD L. FRIEDMAN[1] AND HENRY TAUBE

In a previous paper[2] the high solubility in ether of some compounds of the type $M'M'''Cl_4$ was noted. It was shown that $NH_4GaCl_4$, $NH_4FeCl_4$, and $NH_4AlCl_4$ distribute themselves between the solid phases and the saturated solutions in ether without change in composition. However, some other compounds of this type, including $LiGaCl_4$, change their composition when treated with ether. The saturated ether phase being enriched in $M'''Gl_3$ relative to $M'Cl$. The present investigation was undertaken in order to learn something of the constitution of the solute in these solutions. The general features of the behavior of electrolytes in solvents of low dielectric constant have been explored by C. A. Kraus, R. M. Fuoss and co-workers.[3] It seemed of interest to make comparisons between the present systems and those studied by Kraus[4] because of the relatively small size and simple character of the cations and the relatively complex nature of the anions in the present systems. The results would appear to have a direct bearing also on the extraction of iron and gallium by ether from aqueous hydrochloric acid solutions of Ga(III) and Fe(III). These elements are taken up into the ether phase as $HFeCl_4$[5] and $HGaCl_4$[6] (with a rather large number of water molecules) and presumably exist in ether as the etheronium or hydronium compounds. In composition they therefore resemble $NH_4GaCl_4$, and their behavior in ether solutions can be expected to show resemblances to that of $NH_4GaCl_4$.

## Results

**Two-Phase Liquid Region.**—When the concentration of the solute $NH_4GaCl_4$[7] in ether is increased at constant temperature, a composition is reached at which a new liquid phase appears. Further increase in concentration causes the solute-rich phase to grow at the expense of the other; finally, only the solute-rich phase is left, which then increases in concentration until it is saturated with solute. Analyses were made of the two co-existing liquid phases with the results as reported in Table I.

TABLE I

| | Upper phase | Lower phase | |
|---|---|---|---|
| Density, g./ml. | 0.75 | 0.82 | ±0.02 |
| Atoms Cl/atoms N | 3.99 | 4.00 | ± .01 |
| Concn., molality | 0.45 | 0.88 | ± .05 |

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[1] Department of Chemistry, University of Southern California, Los Angeles 7, California.

[2] H. L. Friedman and H. Taube, THIS JOURNAL, **72**, 2236 (1950).

[3] *Cf.* review by C. A. Kraus, *J. Franklin Inst.*, **225**, 687 (1938).

[4] Kraus, *et al.*, studied as solutes salts of the type tetraalkylammonium or trialkylammonium halide, nitrate, perchlorate, thiocyanate, or picrate. Solutions of silver perchlorate in benzene were also studied but there is evidence for a stable complex between silver ion and benzene: A. E. Hill, THIS JOURNAL, **44**, 1163 (1922); L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

[5] N. H. Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948).

[6] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **71**, 4035 (1949).

[7] The preparation, purification, and precautions in handling of the materials were described in the previous paper.