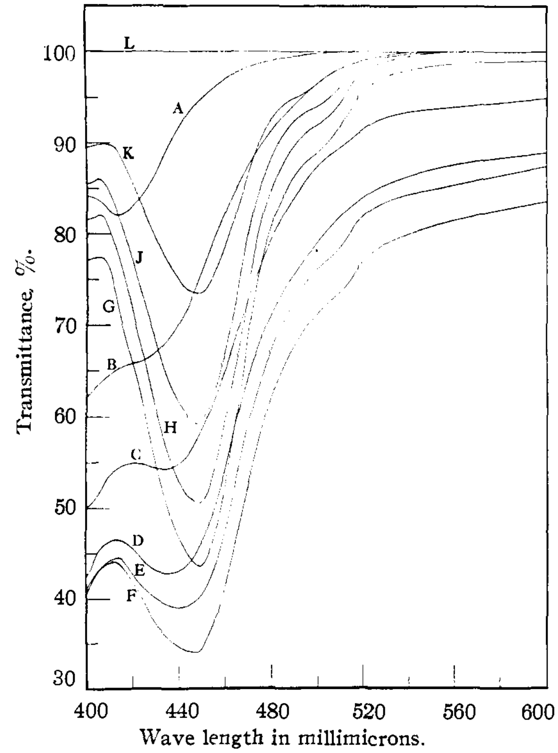

Fig. 1.—Method of continuous variations: solutions containing UO_2^{++} and $SO_3^{=}$.

that the ratio of uranium to sulfite ion varies from approximately 3:2 to 4:3; apparently the solid consists of a mixture the composition of which is partially dependent upon the concentration of sulfite used. This product was not further investigated.

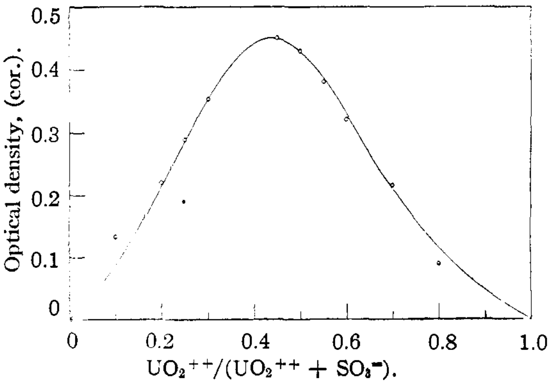

Fig. 2.—Method of continuous variations: λ = 448.

Summary

1. Two different crystalline forms of uranium peroxide 2-hydrate are formed by the reaction between excess uranyl nitrate and hydrogen peroxide, and between uranyl nitrate and excess hydrogen peroxide. The uranium-uranium distance is the same in both types of crystal.

2. The precipitation of uranium as the peroxide 2-hydrate is substantially quantitative at *p*H 2.5 and 3.5. The product obtained at an initial *p*H of 4.5 (following addition of ammonium hydroxide) consists of uranium peroxide 2-hydrate, ammonium diuranate, and at least one other crystalline solid. At *p*H $\leqq$ 1, uranium peroxide 2-hydrate and at least one additional crystalline product are formed.

3. Uranium peroxide 2-hydrate is dissolved without gas evolution by aqueous solutions of sulfites to form an intensely yellow solution and (under appropriate conditions of concentration) a similarly colored solid which is apparently a mixture. The soluble product responsible for the color of the solution has been shown to consist of uranyl sulfite, which has not been reported previously.

AUSTIN, TEXAS RECEIVED JANUARY 5, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The System Uranyl Sulfate-Water. II. Temperature-Concentration Relationships Above 250°[1]

BY C. H. SECOY

In the first paper of this series,[2] temperature-concentration data for the system uranyl sulfate-water below 250° were presented. This paper describes an extension of this study to the critical temperature of water.

As a point of special interest, it was thought that this work might add information about the behavior of aqueous solutions of electrolytes at the critical point concerning which very little experimental information is to be found in the literature. Wuite[3] studied the system sodium sulfate-water and found a rapidly diminishing 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°, and his analysis of the liquid phase in equilibrium at that temperature

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(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory. Presented before the Division of Physical and Inorganic Chemistry at the 114th National Meeting of the American Chemical Society, Portland, Oregon, September, 1948.

(2) Secoy, THIS JOURNAL, **70**, 3450 (1948).

(3) Wuite, *Z. physik. Chem.*, **86**, 349 (1914).

showed no detectable amount of salt. In experiments performed in this Laboratory the aqueous phase in contact with solid sodium sulfate has repeatedly shown critical phenomena at 374.3 ± 0.1°, the critical temperature of water.

Schröer[4] studied the behavior of dilute solutions of sodium chloride, potassium chloride, potassium bromide and potassium iodide and found that solutions unsaturated with respect to the solid 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 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 salt at this temperature, the stable existence of several per cent. of salt in the gas phase must be attributed to a "solubility effect." This effect is discussed by the author elsewhere.[5] Diepen and Scheffer[6] have reported a similar solubility effect in systems containing certain organic solids in supercritical ethylene. Khitarov and Ivanov,[7] using a balanced bomb in which the critical phenomenon was detected by the homogeneity of the system above the critical temperature, verified Schröer's results for potassium chloride and reported a similar elevation of the critical temperature for sodium metasilicate solutions. However, the possibility of the appearance of another liquid phase or a solid phase, which they fail to mention, might render their conclusions ambiguous. Benrath[8] and co-workers have studied the solubility of several salts at temperatures above 100° but did not mention any phase phenomena that might occur in unsaturated solutions at elevated temperatures. Furthermore, they based some of their interpretations on the assumption that the solubility of all salts in the supercritical fluid is zero. This is not necessarily true as shown by the behavior of the alkali halides.

Experimental

Uranyl sulfate was prepared from C. P. uranyl nitrate by treatment with dilute sulfuric acid followed by repeated evaporations to sulfur trioxide fumes. The sulfate-acetone complex was precipitated from the aqueous solution, washed thoroughly with acetone, and finally decomposed by boiling in excess water. This treatment serves to ensure the correct stoichiometric ratio of sulfate to uranyl ion. 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 25° 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 tubes used for this work were of fused silica 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.[9]

A stainless steel cylinder, 3 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. An explosion shield with Plexiglass windows could be attached to the rocker.

Temperature was measured by means of an iron-constantan 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 mid-point. Since a finite temperature difference between the contents of the tube and the outer wall 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°). Thus an empirical correction curve, which was nearly linear over the range 280 to 400°, was obtained. It is believed that the temperature readings are correct to ± 0.2° as evidenced by the reproducibility of the data.

In the two-liquid phase region free flow of the liquid in the tube was always obtained at temperatures below those at which phase changes were observed. The phase change could be approached with either rising or falling temperature, and the temperature of appearance of the second liquid phase never differed from the temperature of disappearance by more than 0.2°. The average of the observed values is reported in Table I. However, in the case of the solid-liquid equilibrium free flow of the tube contents was not obtained. These points were approached with the temperature falling at a very slow rate (usually about two 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.

The composition of the contents of the tubes was determined in two ways. In the first the composition was calculated from the weights of solution and solid used and the analytically determined uranium content of the solutions and solid. In the second the contents of the tube were weighed and the uranium determined by chemical analysis at the completion of the solubility determination. In addition, those cases in which the salt content was greater than the room-temperature saturation value were checked against the previously determined solubility curve for the trihydrate. It should be emphasized that the values reported in Table I as per cent. UO_2SO_4 are obtained from the over-all contents of the tube and do not represent the true concentration of the liquid at the elevated temperatures due to loss of the volatile component, water, to the vapor phase. Even though this may introduce an error of several per cent., the general shape and nature of the phase diagram must be as given.

Discussion

Figure 1 shows the projection of the phase diagram on a temperature–concentration plane. The lower portion of the figure is reproduced, for the sake of completeness, from data previously published,[10] and the upper portion is plotted from the data of Table I. The point, A, is the incongruent melting point of $UO_2SO_4 3 \cdot H_2O$ and the curve AB represents the liquid composition of the univariant system solid monohydrate–liquid–va-

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

(5) Secoy, "The Application of Kinetic Theory to the Critical Curve for Aqueous Solutions of 1-1 Electrolytes," presented at the Symposium on Critical Phenomena at the 116th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949, in press.

(6) Diepen and Scheffer, This Journal, **70**, 4081, 4085 (1948).

(7) Khitarov and Ivanov, *Zentr. Mineral. Geol.*, 46 (1936A).

(8) Benrath, *et al.*, *Z. anorg. allgem. Chem.*, **231**, 285 (1937).

(9) Ref. 2, p. 3450.

(10) Ref. 2, p. 3451.

TABLE I

SOLUBILITY OF URANYL SULFATE IN WATER

UO_2SO_4, wt. %	Temp., °C.	Phase appearing or disappearing	Crit. temp. of aq. phase, °C.
0.77	335.1	UO_2SO_4-rich liq.	
3.15	319.4	UO_2SO_4-rich liq.	
5.86	310.1	UO_2SO_4-rich liq.	
12.30	299.9	UO_2SO_4-rich liq.	374.3
20.40	295.8	UO_2SO_4-rich liq.	
31.65	295.5	Water-rich liq.	374.0
40.72	297.5	Water-rich liq.	374.2
48.06	302.3	Water-rich liq.	374.2
55.45	308.2	Water-rich liq.	
58.64	312.5	Water-rich liq.	374.4
60.60	316.2	Water-rich liq.	
62.32	320.5	Water-rich liq.	
67.43	339.6	Water-rich liq.	
71.00	363.0	Water-rich liq.	
72.60	365	Solid monohydrate	
72.85	347	Solid monohydrate	
73.49	311	Solid monohydrate	

por. This curve does not intersect the two-liquid phase region .and must continue up to the melting point of the monohydrate. Two liquid phases are encountered only in the concentration range in which the liquid is unsaturated with respect to the solid. This is in contrast to the cases of two-liquid phase formation in water–salt systems reported by Benrath in all of which the invariant system, solid–liquid 1–liquid 2–vapor was found to occur.

The two branches of the curve T_cDC, namely, T_cD and DC, represent the liquid phases, the water-rich phase L_1 and the UO_2SO_4-rich phase L_2, respectively, in the univariant system, L_1–L_2–V. These curves must end at 374° since at this temperature the water-rich phase, L_1, undergoes critical change and becomes identical with the vapor. The observed temperatures for this critical transformation are recorded in the last column of Table I. In each case reported the volume of liquid was such that the L_1–V meniscus disappeared near the center of the tube and did not move through either end of the tube. Above 374° one obtains the bivariant system, L_2–V.

Since the critical temperature of the water-rich liquid phase is identical within the limits of experimental error with the accepted value for pure water, it seems safe to assume that the concentration of salt in the water-rich phase has reached zero at or below the critical temperature. Extrapolation of curve CD supports this assumption. Further support is given by the fact that the water-rich liquid appears completely devoid of yellow salt color above 350°

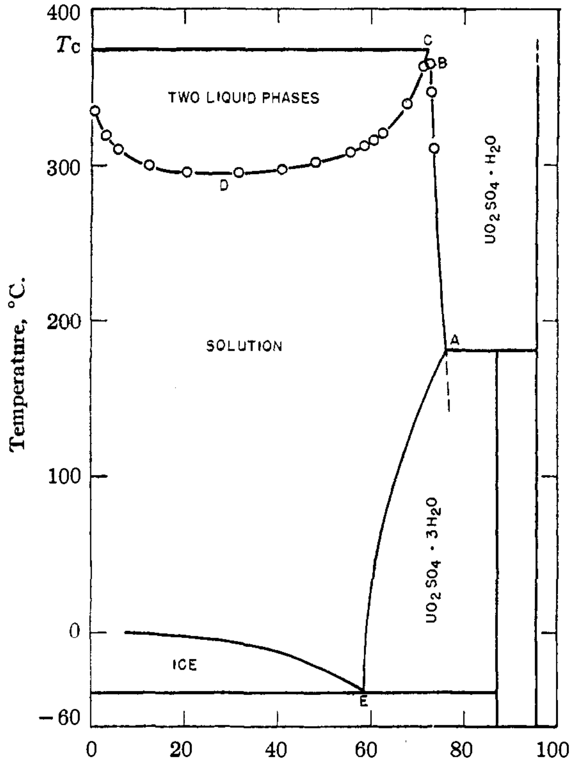

Fig. 1.—Phase diagram for the system uranyl sulfate–water.

Summary

The system uranyl sulfate–water displays a two-liquid phase region at all concentrations up to 72% UO_2SO_4. The lower critical solution temperature is 295° at a concentration of about 28% UO_2SO_4. The univariant two liquid phase region is terminated at 374° at which temperature the water-rich liquid phase undergoes a critical change becoming identical with the vapor.

The solubility curve of solid $UO_2SO_4 \cdot H_2O$ has been followed to 363° and does not intersect the two-liquid phase region. The invariant system, S–L_1–L_2–V, does not occur.

OAK RIDGE, TENN.

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