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THE MEASUREMENT OF THE SOLUBILITY OF FISSION PRODUCT SULFATES AT HIGH TEMPERATURES AND PRESSURES

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M. H. Lietzke and R. W. Stoughton

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Contribution from the Oak Ridge National Laboratory
Chemistry Division

THE MEASUREMENT OF THE SOLUBILITY OF FISSION PRODUCT SULFATES AT HIGH TEMPERATURES AND PRESSURES(1)

M. H. Lietzke and R. W. Stoughton

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(1) This document is based on work performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

Introduction

During the operation of an aqueous homogeneous reactor the fission products will "grow into" the reactor solution. Eventually the solubility products of some of the fission product salts may be exceeded, resulting in the precipitation of solid material. The amount of precipitate may be quite significant, especially in the operation of homogeneous reactors of high power ratings, and may have to be considered both during the operation of the reactor and in the solution decontamination process. Hence it is of interest to determine the solubilities of some of the fission product salts under the conditions existing in a reactor. Since the homogeneous reactor under construction (the HRE) will operate at high temperature and pressure and use a uranyl sulfate solution, it is of interest to determine the solubilities of some of the fission product sulfates at elevated temperatures and pressures, both in water and in a uranyl sulfate solution of pile concentration. In the present work the solubilities of the sulfates of lanthanum, yttrium, cadmium, cesium, and zinc were determined at high temperatures in water; and the solubilities of the sulfates of lanthanum, yttrium, and cadmium were determined at high temperatures in a uranyl sulfate solution containing 30 g/l uranium.

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Experimental Methods

With the exception of the determinations below 100°C all solubility measurements described in this report were made by the quartz tube method described by Étard[2] and A. Benrath[3][4]. The quartz tube method depends upon the visual

(2) Étard, Ann. Chim. (7)2(1894),503.

(3) Benrath, A., Z anorg. allgem. Chem. 231, 285 (1937).

(4) Benrath, A., Z anorg. allgem. Chem. 247, 147 (1941).

observation of the appearance or disappearance of crystals in synthetic "mixtures" of known concentration. Stock solutions of the salts were prepared and the more dilute solutions obtained by diluting the stock solution. Spot check analyses were made of some of the various dilutions and good agreement between the observed and calculated concentrations was obtained in all cases. In the case of cesium sulfate, which showed a positive temperature coefficient of solubility, the water and crystals were weighed directly into the quartz tubes for each determination.

In place of the 2-3 mm tubes used in most of the previous work, 8 mm quartz tubes were employed in the present experiments. These tubes did not permit as high temperatures to be reached, but made easier the observation of the solution and crystals. The tubes were heated in aluminum block furnaces which were mounted on motor driven rockers so that thorough mixing of the solution and crystals could be accomplished. The temperature was measured by an iron-constantan thermocouple placed directly above the quartz tube in the furnace and recorded on a calibrated Brown recording potentiometer. No significant difference was observed between the temperature recorded by a thermocouple placed within the tube and one placed just above the tube, so no correction was necessary.

The lowest solubility measured was limited in each case by the ability to notice the first appearance of crystals in the tube. In some cases the crystals were visible in much more dilute solutions than in the case of other salts. For example, the measurement of the solubility of lanthanum sulfate in uranyl sulfate solution could be extended to 0.04% lanthanum sulfate while the cadmium and zinc sulfate limits were much higher (2-3%). In all cases the measurements were extended to as dilute solutions as possible.

Experimental Results

Lanthanum Sulfate

The solubility of lanthanum sulfate in water and in a uranyl sulfate solution containing 30 g/l uranium is shown in Table 1 and Figure 1. Data at the lower temperatures from Seidell[5] are plotted on the same graph as indicated.

(5) Seidell, Atherton, "Solubilities of Inorganic and Metal Organic Compounds", Vol. 1, D. van Nostrand Co., New York 1940, page 894.

Table 1

A. Lanthanum Sulfate Solubility in Water

t °C	26	108	113	115	117
% $La_2(SO_4)_3$	2.04	0.61	0.46	0.37	0.31

B. Lanthanum Sulfate Solubility in Uranyl Sulfate Solution containing 30 g/l uranium.

t °C	97	105	120	145	169	199	215
% $La_2(SO_4)_3$	2.04	1.74	0.87	0.29	0.15	0.083	0.042

In both cases the solubility of lanthanum sulfate shows a negative temperature coefficient. Since the lanthanum sulfate solutions all showed a strong tendency to supersaturate it was necessary to heat them 50° - 70° above the equilibrium

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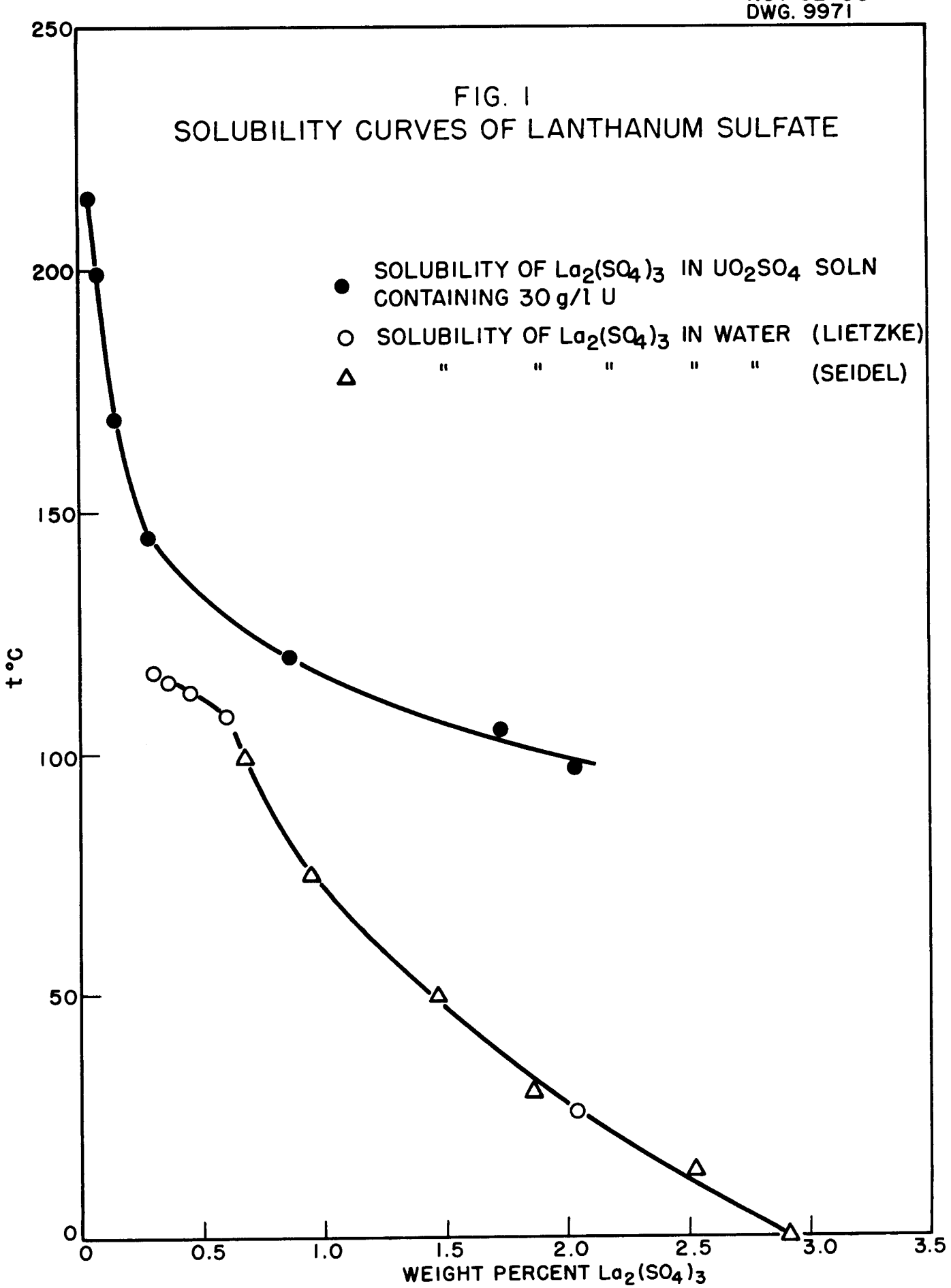

solubility temperature before crystals appeared. The temperatures given in the table represent the points at which the last crystals redissolved upon slow cooling. The lanthanum sulfate crystals did not adhere to the sides of the tube.

Several of the solutions were heated to 300°C to check on the possible existence of double solubility points at a given concentration. No such points were observed. When the 0.31% solution was held at 260°C for 48 hours there was no noticeable change either in the amount or in the type of crystals in the tube. The crystals redissolved easily at the expected temperature when the solution was cooled. Hence it appears that lanthanum sulfate is stable at the temperatures investigated. To check on the stability of the lanthanum sulfate-uranyl sulfate system in water at high temperatures the tube containing the 0.87% lanthanum sulfate solution and 30 g/l uranium as uranyl sulfate was maintained at 250°C for 72 hours. There appeared to be no change either in the amount or in the form of the lanthanum sulfate crystals in the tube. When the tube was cooled the crystals redissolved at the expected temperature. The lanthanum sulfate-uranyl sulfate-water system therefore seemed to be stable at 250°C. The increased solubility of lanthanum sulfate in uranyl sulfate solution is probably due to strong sulfate complexing by the uranyl sulfate.

Cadmium Sulfate.

The solubility of cadmium sulfate in water and in a uranyl sulfate solution containing 30 g/l uranium was determined over a wide range of concentrations. Table 2 and Figure 2 show the results obtained. Data obtained by A. Benrath[3] are plotted on the same graph as indicated.

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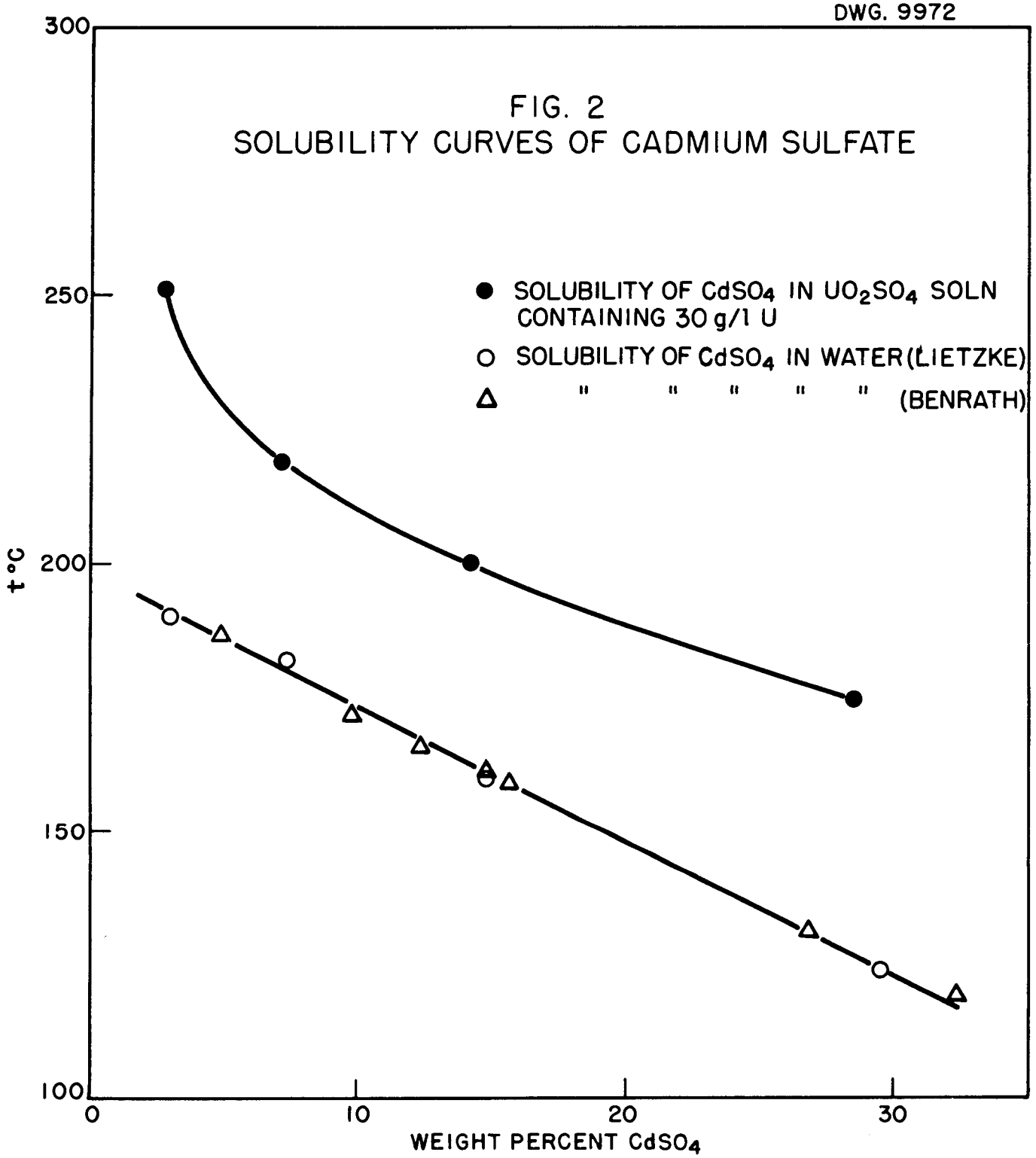

Table 2

A. Cadmium Sulfate Solubility in Water

t°C	124	160	182	190
% $CdSO_4$	29.6	14.8	7.4	3.0

B. Cadmium Sulfate Solubility in Uranyl Sulfate Solution containing 30 g/l Uranium.

t°C	175	200	219	251
% $CdSO_4$	28.5	14.2	7.1	2.8

Cadmium sulfate like lanthanum sulfate shows a negative temperature coefficient of solubility; and the presence of uranyl sulfate in the solution increases the solubility of cadmium sulfate at a given temperature. The cadmium sulfate solutions also showed a tendency to supersaturate, hence the temperatures given represent the points at which the last crystals redissolved as the solutions were cooled. The crystals obtained at the higher temperature (e.g. in the 3% solution) adhered to the walls of the tube, while the crystals from the more concentrated solutions were non-adherent. No double solubility points were found below 300°C at any given concentrations. The cadmium sulfate-uranyl sulfate-water system did not appear to be as stable as the lanthanum sulfate-uranyl sulfate-water system. When the 2.8% cadmium sulfate solution containing uranyl sulfate was held for 24 hours at 230°C or for one hour at 240°C (below the point at which crystals normally appeared in the solution) a brownish-orange precipitate appeared in the tube. The precipitate redissolved when the solution was cooled. Analysis revealed that the precipitate did not contain any uranium. When the brownish crystals were dissolved in dilute sulfuric acid a colorless solution resulted. When sodium hydroxide was added to the solution a white precipitate of cadmium hydroxide was obtained. It appears

that the precipitate may have been cadmium oxide.

Zinc Sulfate.

The solubility of zinc sulfate in water also decreased as the temperature increased. The data obtained are shown in Table 3 and in Figure 3. Data obtained by Benrath[4] are plotted on the same graph as indicated.

Table 3

Solubility of Zinc Sulfate in Water

t°C	178	203	219	238	248	253	255	257
% $ZnSO_4$	34.0	25.5	22.7	17.0	11.3	8.5	5.1	2.1

The zinc sulfate solutions, unlike the lanthanum sulfate and cadmium sulfate solutions, did not exhibit the strong tendency to supersaturate. No double solubility points at a given concentration were found below 300°C. The crystals of zinc sulfate that appeared adhered to the walls of the tube. Occasionally the zinc sulfate solutions showed very peculiar behavior. For example, when the 2.1% solution was heated for the very first time non-adherent crystals appeared in the solution at 225°C. The crystals redissolved on cooling. When the solution was heated again no crystals appeared at 225°C, but the "normal" adherent crystals were observed at 257°C. The non-adherent crystals could not be produced in the tube again upon several subsequent heatings. This phenomenon was also observed in the 5.1% and in the 11.3% solutions. No explanation is given for this behavior although the points may indicate an extension of the lower half of the zinc sulfate solubility curve. The 2.1% zinc sulfate solution contained 0.39 mg silica/ml after 3 heatings to 260°C while a similar solution that had been heated only once contained only 0.03 mg silica/ml.

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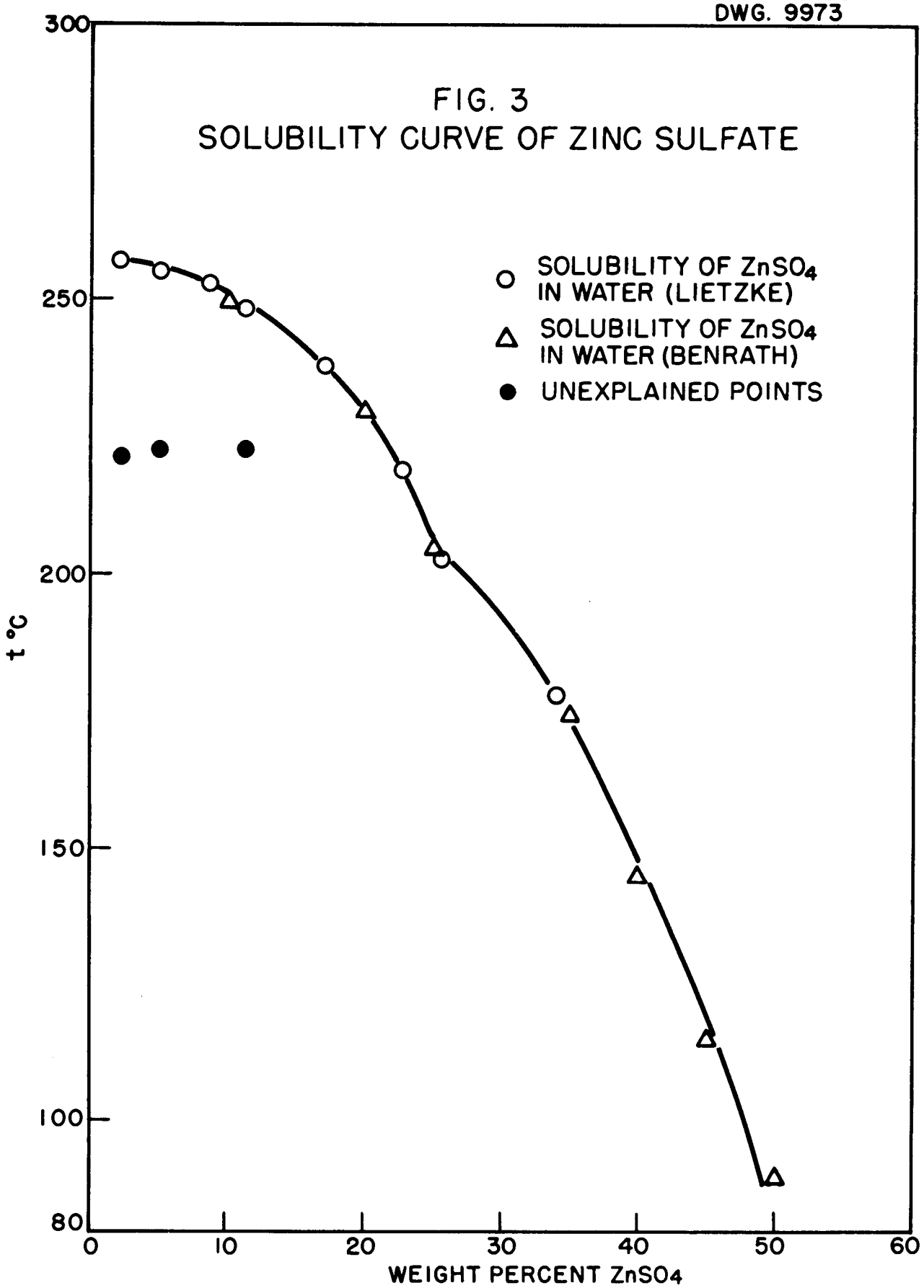

When the 11.3% zinc sulfate solution was held at 250°C (2 degrees above the point at which crystals appeared in the tube) for 24 hours a very large amount of crystalline material was deposited in the tube. X-ray analysis of these crystals showed them to be a mixture of $ZnSO_4.H_2O$ and $ZnSO_4$ which seems to preclude a hydrolytic reaction as the cause of the increased number of crystals. When the 17.0% zinc sulfate solution was held overnight at 210°C (28° below the point at which crystals normally appear) crystals appeared in the solution. These crystals redissolved readily when the solution was cooled and their composition was not determined.

Cesium Sulfate.

The solubility of cesium sulfate in water was determined over a wide range of temperatures. Table 4 and Figure 4 show the results obtained.

Table 4

Cesium Sulfate Solubility in Water

t°C	23	175	211	270	292
% Cs_2SO_4	63.5	71.8	73.5	75.0	75.5

Throughout the range investigated the solubility of cesium sulfate showed a positive temperature coefficient. No crystals reappeared in any of the solutions when they were heated to ca. 310°C (the upper limit for the 8 mm quartz tubes used). The cesium sulfate solutions showed no tendency to supersaturate. In all cases at the elevated temperatures the crystals dissolved and reappeared at exactly the same temperature. The point at 23°C was obtained merely by stirring excess cesium sulfate crystals with water in a beaker. No attempt was made to thermostat the solution; and an ordinary mercury thermometer was used to measure the temperature. The agreement was satisfactory to indicate the correctness of the values in Seidell.[5]

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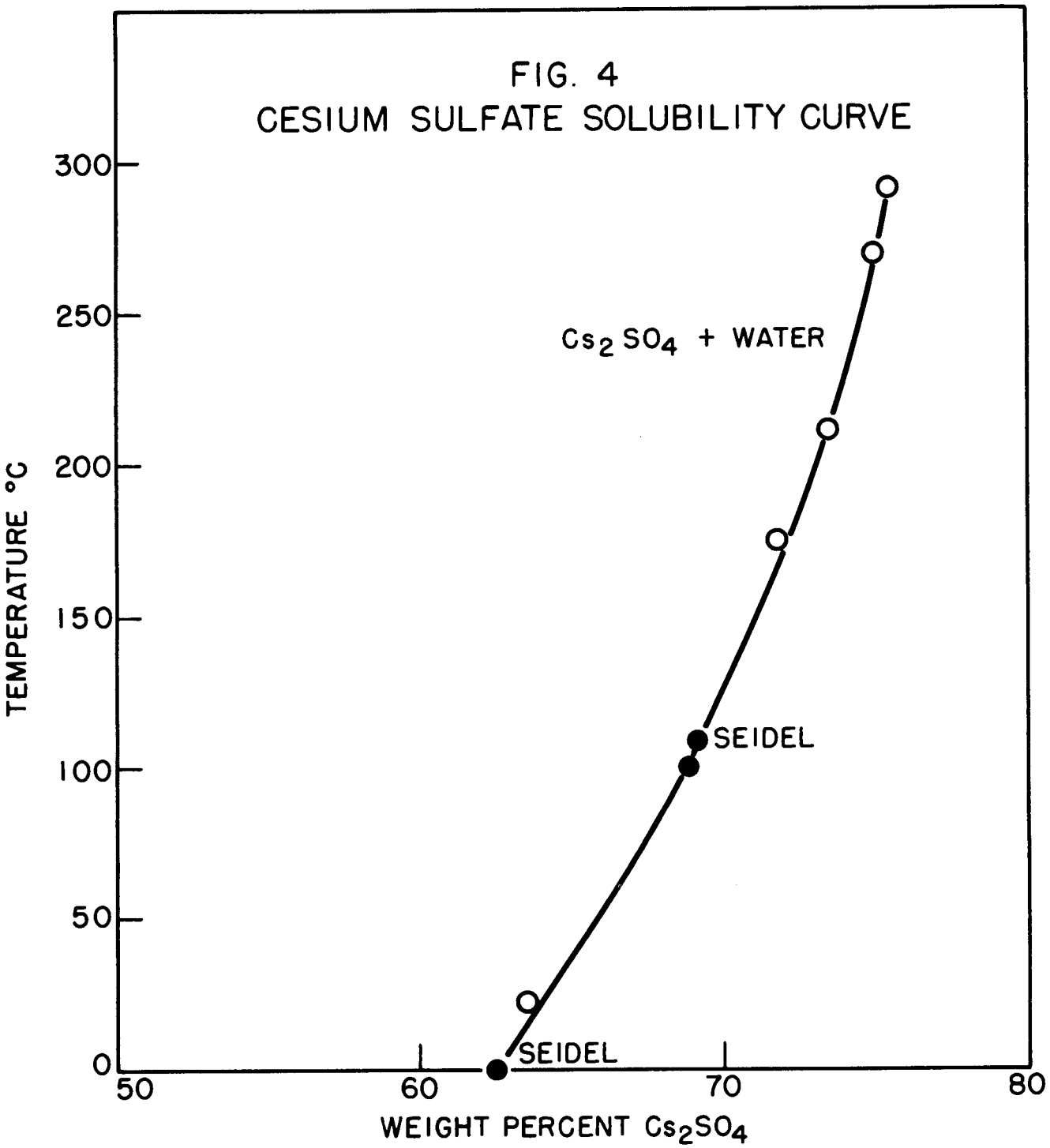

Yttrium Sulfate.

The solubility of yttrium sulfate in water and in a uranyl sulfate solution containing 30 g/l uranium is shown in Table 5 and Figure 5.

Table 5

A. Yttrium Sulfate Solubility in Water

t°C	108	150	155	160	161	163	176	186	195
% $Y_2(SO_4)_3$	4.76	2.38	1.59	1.19	0.95	0.64	0.48	0.23	0.12

B. Yttrium Sulfate Solubility in Uranyl Sulfate Solution containing 30 g/l Uranium.

t°C	153	162	189	229
% $Y_2(SO_4)_3$	4.47	2.23	0.81	0.22

In both cases the solubility of yttrium sulfate shows a negative temperature coefficient. Since the yttrium sulfate solutions all showed a strong tendency to supersaturate it was necessary to heat them 50°-70 ° above the equilibrium solubility temperature before crystals appeared. The temperatures given in the table represent the points at which the last crystals redissolved upon slow cooling. The yttrium sulfate crystals did not adhere to the sides of the tubes. Just as in the case of lanthanum sulfate no double solubility points were observed at any given concentration below 300°C. Also the yttrium sulfate-uranyl sulfate-water system seemed to be stable at 250°C.

Conclusion

With the exception of cesium sulfate all the salts investigated showed a negative temperature coefficient of solubility both in water and in uranyl sulfate solution. It is possible that at higher temperatures cesium sulfate might behave like sodium and potassium sulfates[4] and show a sudden decrease in solubility.

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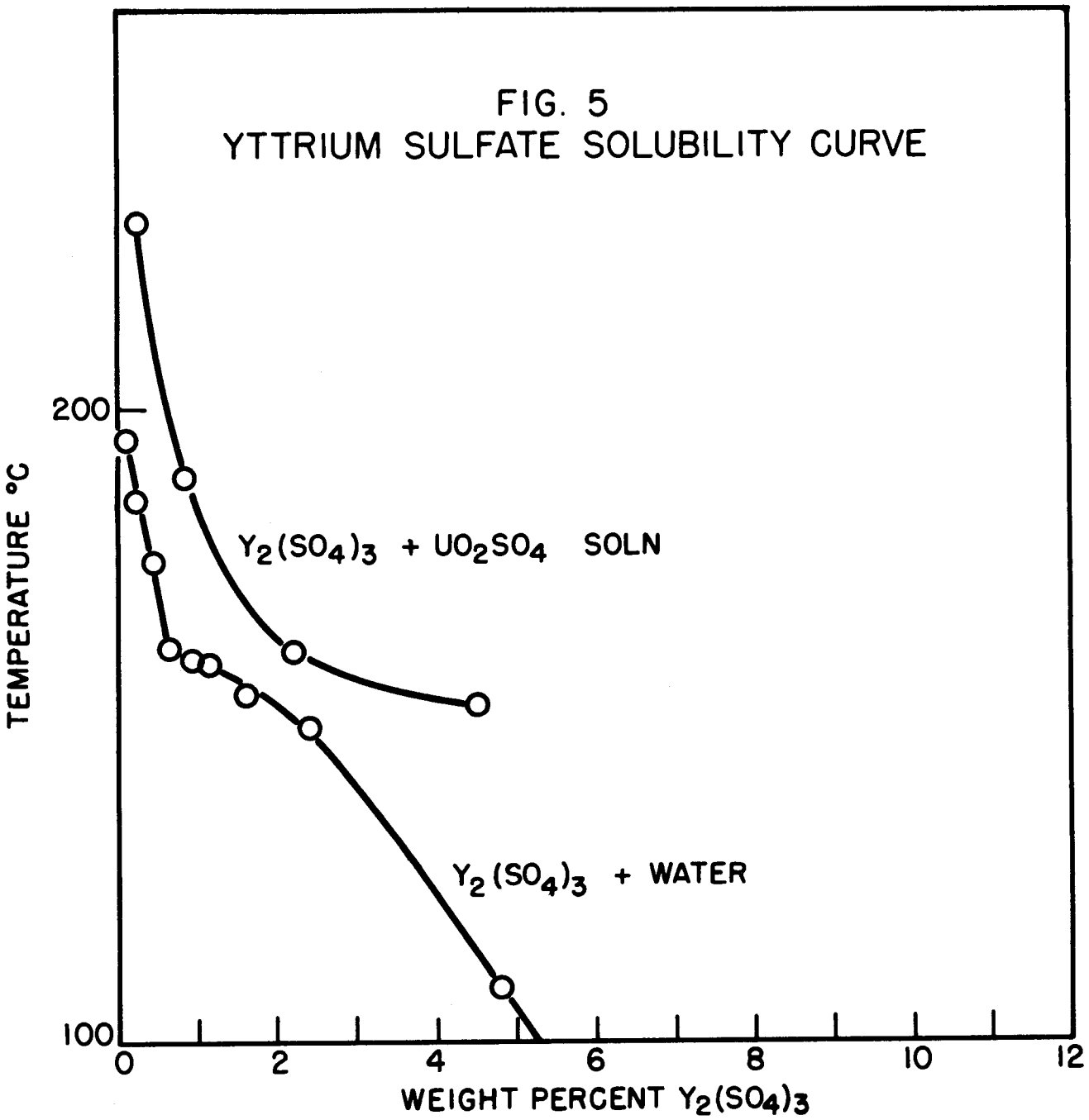

The formation of a sulfate complex of the type $\left[UO_2(SO_4)_2\right]^{=}$ may account for the increased solubility of the various sulfates in uranyl sulfate solution at a given temperature.

Because of the small amount of material used in the synthetic method and because of the difficulty (if not impossibility) of sampling, the solid phase in equilibrium with the solution at a given temperature was not identified.