2. The rate of the reaction is independent of the nature of the walls of the vessel and the space arrangement in the molecule of malic acid.

3. The velocity of the reaction has been determined with various concentrations of water at the temperatures 30°, 40° and 50°. In all cases, small amounts of water produce a great retardation of the reaction.

4. Sodium, potassium and silver sulfates, acetic acid and dimethylpyrone retard the reaction to a great extent.

5. Dissolved hydrogen chloride does not alter the reaction rate and the effect of small amounts of sulfur trioxide cannot be detected, although a large excess causes appreciable diminution.

6. The inhibition increases logarithmically with the molality of the inhibitors, and the similarity of the decomposition of formic acid to that of oxalic acid in this respect is pointed out.

7. The temperature coefficient has been calculated for ten-degree intervals from 20° to 50°. The average value, 3.72, is abnormally large.

8. The value of the critical increment, calculated according to the equation of Arrhenius, changes but slightly with the temperature.

9. A mechanism for the decomposition of malic acid has been offered, postulating an unstable intermediate of the type $C_4H_6O_5.H_2SO_4$.

10. The role of the inhibitors has been discussed in the light of Taylor's theory of negative catalysis and found to conform to his predictions.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

# SOLUTIONS OF SALTS IN 100% SULFURIC ACID. SOLVOLYSIS AND DOUBLE DECOMPOSITION REACTIONS

BY ARTHUR W. DAVIDSON

RECEIVED NOVEMBER 17, 1924 PUBLISHED APRIL 4, 1925

## Introduction

Sulfuric acid has attracted the attention of a considerable number of investigators interested in the properties of non-aqueous solvents. Pure 100% $H_2SO_4$ is fairly easily prepared, is a liquid over a very wide temperature range (10.5° to 332°) and its physical properties, with the single exception of its very high viscosity,[1] are such as to present no serious experimental obstacles to its investigation.

The first systematic study of this solvent was undertaken by Walden.[2]

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[1] The viscosity of $H_2SO_4$ at 25° is approximately 21 times that of water at the same temperature. On this account, most substances dissolve in this liquid at a very slow rate, except at inconveniently high temperatures. On the other hand, crystallization from solutions in this solvent is also likely to be delayed, necessitating extreme supercooling, especially in concentrated solutions. The high viscosity also makes it difficult to free separated crystals from adhering liquid for the purpose of analysis.

[2] Walden, *Z. anorg. Chem.*, **29**, 371 (1902).

He found that it dissolved several acids and salts, and concluded from conductivity measurements that its ionizing power was very great, as would be expected from its high dielectric constant, which is greater than that of water. It was not possible to determine the degree of dissociation of solutes in such solutions, however, due to the considerable number of unknown factors involved.[3] The pioneer work of Walden was soon followed by a considerable number of other investigations on the properties of 100% sulfuric acid as solvent.[4] Hantzsch's first paper presents interesting data on the freezing-point depressions and conductivities of solutions of a very large number of substances, both organic and inorganic. However, the later investigations listed accomplished little more than the accumulation of a mass of apparently unrelated and often contradictory freezing-point and conductivity data. Many of these articles (the later ones by Hantzsch and by Oddo) are, in fact, merely controversial in nature, and throw no further light on the subject. In 1914 Kendall and Carpenter[5] made a study of systems consisting of organic acids (and other organic compounds) and sulfuric acid, and showed that the tendency toward the formation of addition compounds in such solutions is greater, the less the strength of the organic acid.

In 1920 a systematic study was begun by Kendall and co-workers of compound formation and solubility in systems of the type, sulfuric acid, metal sulfate. It was demonstrated as a result of these investigations[6] that solutions of sulfates in 100% sulfuric acid show considerable analogy to solutions of the corresponding hydroxides in water or, more specifically, that the order of solubility of the various sulfates in sulfuric acid corresponds almost exactly with the order of solubility of the hydroxides in water. The sulfates may, in fact, be considered as bases, in sulfuric acid solution, since they presumably have the same negative ion as the solvent.[7] In a later article[8] it was shown, however, that this analogy does not extend to the relative degrees of dissociation of the sulfates in such solutions, as measured by their conductivities.

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[3] Such as corrections to be made for the high conductivity of the solvent itself, changes in the degree of dissociation of the solvent on the addition of other substances, possible chemical reactions between solvent and solute, etc.

[4] (a) Beckmann, *Z. physik. Chem.*, **53**, 129 (1905). (b) Hantzsch, *ibid.*, **61**, 257 (1907); (c) **62**, 626 (1908); (d) **65**, 41 (1908); (e) **68**, 204 (1909). (f) Oddo and Scandola, *ibid.*, **62**, 243 (1908); (g) **66**, 138 (1909); (h) *Gazz. chim. ital.*, **38**, I, 603 (1908); (i) **39**, II, 1 (1909). (j) Hantzsch, *ibid.*, **41**, I, 645 (1909). (k) Bergius, *Z. physik. Chem.*, **72**, 338 (1910). (l) Poma, *J. chim. phys.*, **10**, 177 (1912). (m) Oddo and Casalino, *Gazz. chim. ital.*, **47**, II, 200, 232 (1917); (n) **48**, I, 17 (1918).

[5] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[6] (a) Kendall and Landon, *ibid.*, **42**, 2131 (1920). (b) Kendall and Davidson, *ibid.*, **43**, 979 (1921).

[7] Compare Schlesinger and Calvert, *ibid.*, **33**, 1933 (1911).

[8] Kendall, Adler and Davidson, *ibid.*, **43**, 1846 (1921).

## Solvolysis in Sulfuric Acid Solutions

The interesting results obtained in the study of the sulfuric acid : metal sulfate systems made it appear worth while to attempt to discover further analogies between water and sulfuric acid as solvents, and especially to throw some additional light, if possible, on the behavior of *salts* when dissolved in this solvent, bases (that is, sulfates) and acids having already been investigated. Such an attempt was made in the work to be described. It was soon found that no such close parallel can be drawn between these two solvents as that developed, by the well-known researches of Franklin and co-workers, between water and liquid ammonia.[9] The main reason for the failure of the analogy to hold when salt solutions in water and in sulfuric acid are compared is, in the writer's opinion, to be found in these facts: that while water and liquid ammonia, though excellent dissociating mediums, are themselves only very slightly dissociated, sulfuric acid, on the other hand, is not only an ionizing medium but is itself ionized to a considerable extent, even in the pure state. This difference is sharply brought out by a comparison of the specific conductivities of the pure liquids, which may be considered as giving a rough idea of the extent of their self-ionization. For water at 25°, the value of the specific conductivity is about $5 \times 10^{-8}$ reciprocal ohm; for pure sulfuric acid it is approximately[10] $1 \times 10^{-2}$. The probable influence of this fact upon the solvent properties of sulfuric acid was at once recognized by Walden in his early work in this field, where he mentions[11] that the high degree of self-ionization of the solvent (into $H^+$, $HSO_4^-$ and $SO_4^{--}$ ions) would cause it to enter very readily into double decomposition reactions with dissolved substances. Such reactions are quite analogous to hydrolysis in aqueous solutions or ammonolysis in liquid ammonia. Walden gave the name of "sulfolysis" (German "Sulfolyse") to this sort of reaction in sulfuric acid, but the more general term "solvolysis" will be employed in this article.[12] According to Hantzsch, solvolysis always proceeds practically to completion in solutions of salts in sulfuric acid.[13] There is, however, no satisfactory evidence to justify such a conclusion. Hantzsch, it is true, found that the freezing-point depression in dilute solutions of potassium nitrate in sulfuric acid was four times that calculated according to the van't Hoff theory of dilute solutions, which fact he explained by assuming that the

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[9] Franklin, *Am. Chem. J.*, **47**, 285 (1912).

[10] Lichty, THIS JOURNAL, **30**, 1834 (1908).

[11] Ref. 2, p. 387.

[12] Since the word "sulfolysis" might perhaps be more appropriately used for similar reactions in liquid sulfur dioxide solutions.

[13] "All salts (except sulfates), because of the great excess of the strong acid serving as solvent, are practically completely decomposed into acid sulfates and free acids" (Ref. 4 b, p. 291). In all his subsequent papers, Hantzsch simply assumes the truth of this statement. See, for example, Ref. 4 d, p. 51.

salt was completely solvolyzed to nitric acid and potassium hydrogen sulfate, each of these products being practically completely dissociated into two ions. But obviously, this explanation cannot be valid; for if both of the products of solvolysis were completely dissociated, it would be difficult to account for any solvolysis at all taking place. We may, however, logically conclude this much: that since the degree of ionization of sulfuric acid is comparatively great, soluble salts will always be appreciably solvolyzed in this solvent, with the formation of sulfates (or acid sulfates) and free acids,[14] just as in aqueous solutions hydrolysis of soluble salts would always be appreciable if water were largely, instead of only exceedingly slightly, dissociated into hydrogen and hydroxyl ions. Furthermore, we may confidently predict that at least two particular classes of salts will, unless quite insoluble, undergo extensive and readily detectable solvolytic double decomposition in sulfuric acid solution, namely, salts of metals whose sulfates are insoluble in sulfuric acid, and salts of acids which are insoluble in this solvent. This can perhaps be made clearer by again drawing an analogy with hydrolysis in aqueous solution. If water were *largely* dissociated into its ions, any soluble salt of a metal whose hydroxide is either a very weak base or is insoluble in water[15] would be extensively hydrolyzed because of the formation of this hydroxide. Thus, under these conditions, *no* ferric nor aluminum salts, not even those of strong acids, could be dissolved in water to give clear solutions, as considerable amounts of insoluble ferric or aluminum hydroxide would be formed as soon as the salt was brought in contact with the solvent.[16] We should expect, then, that salts of metals whose sulfates are insoluble in sulfuric acid would, in that solvent, be extensively solvolyzed to the corresponding insoluble bases, that is, sulfates. Similarly, if water were highly dissociated as we have supposed, extensive hydrolysis in aqueous solution would evidently take place also whenever the acid corresponding to the salt was insoluble;[17] silicates, for example, even those of the alkali metals, could not be dissolved to give clear solutions, but would form considerable amounts of silicic acid when brought in contact with water. Correspondingly, salts of acids insoluble in sulfuric acid should be extensively solvolyzed to such acids in that solvent. Experimental verification of these predictions will be described below.

[14] Compare the discussion of solvolysis in formic acid solutions by Schlesinger and Calvert, Ref. 7, p. 1932.

[15] Those hydroxides which are weak bases are, in general, also insoluble. See Kendall, Davidson and Adler, THIS JOURNAL, **43,** 1490 (1921).

[16] Of course such salts are actually hydrolyzed to some extent, even though the degree of dissociation of water is so small.

[17] Or whenever the acid was slightly dissociated. We have too little information about the degree of dissociation of acids in $H_2SO_4$ solution, however, to make it possible to extend this part of the analogy to such solutions.

## Object of the Present Work

The specific objects of this investigation were as follows: (1) to determine whether the solubilities in 100% sulfuric acid of the sulfates of aluminum, lead and zinc are increased by the addition of the sulfate of the strongly positive metal sodium, since the hydroxides of these less positive metals are dissolved by aqueous sodium hydroxide solution; (2) to gain some additional information on the subject of solvolysis by sulfuric acid, both by qualitative experiments and by determining the composition of the crystals separating on cooling the solutions of certain salts in this solvent; (3) to obtain qualitative data as to the relative solubilities of various salts in 100% sulfuric acid, and to determine whether ionized salts in this solvent readily take part in double decomposition reactions forming insoluble products, as such salts do in water and in liquid ammonia.

## Experimental Part

Pure 100% sulfuric acid was prepared as described by Kendall and Carpenter,[18] the freezing point being taken as the criterion of purity. All the acid used throughout the investigation froze at 10.3–10.4°. The salts used were C. P. samples of reliable quality, moisture being, in general, the only impurity present in significant amount. To remove this, the salts were heated to constant weight and then kept in a desiccator over 99% sulfuric acid until used. Special purification was necessary in only a few instances. Precautions were taken to exclude atmospheric moisture, as far as possible, during the experiments. Compositions of solutions are expressed throughout in molecular percentages of solute.

**1. Effect of Sodium Sulfate on the Solubilities of Aluminum, Zinc, and Lead Sulfates in Sulfuric Acid.**—Anhydrous aluminum sulfate is practically insoluble in 100% sulfuric acid.[19] In order to determine whether or not its solubility is increased by the presence of sodium sulfate in solution, a solution was prepared containing 3.47 molecular per cent. of anhydrous sodium sulfate in sulfuric acid. To 25.85 g. of this solution, 0.05 g. of anhydrous aluminum sulfate was added, and the mixture was heated to boiling. There was no indication of solution taking place, the solid remaining undiminished in amount, in spite of the large excess of sodium sulfate (6 moles of sodium sulfate to 1 of aluminum sulfate). Two additional portions of sodium sulfate were added, and the solution was heated to boiling after each addition. Although the final solution contained 9.73% of sodium sulfate, no solution of the aluminum sulfate took place.

Similar experiments were made with anhydrous zinc sulfate and with lead sulfate. The former is soluble in 100% sulfuric acid to the extent of 0.14 molecular per cent. at 20°, the latter to about 1.25%.[19] In neither case was the solubility increased by the addition to the solution of sodium

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[18] Ref. 5, p. 2500.

[19] Ref. 6 b, p. 984.

sulfate to the extent of 4 molecular per cent. In fact, the presence of sodium sulfate actually decreased the solubility of the zinc and lead sulfates, due probably to the effect of the increased concentration of the common ion, $SO_4^{--}$.

**2. Solvolysis of Salts in Sulfuric Acid Solution.**—A few qualitative experiments sufficed to verify the predictions made above in regard to the extensive solvolysis of salts of metals whose sulfates are insoluble, and of salts of insoluble acids. The most insoluble sulfates of those so far studied are aluminum and ferric sulfates.[19] The following aluminum and ferric salts were treated with 100% sulfuric acid: aluminum chloride, nitrate and orthophosphate, ferric chloride, nitrate and ferrocyanide ($Fe_4[Fe(CN)_6]_3$). All of these salts were visibly solvolyzed. In most cases the salts at once became coated with a white, opaque, gelatinous layer of sulfate. This change took place slowly in the cold, rapidly on gentle heating. In no case could a clear solution of the salt be obtained.

Hydrogen chloride, hydrogen bromide and silicic acid are nearly insoluble in 100% sulfuric acid. Experiments were made with the following salts of these acids: sodium, potassium and calcium chlorides, sodium and potassium bromides and sodium metasilicate. The chlorides and bromides dissolved readily, even in the cold, giving clear solutions; considerable quantities of gaseous hydrogen chloride or hydrogen bromide, however, were given off. The solvolysis here, although extensive, is not complete, as will be shown later. In the case of the bromides, the solutions became orange-brown in color, which may possible be due to partial oxidation of the hydrogen bromide to free bromine;[20] in the cold, such oxidation is not extensive. Sodium silicate did not dissolve when treated with 100% sulfuric acid, but left a white, gelatinous residue which was found to be insoluble in water and was therefore presumably some form of silicic acid.

It follows, then, that the only salts that can be dissolved in this solvent *without* extensive solvolytic double decomposition accompanied by immediate separation of the insoluble product, are salts of metals whose sulfates are soluble and of acids which also are soluble. Even in such cases considerable amounts of the acid and the base (sulfate) may be present in the solution, in equilibrium with solvent and unchanged salt and their ions. The amounts of such solvolytic products in the equilibrium mixture cannot readily be determined. When the solution is cooled, however, the particular product that first crystallizes will depend on the extent of solvolysis and on the relative solubilities of the various substances present in the solution; that is, of the salt, acid and base (sulfate). There are evidently too many unknown factors involved to allow prediction of the re-

[20] In this connection, Walden (Ref. 2, p. 385) pointed out that a solution of free bromine in $H_2SO_4$ is pale yellow; he believed the much darker color of bromide solutions to be due to some other cause.

sult in any given case. In the hope of learning whether it is possible, in a case where conditions are favorable, to crystallize the unchanged salt or an addition compound of salt and solvent from a solution of an easily soluble, highly ionized salt in sulfuric acid,[21] a study was made of solutions of the two salts, potassium ferrocyanide and calcium phosphate. Both of these salts dissolve in the solvent rather readily and with no visible evidence of solvolysis; in each case both the acid and the base (sulfate) that might be derived from the salt by solvolysis are soluble in 100% sulfuric acid and are not acted upon by this substance under ordinary conditions.

The method used was as follows. First, the freezing-point depression curve for solutions of the salt in 100% sulfuric acid was determined in the usual way.[22] At first the solid phase that separated on cooling consisted, of course, of crystals of $H_2SO_4$. The curve was continued until a sharp break in its direction indicated that a new solid phase was separating.[23] A solution was then made containing a somewhat greater concentration of salt than that at which the break in the curve occurred. This solution was cooled until crystallization took place, and the crystals were separated from the solution and analyzed as described below.

**Potassium Ferrocyanide.**—In making up solutions of this salt, it was necessary to immerse the test-tube containing the sulfuric acid in a bath of ice water and to add the salt in small portions at a time while the mixture was constantly shaken in order to avoid decomposition at the moment of contact of solid and liquid. The salt became white when immersed in the acid, and after it had been thoroughly wet by the solvent, the mixture could be heated as high as 100° without appreciable decomposition taking place.[24] The solutions were perfectly clear and straw-yellow.

Freezing-point data were as follows.

FREEZING-POINT DATA

| $K_4Fe(CN)_6$, % | 0 | 0.53 | 1.11 | 1.38 | 1.57 |
|---|---|---|---|---|---|
| Temp., °C. | 10.3 | 7.1 | 2.3 | −0.2 | 6.0 (new solid phase) |

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[21] Mercuric chloride dissolves in *boiling* sulfuric acid and can be recovered unchanged when the solution is cooled. Compare Ref. 4b, p. 268. This salt is probably not ionized, however.

[22] For details as to the method used for obtaining such data for $H_2SO_4$ solutions, see Ref. 6a, pp. 2132–4.

[23] It was intended to determine the solubility curve for the salt, provided that the new phase proved to be either the pure salt or an addition product of salt and solvent. When, however, the crystals separating consisted of a product of solvolysis (as was found to be the case with both the salts here used), then of course the mixture could no longer be regarded as a two-component system.

[24] Compare Fowler, *J. Chem. Soc.*, **77**, 150 (1900). It is there shown that while potassium ferrocyanide is rapidly decomposed by sulfuric acid containing considerable quantities of water, little decomposition takes place below 130° in the concentrated (98%) acid.

No quantitative conclusions as to the state of the dissolved salt can be drawn from these data, because of the large number of factors which influence the freezing-point depression to an unknown extent.[25] The depressions are so large, however, in comparison with those obtained experimentally by Hantzsch for non-dissociating substances at corresponding concentrations,[26] or with those calculated from the equation for ideal solutions,[27] as to leave no doubt, at least, that combination between solvent and solute and ionization of the latter have both taken place to a considerable extent.

In order to obtain a yield of crystals sufficient for analysis, a mixture containing 2.5% of potassium ferrocyanide was warmed (to about 60°) until all of the salt had dissolved. When the mixture had cooled to room temperature the solution remained supersaturated, but after several days crystals began to separate. These took the form of thick, clear, colorless or very pale yellow, hexagonal plates, some of which attained a diameter of about 6 mm. Some of the crystals were removed from the solution by means of platinum-tipped tweezers and dried on a porous tile. In the air they soon became white and opaque.

The substance was readily soluble in water. Qualitative tests of the solution showed the presence of $H^+$, $SO_4^{--}$, and $Fe(CN)_6^{----}$ ions; $K^+$ ion, however, was absent. The crystals, then, consisted not of an addition compound of potassium ferrocyanide and sulfuric acid, but of a product of solvolysis or, specifically, of an addition compound of hydroferrocyanic and sulfuric acids. The quantitative determination of the composition of this addition compound proved to be a matter of considerable difficulty, chiefly because of the instability of the substance, since it slowly decreased in sulfate content when exposed to the air, even when kept in a desiccator. The following method was found to give fairly concordant results. Large crystals were allowed to form as described above. Some of these were transferred to a piece of porous tile by means of tweezers and moved about in order that the adhering sulfuric acid might be removed as thoroughly as possible without long exposure to the air. The crystals were then removed to a stoppered weighing bottle and a portion was immediately weighed out for analysis. First, the hydrogen content was determined by titration with standard sodium hydroxide solution.[28] The solution was then acidified with a drop of nitric acid, and a slight excess of silver nitrate

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[25] See Kendall, Booge and Andrews, THIS JOURNAL, **39**, 2308 (1917).

[26] Ref. 4 b, p. 270.

[27] Ref. 25, p. 2309.

[28] The result of this analysis for acidity served to confirm the conclusion that the substance was an addition compound of $H_4Fe(CN)_6$ and $H_2SO_4$, but was not of much value in fixing the quantitative composition, since the percentages of hydrogen in $H_2SO_4$ (2.055%) and in $H_4Fe(CN)_6$ (1.867%) are not very widely disparate. The hydrogen content of any compound of the two acids would, of course, lie between these limits.

solution added. After the precipitate of silver ferrocyanide had been filtered off, hydrochloric acid was added in slight excess, the silver chloride was filtered off, and the filtrate was made alkaline with ammonium hydroxide in order to precipitate the trace of ferric salt which was always found to be present, and filtered again. This filtrate was then acidified with hydrochloric acid, and sulfate ion was determined as barium sulfate in the usual way.

*Anal.* Subs., (I) 0.1100, (II) 0.0882, (III) 0.0426: cc. of 0.2075 *N* NaOH soln., (I) 10.04, (II) 7.78; $BaSO_4$, (I) 0.1906, (III) 0.0723. Calcd. for $H_4Fe(CN)_6.6H_2SO_4$: H, 2.00; $SO_4$, 71.65. Found: H, 1.908, 1.845, mean 1.88; $SO_4$, 71.29, 69.82, mean 70.56.

Although conditions are such as to prevent the attainment of very great accuracy in this analysis, it seems probable that the addition compound has the formula $H_4Fe(CN)_6.6H_2SO_4$.

**Calcium Phosphate.**—Solutions of calcium orthophosphate in 100% sulfuric acid were studied in a similar manner. The following freezing-point data were obtained.

FREEZING-POINT DATA

| $Ca_3(PO_4)_2$, % | 0 | 0.51 | 0.94 | 1.10 | 1.16 |
|---|---|---|---|---|---|
| Temp.,[29] °C. | 10.3 | 6.5 | 2.4 | 0.8 | 4.5 (new solid phase) |

A solution containing 1.8% of calcium orthophosphate was cooled until crystallization took place, and then filtered through a layer of asbestos in a dry Gooch crucible. The crystals were removed and pressed between porous tiles. They were white, and difficultly soluble in water. Qualitative analysis showed the presence of $Ca^{++}$, $SO_4^{--}$ and $H^+$ ions, but $PO_4^{---}$ ion was absent. In this case also, then, the crystals consisted of a product of solvolysis or, specifically, of an addition compound of calcium sulfate and sulfuric acid, rather than of an addition compound of solvent and solute. A weighed portion was dissolved in water and titrated with standard sodium hydroxide solution. The solution was then acidified with hydrochloric acid and sulfate ion was determined in the usual way.

*Anal.* Subs., 0.2628: 10.85 cc. of 0.2075 *N* NaOH soln.; $BaSO_4$, 0.5204. Calcd. for $CaSO_4.H_2SO_4$: H, 0.861; $SO_4$, 82.02. Found: H, 0.864; $SO_4$, 81.47.

**3. Solubility of Salts in Sulfuric Acid and Double Decomposition Reactions in this Solvent.**—A number of qualitative tests were made in order to gain a rough idea of the solubilities of a wide range of salts in 100% sulfuric acid. The results are listed below; the solutions were clear and colorless unless otherwise noted.

| | |
|---|---|
| NaCl | Very soluble; HCl evolved even at 0°. |
| NaBr | Easily soluble; orange solution; some HBr evolved. |

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[29] Here again the freezing-point depressions, being a little larger even than for $K_4Fe(CN)_6$, indicate extensive compound formation with the solvent, or dissociation of the solute or, more probably, both.

| | |
|---|---|
| $NaNO_3$ | Easily soluble; no color change or other visible evidence of reaction. |
| $Na_2HAsO_4$ | Easily soluble. |
| $Na_2SiO_3$ | Changed to white insoluble gelatinous subs., probably silicic acid. |
| KCl | Very soluble; HCl evolved as with NaCl. |
| KBr | Very soluble; orange solution. |
| KI | At once oxidized to free iodine, even at 0°. |
| $KNO_3$ | Very soluble. |
| $K_4Fe(CN)_6$ | Easily soluble; pale yellow solution; no decomposition at ordinary temperatures. |
| $K_3Fe(CN)_6$ | Easily soluble; dark red-brown solution; no decomposition at ordinary temperatures. |
| KSCN | Easily soluble. |
| $CaCl_2$ | Easily soluble; HCl evolved slowly. |
| $CaF_2$ | Very soluble; no gas formed; no apparent action on glass, even on standing. |
| $CaCO_3$ | Difficultly soluble; $CO_2$ evolved slowly. |
| $Ca_3(PO_4)_2$ | Easily soluble; yellowish solution. |
| $AgNO_3$ | Very soluble; no reaction apparent. |
| AgCl | Very insoluble; not affected by boiling. |
| $AlCl_3$ | Insoluble and inert at ordinary temperatures; on boiling, changed to insol. $Al_2(SO_4)_3$ with evolution of HCl. |
| $Al(NO_3)_3$ | Changed to white insol. gelatinous subs., probably $Al_2(SO_4)_3$. |
| $AlPO_4$ | Insol. and inert at ordinary temperatures; on heating, swelled and became gelatinous, probably being changed to $Al_2(SO_4)_3$. |
| $FeCl_3$ | Changed to yellowish-white, insol. $Fe_2(SO_4)_3$; HCl evolved. |
| $Fe(NO_3)_3$ | Changed to yellowish-white, insoluble $Fe_2(SO_4)_3$. |
| $Fe_4[Fe(CN)_6]_3$ | Changed to yellowish-white, insoluble $Fe_2(SO_4)_3$; soln. remained colorless. |
| $CuBr_2$ | Insol. at ord. temps.; dissd. on heating, with evol. of $Br_2$. |

Since previous work has established rather definitely that most salts are highly ionized in solution in sulfuric acid,[30] we might expect that when two such salt solutions were brought together, instantaneous (or at least rapid) double decomposition would take place whenever one of the possible products was insoluble in 100% sulfuric acid. Experiments were made with a number of pairs of salt solutions which, it was thought, might lead to the formation of an insoluble product; the solutions were roughly 0.25 *M*, except in the case of the sulfates of zinc, mercury and copper, for which saturated solutions were used. The following results were obtained.

These pairs of salts in sulfuric acid solution gave no precipitate: silver nitrate with calcium phosphate, calcium fluoride, disodium arsenate, potassium ferrocyanide, or potassium ferricyanide; mercurous sulfate with calcium phosphate; zinc sulfate with sodium chloride or potassium ferrocyanide; lead sulfate with sodium chloride; cupric sulfate with potassium ferrocyanide or calcium fluoride.

A suspension of ferric sulfate in sulfuric acid, when treated with a solu-

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[30] See, for instance, Ref. 2, p. 386.

tion of potassium thiocyanate, showed no change. Ferric sulfate suspension treated with potassium ferrocyanide solution showed no change, but the usual dark blue precipitate was formed when the mixture was poured into a large volume of water. When solutions of ferrous sulfate and potassium ferricyanide were mixed, the brownish color of the latter disappeared, but no further change took place; again, a dark blue precipitate appeared when the mixture was poured into a large volume of water.

In the following cases, precipitation occurred on mixing two salt solutions in sulfuric acid. When sodium chloride solution was added to silver nitrate solution, a heavy white precipitate of silver chloride was formed at once. It is interesting to note that a heavy precipitate was formed even when the sodium chloride solution was boiled for several minutes before being added to the silver nitrate. This shows that solvolysis of the sodium chloride must be far from complete, even at the boiling point of the solvent, in spite of the very low solubility of hydrogen chloride in 100% sulfuric acid at this temperature.

When potassium bromide solution was added to the silver nitrate, a yellowish-white precipitate of silver bromide was immediately formed. To show that the formation of this precipitate was due to the presence of bromide ion in the potassium bromide solution, and not to the small amount of free bromine which may have been present, another portion of silver nitrate solution was treated with a solution of free bromine;[20] in this case no precipitate whatever appeared.

When sodium chloride solution was added to mercurous sulfate, a heavy white precipitate of mercurous chloride was formed. A saturated solution of cupric sulfate, on the addition of sodium chloride solution, slowly yielded a yellow gelatinous precipitate of cupric chloride; and when cupric sulfate and potassium bromide solutions were mixed, a surprisingly bulky, gelatinous, purplish-brown precipitate of cupric bromide was slowly produced.

It was thought that it might be possible to precipitate some of the more insoluble of the sulfides in sulfuric acid, in spite of the ease with which sulfides are oxidized by this substance. When hydrogen sulfide is passed into 100% sulfuric acid, it is, of course, rapidly oxidized; sulfur dioxide is given off and a heavy white precipitate of sulfur is formed. When the gas was introduced into mercurous sulfate or lead sulfate solution the result was the same; only sulfur was precipitated. With silver nitrate, however, a black precipitate of silver sulfide was formed immediately upon contact of the gas with the solution. This precipitate then gradually reacted with the solvent, with the formation of sulfur dioxide and free sulfur. This result makes it seem probable that hydrogen sulfide is ionized in sulfuric acid, and that combination between silver ion and sulfur ion takes place to a considerable extent before the latter ion is oxidized by the solvent.

## Discussion of Results

1. Contrary to expectations, there is no evidence for the formation of soluble addition compounds, stable in sulfuric acid solution, between the sulfates of aluminum, zinc or lead, on the one hand, and sodium sulfate on the other,[31] such as would correspond to the soluble aluminates, zincates, and plumbites which are formed by the addition of an excess of sodium hydroxide to aluminum, zinc, or lead salts in aqueous solution, or to the ammono-aluminates, ammono-zincates, and ammono-plumbites which can be formed in an analogous manner in liquid ammonia solutions.[32] It is interesting to note in this connection that similar compounds of other metals (a potassium ammono-magnesiate, for example) have also been prepared,[33] which have no analogs in the water system. This is explained by Bergstrom[34] on the ground that the much greater solvolytic power of water relative to that of ammonia (due to the greater degree of dissociation of the former) renders the existence of aqueous "magnesiates," etc., impossible. If we bear in mind that sulfuric acid is dissociated to an enormously greater degree than water, it is evident that the non-existence of compounds of any of these types in sulfuric acid could readily be accounted for on this same basis.

2. It has been shown that although some salts are completely solvolyzed by 100% sulfuric acid, many others dissolve in this solvent without any visible evidence of reaction. So far as the writer can see, there is no *a priori* reason why it should not be possible to isolate from such solutions, in certain cases, either the unchanged salt or an addition product of salt and solvent, analogous to the salt hydrates that separate from aqueous solutions. In neither of the two cases studied, however, was an addition product obtained, although conditions were such that there seemed to be considerable likelihood of such a result. The crystals separating on cooling were those of a product of solvolysis in each case; in one system the solvated acid, $H_4Fe(CN)_6.6H_2SO_4$, in the other the solvated base, $CaSO_4.H_2SO_4$. Further investigation of salt solutions might lead to the discovery of interesting new compounds.

3. With regard to the solubility of salts in sulfuric acid, the following general statements may be made on the basis of the relatively few cases studied; they apply only to salts which are not oxidized or otherwise decomposed (except solvolytically) by this solvent.

(a) All salts of metals whose sulfates are insoluble in sulfuric acid are

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[31] Though, of course, such addition compounds are known in the solid state.

[32] (a) Fitzgerald, THIS JOURNAL, **29**, 660 (1907). (b) Franklin, *ibid.*, **29**, 1274 (1907); (c) *J. phys. Chem.*, **15**, 509 (1911). (d) Bergstrom, THIS JOURNAL, **45**, 2788 (1923).

[33] Franklin, THIS JOURNAL, **35**, 1463 (1913). See also *ibid.*, **46**, 2143–4 (1924).

[34] Ref. 32 d, p. 2788, Footnote 3.

either insoluble themselves (such as aluminum orthophosphate), or else are extensively solvolyzed (ferric nitrate) into the insoluble sulfate, as we should expect from the high degree of ionization of the solvent.

(b) Salts of acids which in the free state are insoluble in sulfuric acid are either themselves insoluble (silver choride, cupric bromide), or else are extensively solvolyzed (sodium chloride), yielding the insoluble acid.

(c) Salts of metals whose sulfates are soluble and of acids which are soluble are, in general, soluble in 100% sulfuric acid. Thus, all of the following salts are known to be soluble, either by direct test or because of their failure to precipitate from solutions containing their ions: sodium acetate,[35] pyrophosphate,[35] arsenate and nitrate, potassium phosphite,[36] metaphosphate,[36] orthophosphate,[36] ferrocyanide, ferricyanide, thiocyanate, nitrate and perchlorate,[37] calcium orthophosphate and fluoride, silver nitrate, orthophosphate, arsenate, fluoride, ferrocyanide and ferricyanide, zinc ferrocyanide, cupric fluoride and ferrocyanide, ferrous ferricyanide, mercurous orthophosphate.

(d) Double decomposition reactions take place readily between ionized salts in sulfuric acid solution. The course of such reactions is determined largely by the solubilities of the several salts in question in 100% sulfuric acid and is, of course, not necessarily the same as in aqueous solutions. The reactions in sulfuric acid are not always instantaneous; this slower rate of reaction is probably due to the greater viscosity of the solvent.

## Summary

1. The solubilities of aluminum sulfate, zinc sulfate and lead sulfate in 100% sulfuric acid are not increased by the presence of sodium sulfate in the solution.

2. Solvolysis of salts takes place readily in sulfuric acid solution, due to the high degree of ionization of both solvent and solute. Salts of metals whose sulfates are insoluble in this solvent, or of insoluble acids, are either themselves insoluble or else are extensively solvolyzed to insoluble products.

3. It has not been possible to isolate either unchanged salt or an addition product of salt and solvent by cooling solutions of easily soluble, highly-ionized salts in sulfuric acid in two cases tried. In both cases, products of solvolysis were obtained.

4. A new crystalline addition product of hydroferrocyanic acid and sulfuric acid, apparently having the formula $H_4Fe(CN)_6.6H_2SO_4$, has incidentally been prepared and analyzed.

5. In general, salts of metals whose sulfates are soluble in sulfuric acid

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[35] Ref. 2, p. 384.

[36] Ref. 4 d, pp. 53, 58.

[37] Ref. 4 b, p. 291.

and of acids that are soluble in and not oxidized or decomposed by sulfuric acid, are soluble in this solvent.

6. A number of double decomposition reactions between ionized salts in sulfuric acid solution have been described.

LAWRENCE, KANSAS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# ALPHA-FURILDIOXIME AS A REAGENT FOR THE DETECTION AND DETERMINATION OF NICKEL

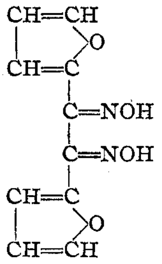
BY BYRON A. SOULE[1]

RECEIVED DECEMBER 1, 1924 PUBLISHED APRIL 4, 1925

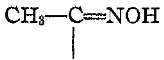
## Introduction

The change in status of furfural from a laboratory curiosity to a commercial product has made it seem worth while to investigate the properties of its derivative, α-furildioxime (I), as a reagent for the detection and determination of nickel. Although Tschugaeff[2] mentioned twelve members of the dioxime series, hitherto only two have been studied from the standpoint of their use in chemical analysis. Brunck[3] recommended α-dimethylglyoxime (II) in 1907, and Atack[4] suggested α-benzildioxime (III) in 1913. The former reagent is expensive; the latter, while probably the most easily prepared of the α-dioximes, is so insoluble that it tends to crystallize and contaminate the precipitate. This objection might be overcome by introducing the proper substituent into the benzene ring (perhaps $—HSO_3$), but to the present time nothing has been found in the literature to indicate that the idea has been tried.

Thus it was with the hope of finding a cheaper, water-soluble α-dioxime that the properties of α-furildioxime were investigated.

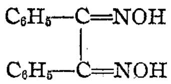


I. α-Furildioxime



$$\begin{array}{l} CH_3—C{=}NOH \\ \quad\;\; | \\ CH_3—C{=}NOH \end{array}$$

II. Dimethylglyoxime



$$\begin{array}{l} C_6H_5—C{=}NOH \\ \qquad\; | \\ C_6H_5—C{=}NOH \end{array}$$

III. α-Benzildioxime

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[1] From a dissertation presented by Byron A. Soule in partial fulfilment of the requirements for the degree of Doctor of Science in the University of Michigan. This work was done under the direction of Professor E. D. Campbell.

[2] Tschugaeff, (a) *Z. anorg. allgem. Chem.*, **46**, 144 (1905); (b) *Ber.*, **41**, 1678 (1908).

[3] Brunck, *Z. angew. Chem.*, **20**, 1844 (1907).

[4] Atack, *Analyst*, **38**, 316 (1913).