

convenience, and toxicity), dimethylformamide appears to be the best choice as a general solvent for explosives. DMSO, butyrolactone, or DMSO-butyrolactone mixtures can be used for HMX. The solubility of HMX in a DMSO-butyrolactone mixture (27% DMSO by weight) is given in Table II. The mixture has mp  $-30^{\circ}\text{C}$  ( $-22^{\circ}\text{F}$ ) and could conveniently be used or stored in cold environments. The mixture is a better solvent for HMX than butyrolactone.

Solubilities of explosives in dimethylformamide are given in Table VI. Solubility values at temperatures above  $25^{\circ}\text{C}$  are listed for explosives which are less soluble than 40 grams/100 grams at  $25^{\circ}\text{C}$ . Solubility values at  $0^{\circ}\text{C}$  are

listed for the more soluble explosives. It should be noted that DMF is a good solvent for both organic and inorganic explosives (inorganic components of explosives).

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## Solubility of Silver Sulfate in Acidified Ferric Sulfate Solutions

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**The solubility of silver sulfate in acidified ferric sulfate solutions was investigated over the temperature interval  $0-100^{\circ}\text{C}$ . At constant acid concentration, the solubility increased slightly with increasing ferric ion strengths in the range  $0-0.3M$   $\text{Fe}^{3+}$ . At a constant ferric ion concentration of  $0.1M$   $\text{Fe}^{3+}$ , the solubility increased with increasing concentrations of sulfuric acid in the range  $0-1.0M$   $\text{H}_2\text{SO}_4$ . Under conditions of high temperature, low acidity, and high ferric ion concentration, silver precipitated as insoluble silver jarosite ( $\text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6$ ).**

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High silver values are frequently encountered in copper sulfide ore deposits, and this silver represents a valuable by-product of copper mining operations. During the dump or heap leaching of low-grade ores (6), silver recovery can lag substantially behind that of copper, and the reason for this is not fully understood (5). One explanation is that silver sulfate is not very soluble in the acidified ferric sulfate medium generally used for leaching. The solubility of  $\text{Ag}_2\text{SO}_4$  in water is about  $0.03M$  ( $\sim 10$  g  $\text{Ag}_2\text{SO}_4/\text{l}$ .) over the temperature interval  $0-240^{\circ}\text{C}$  (3). The addition of sulfuric acid substantially increases the solubility of  $\text{Ag}_2\text{SO}_4$  at all temperatures (2).

This observation was shown (2) to be consistent with the known temperature dependence of the  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$  equilibrium constant (4) and with the assumption that the solubility of  $\text{Ag}_2\text{SO}_4$  varied with ionic strength according to a Debye-Hückel type relationship. The solubility of silver sulfate in acidic solutions containing dissolved ferric sulfate is, however, not known. To determine if the poor silver recoveries obtained during the dump leaching of copper ores were caused by inherently low silver solubilities in the leaching medium, the solubility of  $\text{Ag}_2\text{SO}_4$  in acidified ferric sulfate solutions was determined over the range of temperatures and concentrations likely to be encountered during commercial copper percolation leaching operations.

#### Experimental

**Reagents.** Baker reagent-grade silver sulfate was used without further treatment; this material was white and dissolved completely in an excess of water. Test solutions were prepared with distilled water, reagent-grade sulfuric acid, and hydrated ferric sulfate. The ferric sulfate was dissolved in water and filtered before use to remove any insoluble iron residues. The actual acid and ferric ion concentrations of the solutions were determined by standard titration procedures and agreed with the prepared compositions.

**Apparatus.** Measurements were made with a three-neck flask, closed to the atmosphere except when the solution was being sampled. The contents of the flask were stirred magnetically except during the sampling period. The flask was heated in a temperature-controlled oil bath that was held to within  $\pm 0.1^{\circ}\text{C}$ , and the actual temperature of the solution was measured by an immersed thermometer.

**Procedure.** One liter of solution of known composition was placed in the three-neck flask, together with an excess of silver sulfate. Depending on the temperature, the contents were then stirred for 8-24 hr to permit the solution to attain saturation equilibrium. After this period, the stirrer was stopped, and the solids were allowed to settle. The solution was then sampled with a calibrated pipet, the end of which was fitted with a filter paper sleeve to minimize the transfer of suspended solids. The contents of the pipet were discharged directly into a weighing bottle which was immediately sealed, brought to room temperature, and then weighed. The pipet was calibrated at each temperature with pure water and the same experimental technique that was employed when sampling the silver saturated solutions.

Ten milliliters of solution were withdrawn for each sample, and the silver content was determined by the standard Volhard titration method. The solution density was calculated from the weight of the aliquot and the volume of the pipet as determined by the water calibration at that temperature. The flask was inspected at each temperature to determine if any iron-bearing compounds had formed by hydrolysis.

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After a sample had been taken, the temperature of the flask was raised 10°C, and the equilibration and sampling procedures were repeated. The flask temperature was then lowered by 5°C and another solubility measurement was taken. This procedure, of raising the temperature 10°C and then lowering it by 5°C, was used to obtain data on both heating and cooling to insure that equilibrium solubilities were, in fact, being measured. A conventional heating program whereby the solution was heated in a stepwise manner to the maximum temperature, and then cooled in a similar manner, was not possible in this system. At the higher temperatures, insoluble iron and silver compounds formed, and this altered both the solution composition and the character of the equilibrating solid. At various stages of the experiment, part of the solid phase was withdrawn for X-ray diffraction analysis.

### Results and Discussion

Figure 1 shows the experimentally determined solubilities of Ag<sub>2</sub>SO<sub>4</sub> in 0.1M H<sub>2</sub>SO<sub>4</sub> solutions containing various amounts of ferric sulfate. The solubility of silver sulfate in 0.1M H<sub>2</sub>SO<sub>4</sub> containing no ferric ion was determined over the temperature range 0–100°C, and the results of this study are in good agreement with published values for this system (2). The addition of ferric sulfate to the acidic solution increases the solubility of silver sulfate, although the effect is not pronounced. The presence

of 0.3M Fe<sup>3+</sup> increases the Ag<sub>2</sub>SO<sub>4</sub> solubility by about 25% relative to a similar 0.1M H<sub>2</sub>SO<sub>4</sub> solution containing no iron; smaller amounts of dissolved iron have proportionately smaller effects. The Ag<sub>2</sub>SO<sub>4</sub> solubility curves are nearly linear under the conditions shown in this figure.

The experimental data obtained for each solution composition illustrated in Figure 1 were fitted to an equation of the form:

$$\text{solubility} = a + bt + ct^2$$

where the solubility is expressed as grams Ag<sub>2</sub>SO<sub>4</sub>/100 grams saturated solution, and *t* is in °C. The coefficients thereby determined are presented in Table I for each solution composition. The densities (g/cm<sup>3</sup> of saturated solution) of the silver sulfate saturated solutions were determined as a function of temperature with a similar regression analysis technique, and these density equations are also listed in Table I.

Figure 2 shows the experimentally determined solubilities of Ag<sub>2</sub>SO<sub>4</sub> in solutions containing 0.1M Fe<sup>3+</sup> (as the sulfate) and various concentrations of H<sub>2</sub>SO<sub>4</sub>. The addition of H<sub>2</sub>SO<sub>4</sub> to the 0.1M Fe<sup>3+</sup> sulfate solution increases substantially the solubility of Ag<sub>2</sub>SO<sub>4</sub>. The 1.00M H<sub>2</sub>SO<sub>4</sub> solution dissolves about 60% more silver sulfate than a similar solution containing 0.01M H<sub>2</sub>SO<sub>4</sub>. The presence of large amounts of H<sub>2</sub>SO<sub>4</sub> causes the solubility to increase

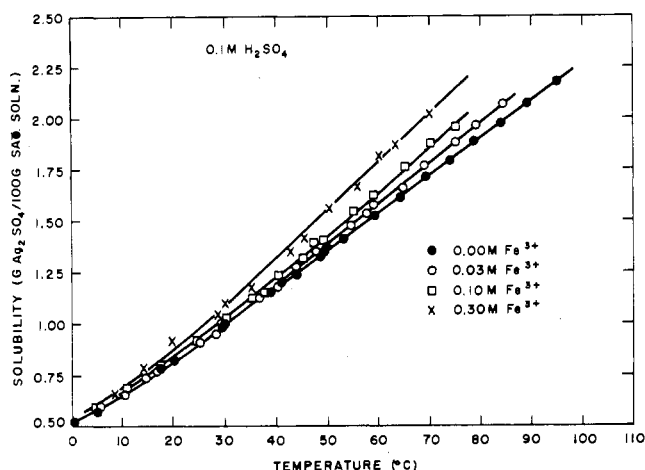


Figure 1. Solubility of silver sulfate in solutions containing 0.1M H<sub>2</sub>SO<sub>4</sub> and various concentrations of Fe<sup>3+</sup> (as sulfate)

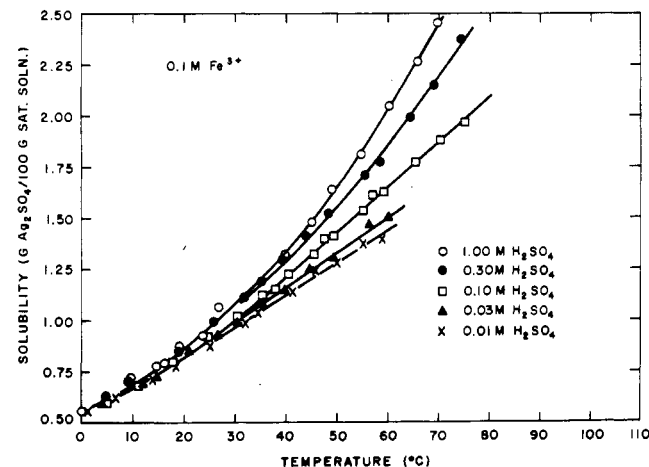


Figure 2. Solubility of silver sulfate in solutions containing 0.1M Fe<sup>3+</sup> (as sulfate) and various concentrations of H<sub>2</sub>SO<sub>4</sub>

Table I. Regression Data for Solubilities and Densities of Silver Sulfate in Acidified Ferric Sulfate Solutions

Composition		Solubility, $s = a + bt + ct^2$ (g Ag <sub>2</sub> SO <sub>4</sub> /100 g sat soln)			Density, $d = a + bt + ct^2$ (g/cm <sup>3</sup> )		
[H <sub>2</sub> SO <sub>4</sub> ]	[Fe <sup>3+</sup> ]	<i>a</i>	<i>b</i> × 10 <sup>2</sup>	<i>c</i> × 10 <sup>5</sup>	<i>a</i>	<i>b</i> × 10 <sup>4</sup>	<i>c</i> × 10 <sup>6</sup>
0	0	0.5413	1.293	-4.909	1.006	1.282	-5.516
0.1	0	0.5052	1.575	2.064	1.014	1.137	-4.605
0.1	0.01	0.5173	1.567	2.780	1.016	0.660	-3.871
0.1	0.03	0.5280	1.358	5.889	1.017	0.587	-3.560
0.1	0.1	0.5011	1.610	4.792	1.031	0.716	-3.756
0.1	0.3	0.5883	1.536	6.410	1.066	2.046	-6.420
0.01	0.1	0.5542	1.160	6.696	1.024	2.325	-7.844
0.03	0.1	0.5329	1.392	4.072	1.027	0.703	-4.894
0.3	0.1	0.5976	1.044	17.53	1.045	-0.309	-2.234
1.0	0.1	0.5773	0.9677	24.01	1.090	-1.124	-1.405
0.1	Mixed SO <sub>4</sub> <sup>2-</sup>	0.5369	1.282	1.763	1.069	0.450	-5.002
0.02	0.003	0.5101	1.458	-4.064	1.010	0.394	-4.482

rapidly with increasing temperature, and in this regard, such solutions differ from their weakly acidic counterparts.

The increasing solubility of  $\text{Ag}_2\text{SO}_4$  in sulfuric acid solutions with increasing temperature was attributable both to the variation of the  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$  equilibrium constant with temperature and to the effect of the ionic strength on the solubility (2). In concentrated sulfuric acid solutions, it appears that the bisulfate equilibrium is the more important term, but both factors, it must be emphasized, contribute to the increasing solubility with increasing temperature. It appears that similar considerations are important in ferric sulfate solutions containing large concentrations of sulfuric acid. At room temperature, the solubility of  $\text{Ag}_2\text{SO}_4$  is not much affected by either ferric sulfate or sulfuric acid concentrations.

The data shown in Figure 2 were processed by the same technique described previously. The corresponding regression coefficients for these solubility curves are shown in Table I. The densities of the silver-saturated solutions indicated in Figure 2 were also measured, and the regression coefficients for the variation of the density with temperature are presented in Table I for each solution composition.

The acidified ferric sulfate solutions used for commercial dump leaching undergo many changes throughout their processing schedule. Two such changes that commonly occur are the neutralization of the solution by contact with carbonate rock, and the dissolution of many unwanted elements. The effect of neutralization was investigated by measuring the  $\text{Ag}_2\text{SO}_4$  solubility in water, and in a solution that was 0.003M in  $\text{Fe}^{3+}$  and 0.02M in  $\text{H}_2\text{SO}_4$ . The effect of the presence of substantial quantities of other elements was tested by measuring the  $\text{Ag}_2\text{SO}_4$  solubility in a mixed sulfate solution having the following composition, in g/l.:  $\text{Fe}^{3+}$ , 3;  $\text{Fe}^{2+}$ , 3;  $\text{Mg}^{2+}$ , 5;  $\text{Al}^{3+}$ , 2;  $\text{Cu}^{2+}$ , 1 and  $\text{H}_2\text{SO}_4$ , 10. The composition of this solution closely approximates many practical percolation leaching lixiviants. The results of these experiments are summarized in Figure 3.

The solubility of  $\text{Ag}_2\text{SO}_4$  in water increases slightly with increasing temperature to about 100°C, levels off, and then declines. The results obtained for this system agree closely with the handbook values (7), except at temperatures above 80°C where the current results are about 2% lower than the published data. The solubility of silver sulfate in weak ferric ion solutions of low acidity is about that obtained in water at the lower temperatures but is

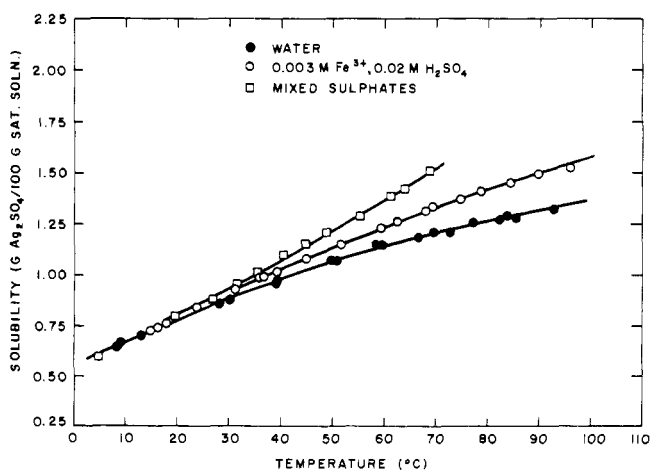


Figure 3. Solubility of silver sulfate in water, in dilute acidified ferric sulfate solution, and in a mixed sulfate solution typical of dump-leaching solutions

significantly higher at temperatures above 50°C. The presence of large amounts of metal sulfates in the acidified ferric sulfate solution does not adversely affect the silver solubility. Such solutions exhibit nearly the same silver solubility as water at lower temperatures but dissolve appreciably more silver sulfate at the higher temperatures.

In the above figures it is apparent that some of the solubility curves were not determined at very high temperatures. Under certain conditions, silver and iron were precipitated as silver jarosite:  $\text{Ag}(\text{Fe}^{3+})_3(\text{SO}_4)_2(\text{OH})_6$ . Jarosite formation was encouraged by high iron concentrations, high temperatures, low acid strengths, and increasing retention times. Individual solubility tests were concluded once the orange-yellow color of jarosite was detected in the reaction vessel. The temperature at which this precipitation commenced for each solution composition can be determined by the temperature of the last measurement of that composition.

The jarosite that precipitated was not pure silver jarosite but was, rather, a silver-hydronium jarosite  $(\text{Ag}, \text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ . Silver jarosite accounted for about 80% of the solid solution, and hydronium jarosite the remaining 20%. Silver solubility from the silver-hydronium jarosite is very low. Measurements showed the solubility to be less than 100 ppm Ag over the temperature range investigated in this study. Thermodynamically, silver jarosite probably forms at all temperatures; the rate of formation is exceptionally slow at temperatures below 50°C. When considered in this light, the solubility data obtained in the present study are really for a metastable solid phase; sufficient time (months?) should permit the formation of insoluble jarosite at all temperatures. The present data are, however, useful since they permit the determination of the silver solubility in a system which enjoys considerable practical stability especially at the lower temperatures encountered during commercial dump-leaching.

The present results show that the poor silver recoveries sometimes observed during dump leaching are not caused by an inherently low solubility of  $\text{Ag}_2\text{SO}_4$  in the acidified ferric sulfate leaching medium. The measured solubilities are sufficient to permit the dissolution of all the silver contained in most copper ores. The reason for the low silver recovery is still not known, and further work is planned to study this problem. Some of the possible reasons for the poor silver recoveries are:

Inherently low dissolution rates of silver minerals in acidified ferric sulfate solutions

Cementation of dissolved silver on reactive base metal sulfides

Precipitation of silver as silver-hydronium jarosite on active surfaces at low temperatures

Precipitation of silver-bearing jarosite at temperatures above 60°C. Such elevated temperatures have been reported in the interior of larger dumps

Precipitation of silver by chloride ion leached from the ore rock.

### Conclusions

The solubility of silver sulfate in acidified ferric sulfate solutions increases with increasing concentrations of either ferric sulfate or sulfuric acid.

The solubility of silver sulfate in such media is sufficiently high to accommodate all the silver generally contained in copper ores. At high temperatures and suitable solution concentrations, the silver precipitates as a silver-hydronium jarosite; this precipitation may be partly responsible for poor silver recoveries during dump leaching.

## Acknowledgment

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# Vapor-Liquid Equilibrium of Binary Mixtures of Butyl Alcohols with Triethylamine

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**Pressure-composition and excess free energies are given for binary mixtures of primary, secondary, and tertiary butyl alcohols with triethylamine at temperatures from 10° to 40°C.**

This is the third in a series of reports on the properties of binary mixtures of triethylamine with saturated aliphatic alcohols (1, 2). As with most mixtures involving strong hydrogen bonds, the excess functions are quite dependent upon alkyl substitution near the hydrogen bonding group. Vapor-liquid equilibrium of the *n*-butanol-triethylamine system has been reported previously at higher temperatures (3).

## Experimental

The vapor-pressure apparatus has been described previously (4). In brief, the apparatus consists of detachable glass sample flasks that allow the sample to be degassed without change in composition. Two of these sample flasks are joined to a glass manifold by ball joints so that two samples can be run at once. The manifold consists of three ball-jointed sections which connect the sample flasks to mercury manometers. The manometer legs not in contact with sample vapors are connected to a common section of the manifold. Vacuum stopcocks are connected to each of the three sections of the glass manifold and are, in turn, connected by ball joints and flexible hoses to an external vacuum manifold. Connections from the external manifold lead to a vacuum pump, McLeod gage, and an external manometer.

Samples of approximately the desired compositions are made up by weight and transferred to the sample flasks through their stopcock bore by a hypodermic syringe equipped with a long needle. After degassing, the flasks are connected to the evacuated glass manifold.

The glass apparatus, consisting of flasks, manometers, stopcocks, and connecting pieces, is suspended in a constant temperature bath and can be agitated to hasten equilibrium. The submerged manometers are read in the bath with a cathetometer. For pressures that do not ex-

ceed the length of the manometers (about 130 mm), a high vacuum can be maintained in the center section between the manometers, and the pressures can be read directly. For higher pressures a back pressure, which can be measured on the external manometer, must be maintained in the vacuum manifold and the center section. The pressures were read with a cathetometer to 0.05 mm. The measurements involved two or four readings, however, and errors up to 0.2 mm could easily result. The readings were corrected for temperature and gravity. The correction for vapor density is not significant.

A uniform bath temperature was maintained by a circulating pump, and the temperature was controlled to within 0.01°C by a thermistor-actuated proportional temperature controller. The temperature was measured with a calibrated glass thermometer, and recorded temperatures are accurate within 0.03°C. An error of 0.03°C would cause a maximum pressure error of 0.2 mm for the alcohol-triethylamine systems at 40°C.

Chemical analysis of the liquid phase was by acid titration of the amine except at amine concentrations in excess of 90% by weight in which case gas chromatography gave better results. The titrations were carried out as follows. The sample was slowly injected into 1*N* HCl until the pH reached 2. Then the excess acid was titrated with 1*N* THAM (tris-hydroxymethyl amino methane) to an end point of 4.7. The acid was standardized against purified amine, and the THAM against the acid. Reproducibility was about 1 part in 500 of amine. The analyses were made in triplicate, and more were made if agreement was not within 1 part in 500. The gas chromatograph used at high amine content contained a 20-ft by 1/4-in. column packed with Fluoropak with a silicone coating. The chromatographic analyses were run at least four times and usually more, and the results were compared with known samples made by weight. Accuracy is believed to be within 0.2 mol %.

All materials were distilled from commercial products on a Stedman column at high reflux. A cut with a boiling range of not more than 0.1°C was used. Triethylamine and *n*-butyl alcohol showed a single peak on the gas chromatograph. Secondary and tertiary butyl alcohol showed a small additional peak amounting to about 0.2%. The samples were collected and stored under nitrogen. They were withdrawn through the stopcock bore with a hypodermic needle and transferred to the sample

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