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TEMPERATURE - CONCENTRATION RELATIONSHIPS ABOVE 250°C.

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Oak Ridge National Laboratory

Oak Ridge, Tennessee

(Contract Number AT-33-1-GEN-53)

THE SYSTEM URANYL SULFATE - WATER

II. TEMPERATURE - CONCENTRATION RELATIONSHIPS ABOVE 250° C.

by C. H. Secoy

July 7, 1948

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The System Uranyl Sulfate - Water

II. Temperature - Concentration Relationships above 250° C.

by C. H. Secoy

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ABSTRACT

Apparatus for the study of the solubility of salts in water to temperatures above the critical point of water is briefly described.

The solubility of $UO_2SO_4 \cdot 1H_2O$, the stable solid phase in this region, has been followed from 181° to 375° C. Its solubility decreases with rising temperature to about 240° and increases above this temperature.

Solutions with a concentration below 82.7% UO_2SO_4 display a two liquid phase region below the critical temperature of water. This phenomena has heretofore not been reported for solutions of electrolytes. Both arms of the curve bounding the two liquid-phase region are followed to the critical temperature of water. The solubility of salt in water has very nearly reached zero at 350° and, since the aqueous phase always undergoes the critical change at 374.4° (the critical temperature of pure water), it must have reached zero at or below this temperature. The lower critical solution temperature of the two liquid-phase region is 294° and the critical concentration is 30% UO_2SO_4.

This abstract is based on work performed under Contract Number AT-33-1-GEN-53 for the Atomic Energy Project at Oak Ridge National Laboratory.

The System Uranyl Sulfate - Water

II. Temperature - Concentration Relationships above 250° C. (1)

by C. H. Secoy

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In the first paper of this series(2), temperature - concentration data for

(2) The System Uranyl Sulfate - Water. I., by C. H. Secoy, to be published in the Journal of the American Chemical Society, August, 1948; CNL-18; MDDC-1767.

the system uranyl sulfate - water below 250° were presented. This paper describes an extension of this study to the critical temperature of water.

Very little experimental information is to be found in the literature concerning the behavior of aqueous solutions of electrolytes at the critical point. Wuite(3)[2] studied the system sodium sulfate - water and found a rapidly diminishing

(3) Wuite, Z. physik. chem., 86, 349 (1914)

solubility as the critical temperature of water was approached. He reasoned that the solubility curve of the salt in liquid water would blend smoothly into a solubility curve for the salt in water vapor but presented no experimental evidence of this. The accepted value of the critical temperature of water at that time was 365° C. and his analysis of the liquid phase in equilibrium at that temperature showed no detectable amount of salt. Although Wuite's reasoning concerning the phase diagram is probably correct, it is also probable that the vapor pressure of the salt at this temperature is extremely small in comparison to that of water and, therefore, the solubility of the salt in water vapor is insignificantly low.

Schröer(4) studied the behavior of dilute solutions of NaCl, KCl, KBr, and KI

(4) Schröer, Z. physik. Chem., 129, 79 (1927)

(1) This document is based on work performed under Contract Number AT-33-1-GEN-53 for the Atomic Energy Project at Oak Ridge National Laboratory.

and found that the solutions did go through a critical change at a temperature above the critical temperature of water without separation of either a solid or liquid phase. This phenomenon has been verified qualitatively for NaCl in this laboratory. In view of the fact that the partial pressure of water would be of the order of 10^6 times that of solid NaCl at this temperature, the stable existence of several percent of salt in the gas phase is difficult to understand. Khitarov and Ivanov(5), using a balanced bomb in which the critical phenomena was detected

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(5) N. I. Khitarov and L. A. Ivanov, Zentr. Mineral. Geol., 1936A, 46.

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by the homogeneity of the system above the critical temperature, verified Schröer's results for KCl and reported a similar elevation of the critical temperature for sodium metasilicate solutions. However, the possibility of the appearance of another liquid or solid phas, which they failed to mention, might render their conclusions ambiguous.

EXPERIMENTAL: Uranyl sulfate was prepared from c.p. uranyl nitrate by treatment with dilute H_2SO_4 followed by repeated evaporations to SO_3 fumes. The acetone complex was precipitated from the aqueous solution, washed thoroughly with acetone, and finally decomposed by boiling in excess water. The water solution was evaporated to incipient crystallization several times to remove all traces of acetone and the crystals finally allowed to form. After three recrystallizations from water, a stock solution saturated at room temperature was prepared. Solutions of lower concentration were made from this by proper dilution. For concentrations above the room-temperature saturation value, a weighed excess of crystalline $UO_2SO_4 \cdot 3H_2O$ was used along with a calculated amount of the saturated solution.

The composition of the contents of the tubes was checked in two ways, by chemical analysis of the solutions and solid from which the tubes were filled and by chemical analysis of the contents of the tube at the completion of the solubility determination. In addition, those cases in which the composition was greater than the room-temperature saturation value, were checked against the previously determined solubility curve for the trihydrate.

The tubes used for this work were of silica glass having a 2 mm bore and a wall thickness of 4 mm. The technique of filling the tubes, degassing the solutions, and evacuating and sealing the tubes has been described elsewhere[2].

A stainless steel cylinder, 2 in. in diameter and 13 in. long, wound with a heating coil over its entire length, was used as a heating block. The silica tube rested at the center of the block and could be viewed through narrow slots in opposite sides of the block with the aid of a light source placed behind the apparatus. The entire assembly was clamped in a horizontal position in a rocker mechanism which oscillated through a vertical arc of about 30° causing the liquid contents to flow back and forth in the silica tube. In the two liquid phase region free flow was always obtained at temperatures well below those at which phase changes were observed. An explosion shield with Plexiglass windows could be attached to the rocker.

Temperature was measured by means of an iron-constantin thermocouple using a Type K-2, Leeds and Northrup potentiometer. The hot junction of the thermocouple rested on top of the silica tube at its midpoint. Since a finite temperature differenc between the contents of the tube and the outside of the tube would be expected, the thermocouple was calibrated against the critical change of carefully purified acetic acid (321.6°), propionic acid (339.5°), chlorobenzene (359°), water (374.4°), and bromobenzene (397°).

Correction for Weight of Water in the Vapor Phase — The maximum volume of vapor above the solution was about 0.22 cc while the volume of solution used varied from about 0.10 to 0.20 cc. At high temperatures the loss of water to the vapor phase would materially change the composition of the liquid and a correction in compositions is necessary. The vapor pressure of the saturated solution was measured, using an isotensiscope method, at several temperatures from 25° to 70° C. Two bulbs, one containing water and the other saturated uranyl sulfate solution over an excess of salt crystals, were attached to the arms of a small U-tube differential manometer. The whole apparatus was agitated in a constant temperature bath and the difference in mercury levels in the U-tube, with appropriate zero-

point corrections, gave the vapor pressure lowering due to the solute. The data are given in Table I. No other vapor pressure data are available.

TABLE I

Vapor Pressure of Saturated Uranyl Sulfate Solutions

T, °C.	Mole Fraction N_2	ΔP, observed mm. of Hg	van't Hoff factor, i
25	0.0688	4.60	2.814
30	.0694	5.82	2.635
35	.0700	7.41	2.510
40	.0708	9.56	2.441
50	.0724	15.6	2.329
60	.0744	24.9	2.240
70	.0765	39.4	2.204

In order to make an extrapolation to 181°, (the transition temperature trihydrate-monohydrate) the van't Hoff factor, i, was calculated and plotted against temperature (see Figure I). The values of i fall rapidly with increasing temperature and seem to approach the ideal value, 2. Such an extrapolation is undoubtedly questionable but in view of the fact that the resulting correction in the concentration of the solution up to 181° is less than the probable experimental error, it seems justified as a first approximation.

An examination of the phase diagram (see Figure II) indicates a triple-point at B, 374°, at which the three phases in equilibrium would be solid monohydrate, a liquid phase consisting of salt saturated with water, and another liquid phase consisting of water saturated with salt. Furthermore, the aqueous liquid phase was found invariably to undergo critical transformation at 374°, the critical temperature of pure water, provided that the volume of aqueous liquid bore the proper ratio to the volume of the vapor. This means that the aqueous liquid phase must be essentially pure water at the critical temperature. The partial pressure of water vapor at this temperature is, therefore, that of pure water. If the gas phase is assumed to contain only water vapor, the vapor pressure of the monohydrate saturated solution must also be equal to that of pure water since the two phases are in equilibrium. Thus, having established a value for the vapor pressure of the saturated solution at 181° and at 374°, one can draw a typical vapor pressure curve between these points as representing the

vapor pressure of the monohydrate saturated solution.

In the two-liquid phase region, three phases are present and the system is monovariant. The temperature, therefore, fixes not only the composition of each phase but also the vapor pressure of the system. The lower critical solution temperature is 294° and the concentration about 30% UO_2SO_4. Assuming that the deviation from Raoult's law is independent of concentration, one can calculate the pressure of the 30% solution from the estimated value for the monohydrate saturated solution at this temperature. Again the pressure must rise with increasing temperature and reach that of water at 374°.

This is, at first sight, a crude approximation. However, the resultant corrections in the concentration of the solutions are most significant in the high temperature and high concentration region, i.e., in the vicinity of point B. (Figure II). This is the region where the approximated vapor pressures are most nearly correct and at the point B must be precisely correct. Error in the approximations could only result in shifting the curves slightly in this region and would not alter the fundamental nature of the phase diagram.

DISCUSSION: The data are summarized in Table II in which the initial or overall composition of the contents of the tube as obtained by chemical analysis is given in the first column. The second column gives the composition of the liquid phase at the temperature of phase separation. These values were calculated from the initial composition and the vapor pressure of the solution estimated as described above.

In the two liquid phase region the equilibrium could be approached from either direction and the temperatures established with precision. These temperatures are believed to be correct to the nearest tenth of a degree. However, for the points on the solid phase solubility curve, equilibrium was reached much more slowly. Free flow of the solution was not obtained and the stirring was negligible. These points were approached with the temperature falling at a very slow rate (usually about two

TABLE II

Solubility of Uranyl Sulfate in Water

% UO_2SO_4 Initial	% UO_2SO_4 Corrected	Temperature °C.	Phase Appearing or Disappearing	Critical Temp. of Aqueous Phase
0.77	1.1	335.1	Liquid Salt	
3.15	3.6	319.4	" "	
5.86	6.8	310.1	" "	
12.30	13.8	299.9	" "	374.3
20.40	22.5	295.8	" "	
31.65	34.6	295.5	Aqueous	374.0
40.72	44.2	297.5	"	374.2
48.06	52.2	302.3	"	374.2
55.45	60.1	308.2	"	
58.64	63.7	312.5	"	374.4
60.60	65.9	316.2	"	
62.32	68.0	320.5	"	
67.43	75.2	339.6	"	
71.00	80.8	363.0	"	
72.60	81.7	365.	Solid Monohydrate	
72.85	80.2	347.	" "	
73.49	77.8	311.	" "	
73.94	76.7	287.	" "	
76.02	76.3	181.	" "	
76.86	76.7	152.	" " (metastable)	

hours for the final degree) and the approach was repeated several times at even slower rates. The values reported are believed correct to the nearest degree.

At temperatures above 374° the system becomes one in which a gas is dissolved in a solid under pressure. The melting point of the solid is lowered by the presence of the dissolved gas so that a liquid state is possible. A univariant system can exist, the phases being solid salt, liquid salt saturated with gas, and gas. However, such a system would be very pressure dependent and the techniques employed in this work are not adequate to study the system in this range.

The point B has the character of a triple-point. At lower temperatures we may have equilibrium between the two liquid phases at concentrations less than that at B, or equilibrium between the salt liquid phase and solid monohydrate at concentrations greater than that at B. At higher temperatures we have only the equilibrium between the aqueous gas phase and solid monohydrate. Although this point was not realized experimentally, the data indicate that it occurs at the critical temperature of water. If this is true, it must be by virtue of the fact that the vapor pressure of the monohydrate saturated solution becomes equal to the critical pressure of water at this temperature.

SUMMARY: The system uranyl sulfate - water displays a two liquid phase region with concentrations up to 82.7% UO_2SO_4. The lower critical solution temperature is 294° and the critical concentration is 30% UO_2SO_4. The aqueous phase undergoes critical transformation at the critical temperature of pure water indicating that it is pure water at this temperature.

The solubility curve of solid $UO_2SO_4 \cdot H_2O$ is followed to its intersection with the two liquid phase region. This intersection has the character of a triple-point and occurs at 374.4° and a concentration of 82.7% UO_2SO_4.

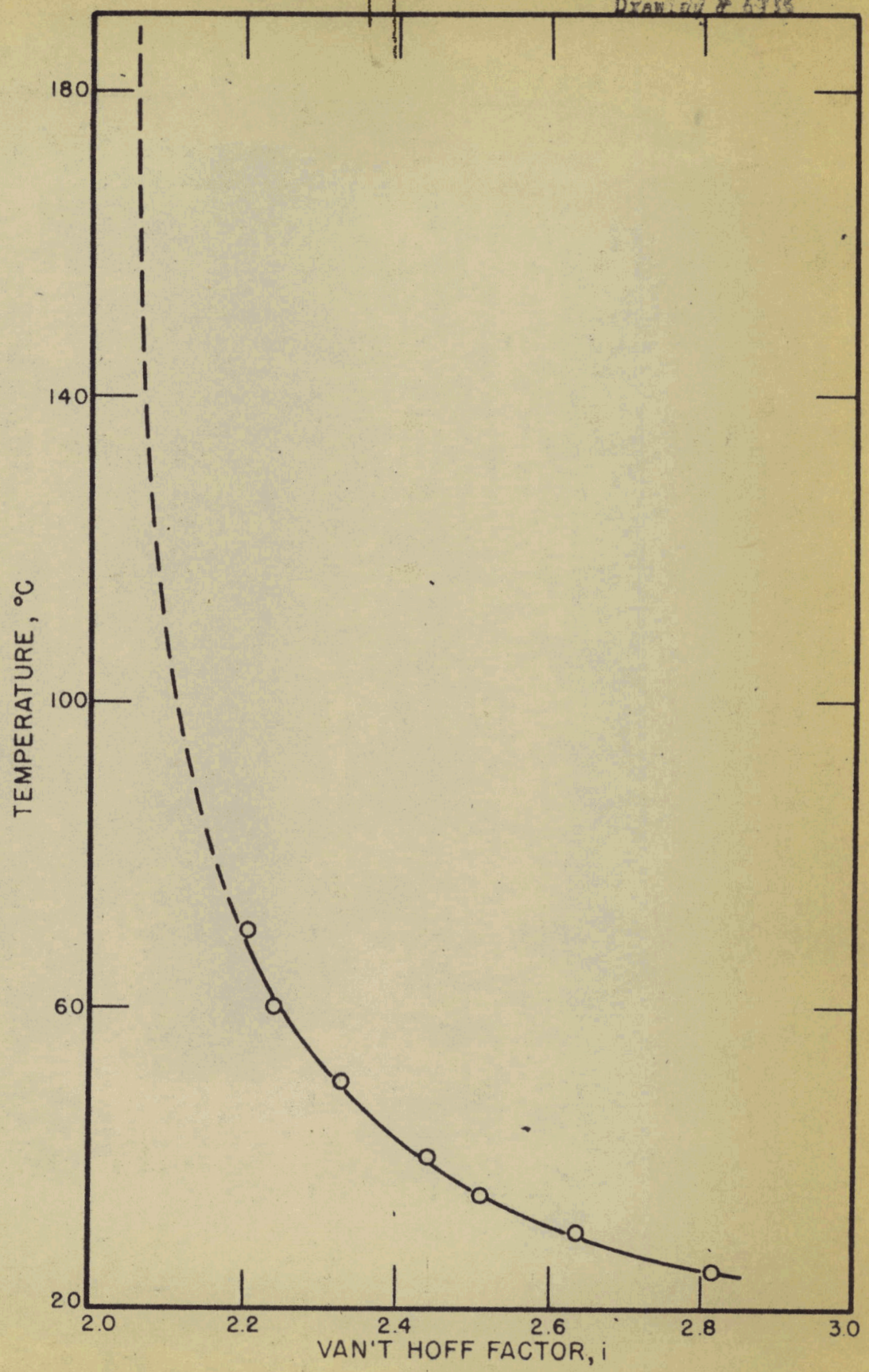

FIG. I
VARIATION OF THE VAN'T HOFF FACTOR WITH TEMPERATURE

Drawing # 5936

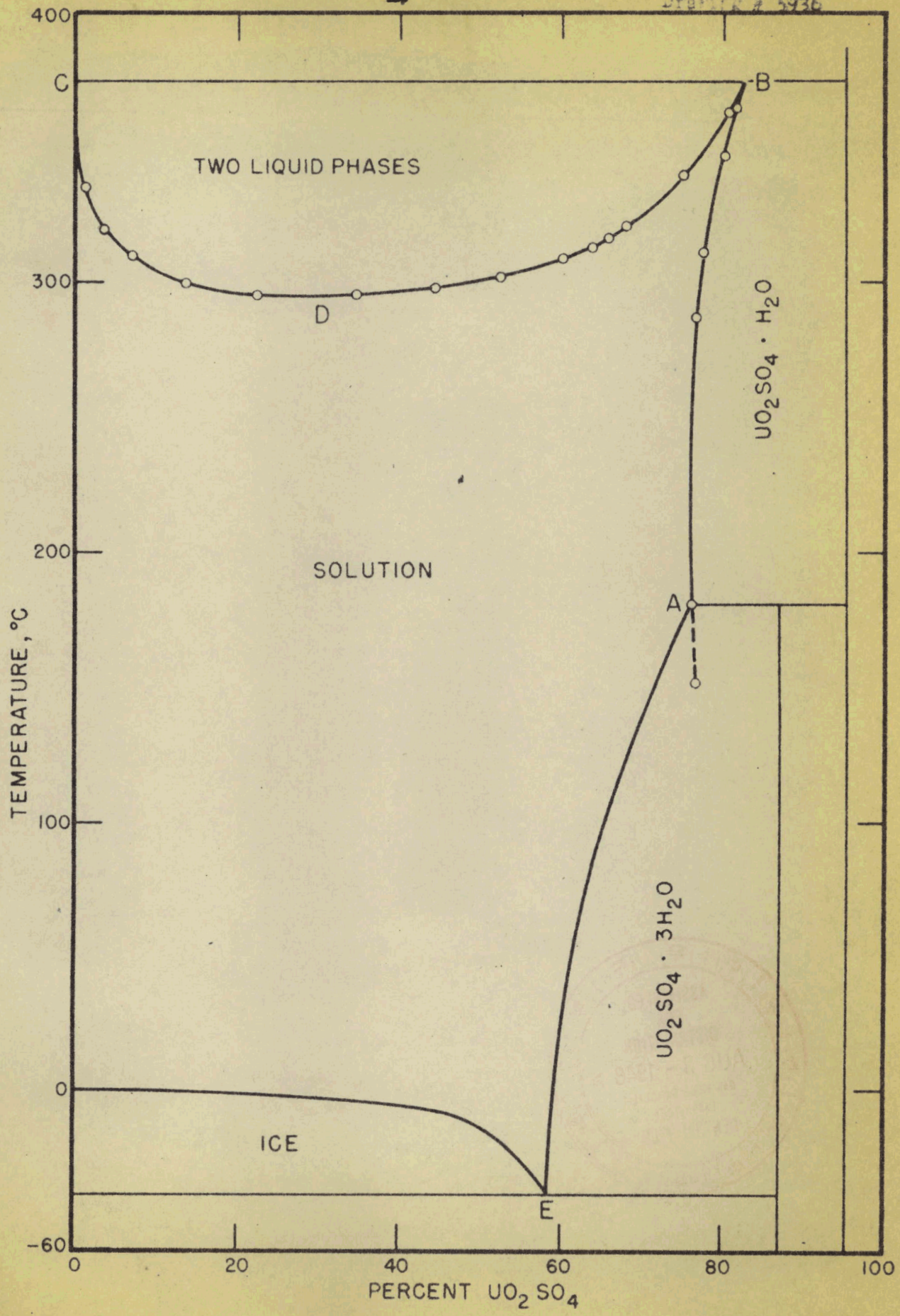

FIG. II

PHASE DIAGRAM FOR SYSTEM URANYL SULPHATE-WATER