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THE pH OF UO_3-H_2SO_4-H_2O MIXTURES AT 25°C AND ITS APPLICATION TO THE DETERMINATION OF THE SOLUBILITY OF UO_3 IN SULFURIC ACID AT ELEVATED TEMPERATURE

W. L. Marshall

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W. [illegible] Marshall

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The pH of UO_3-H_2SO_4-H_2O Mixtures at 25°C and its Application To The Determination of the Solubility of UO_3 In Sulfuric Acid at Elevated Temperature

W. L. Marshall

Oak Ridge National Laboratory
Oak Ridge, Tennessee

The pH at 25.00° ± 0.04°C of uranium trioxide - sulfuric acid-water mixtures has been determined to a precision of ± 0.004 pH units from 0.024 to 10^{-4} molal sulfuric acid and at UO_3/H_2SO_4 mole ratios from 0.70 to 1.20. The solubility of UO_3 in sulfuric acid at elevated temperature (150° to 300°C) has been determined by isolating a UO_3 saturated sample, and comparing the [illegible] isolated sample at 25° with the pH data mentioned above. [illegible] method seven isotherms in the concentration range from 1.0 molal down to 10^{-4} molal have been obtained.

Experimental

The pH's at 25.00° ± 0.04°C were measured using a vibrating reed electrometer coupled with a Leeds and Northrup K-2 potentiometer and Brown recorder for recording the final potential by means of the apparatus of Kraus, Holmberg and Borkowski[1].

(1) K. A. Kraus, R. W. Holmberg, and C. J. Borkowski, Analytical Chemistry, 22, 341 (1950).

[redacted]

Thermostated water was circulated around both the calomel electrode and the test tube containing the sample solution, the salt bridge tip, and the glass electrode. A schematic drawing is shown in Fig. 1. The fluctuation of potential on the Brown recorder was of the order $\pm$ 0.04 millivolts.

Mallinckrodt UO_3 hydrate which had been washed thoroughly with hot water to remove as much nitrate impurity as possible (NO_3^- after washing < 24 ppm) was analyzed, weighed, and dissolved in 0.02441 molal H_2SO_4 solutions to produce the desired mole ratios, UO_3/H_2SO_4. Calibrated volumetric pipettes and flasks were used in this operation and the final concentrations were checked by weighing the solutions. These UO_3-H_2SO_4-H_2O solutions were diluted successively using calibrated volumetrics. Three control buffer solutions were used for relating the measured potentials to pH. These were 0.009928, 0.003157, and 0.001005 molar HCl solutions to which sufficient C.p. KCl was added to obtain a total chloride concentration of 0.100 molar in each solution. The pH value used for the 0.009928 molar HCl solution was 2.079[2] and those for the

(2) R. G. Bates, Chem. Rev. 42, 1 (1948).

other two solutions were related accordingly. The pH's of the buffers were checked before and after all series of measurements and the sample potentials were related to these values. The Nernst slope was found to lie between 59.00 and 59.50 mv per pH unit, but precise to $\pm$ 0.10 mv per pH unit for any series of

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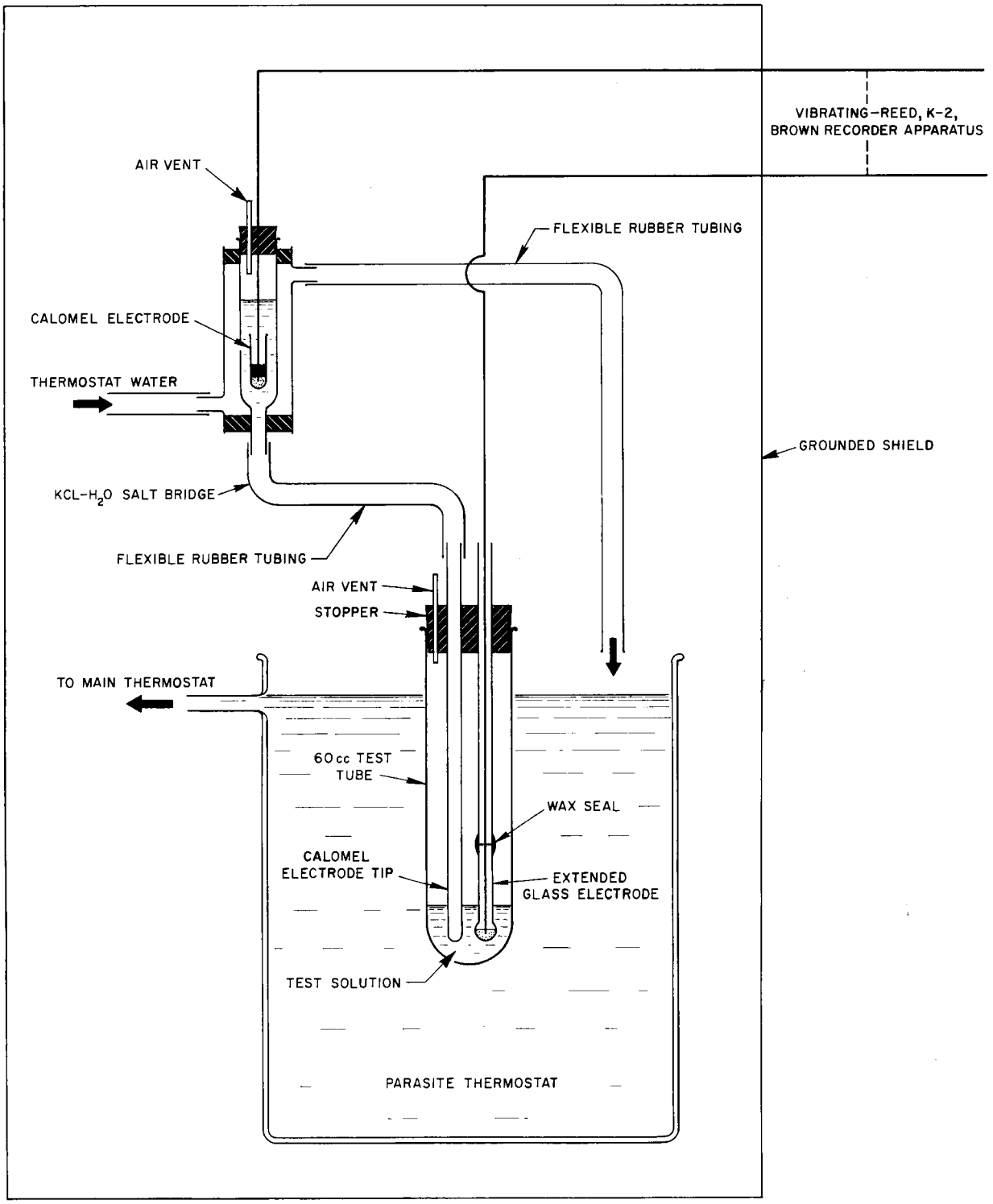

Fig. 1. Schematic Drawing of Thermostated Electrodes.

measurements. The pH's of the control solutions were measured under the above conditions and are believed to be reproducible to approximately ± 0.004 pH units.

A schematic diagram of the bomb and assembly for measuring solubilities at elevated temperature is shown in Fig. 2. There are two unique features of this bomb assembly one of which is the use of pure teflon gasketing fitted into a circular groove in the bomb head. This groove prevents the teflon from extruding upon being subjected to high temperature and pressure. There is no need for auxiliary screws to tighten on a pressure plate since, upon heating the bomb to temperatures above 100°C the teflon expands and effects a leak proof seal. It has been found that by tightening the bomb with the bare hands no leakage occurs. Upon cooling back to room temperature the teflon contracts thus allowing one, in most cases, also to open the bomb with the bare hands. However, usually a wrench is used for tightening and loosening the bomb head. The bomb assembly is cooled within several minutes by removing from the thermostat and placing it directly in a wet ice bath.

The teflon gasket can be used repeatedly under these conditions to approximately 325°C at which temperature a physical change occurs within the teflon[3]. Experiments have been performed on

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(3) E. I. duPont deNemours and Company Published Reports on Properties of Teflon. (Transition Temperature = 327°C)

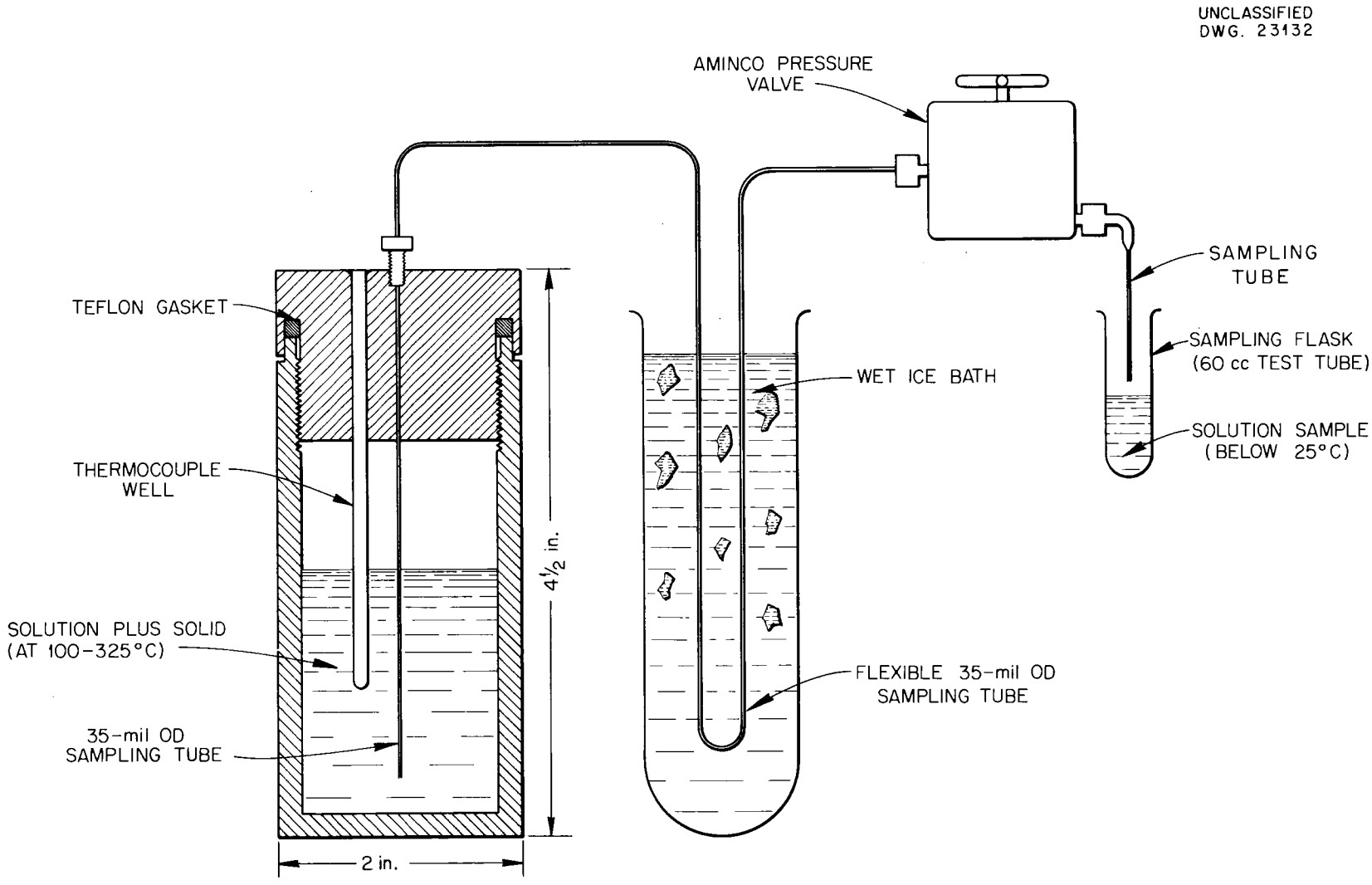

Fig. 2. Schematic Drawing of Aqueous Solution Sampling Assembly.

aqueous systems at 4500 p.s.i. without failure until 325° is reached. These observations indicate that it is not the water vapor pressure (the pressure of saturated steam at 325°C is 1750 p.s.i.) which causes the leakage at 325° but rather this physical change of teflon.

The second feature is the use of 30 mil outer diameter, 20 mil inside diameter stainless steel capillary tubing for sampling solutions. By virtue of the small size of the capillary tubing the solution sample, regardless of the temperature of the system, is cooled rapidly as it passes through that portion of capillary inserted in the wet ice bath. The internal pressure of the system affords the necessary pressure for pushing the solution through the capillary. A conventional Aminco valve is opened slowly and solution comes out either dropwise or in a stream to deliver as much as 15 to 20 cc. per minute.

Procedure for Determining Solubilities

A 60.00 cc. volume of standard H_2SO_4 solution was added to a weighed quantity of UO_3 hydrate. The mole ratio total of UO_3 to total H_2SO_4 was kept at about 3:1 thus assuring the presence of an excess of UO_3 under all conditions. A 4.00 cc. volume of C.p. 30% H_2O_2 was added which upon decomposition at elevated temperature formed oxygen and prevented reduction of uranyl ion to U^{+4} Uranium peroxide, which was formed at the lower temperature by reaction with H_2O_2, decomposed to UO_3 hydrate at the elevated temperature and thus the final system did not involve the peroxide.

A volume dilution correction was made for the hydrogen peroxide addition.

The bomb, loaded with excess solid and solution, was inserted into an insulated heated aluminum cylinder. The temperature was controlled through a Brown Pyr-O-Vane controller to $\pm 1^{o}C$. The whole assembly, including bomb, thermostat, capillary tubing, and sampling valve was placed on a large shaker. This shaker was run at a rate of 100 cycles per minute thereby affording ample mixing of the solution and solid.

Solution and solid were equilibrated at a particular temperature, a 3 cc. holdup sample removed, and a 5 cc. sample of the equilibrated solution was delivered to a standard 60 cc. test tube. This sample solution was thermostated at $25^{o}C$ and the pH determined in the manner described above. The mole ratio, UO_3/H_2SO_4, was determined from curves of pH vs. ratio (Fig. 4) for the particular concentration of H_2SO_4. The pH data of Orban[4]

(4) E. Orban, "Measurements of pH of UO_3-UO_2SO_4-H_2O Solutions" MLM-729, MLM-738 (1952, 1953).

was used for concentrations greater than 0.024 molal. It was found that after the initial hydrogen peroxide and uranium peroxide had decomposed the system equilibrated within 15 to 20 minutes between 150° and 290°. Samples obtained within this time limit agreed with samples obtained several hours later. For the most part, the system was allowed to equilibrate 1 to $1\frac{1}{2}$ hours

and in some cases overnight. The equilibration temperature was approached from higher and lower temperatures and the solubilities thus obtained indicated complete reversibility.

The pH Data at 25°C

The pH data at 25.00 ± 0.04°C are given in Table 1 and are shown in Figs. 3 and 4. There is a satisfactory overlap of data for stoichiometric UO_2SO_4 obtained by previous investigators[4, 5, 6, 7]. However, the previous data lacked the precision of the

(5) L. Helmholz and G. Friedlander, "Physical Properties of Uranyl Sulfate Solutions," LAMS-30 (1943) MDDC-808.

(6) D. A. MacInnes and L. G. Longsworth, "The Measurement and Interpretation of pH and Conductance Values of Aqueous Solutions of Uranyl Salts," A-380 (1942) MDDC-911.

(7) M. H. Lietzke, H. W. Wright, and W. L. Marshall, Homogeneous Reactor Project Quarterly Progress Report, ORNL-1121, p. 124 (1951).

data obtained using the present apparatus. These more precise data were necessary to derive the greatest benefit from using the data for analytical means. An attempt is to be made to interpret the pH data to give hydrolysis constants for UO_2^{++} and equilibria involving sulfate.

The Solubility Data

The solubility data are given in Table 2 and in Figs. 5 and 6. There appears to be a direct correlation between the hydrogen ion activity at a particular temperature and mole ratio

Table 1. The pH of UO_3-H_2SO_4-H_2O Solutions at 25.00 ± .04°C

Molar Ratio UO_3/SO_4: Molarity H_2SO_4	0.7006	0.8017	0.9024	1.0029	1.1042	1.202
	pH *					
0.02432	1.995	2.151	2.425	3.043	3.612	3.823
0.01214	2.259	2.422	2.692	3.267	3.731	3.922
0.004866	2.619	2.784	3.046	3.526	3.874	4.038
0.003656	2.730	2.900	3.155	3.604	3.913	4.074
0.002437	2.905	3.065	3.321	3.708	3.977	4.124
0.001216	3.174	3.348	3.592	3.906	4.093	4.214
0.0004850	3.587	3.715	3.903	4.130	4.250	4.354
0.0003646	3.671	3.822	3.996	4.201	4.304	4.395
0.0002424	3.851	4.004	4.127	4.326	4.411	4.500

* These values and the pH values in Table 2 are based on a determined pH of 2.075 for 0.01000 molar HCl, 0.0900 molar KCl. (See reference 2). For pH's relative to the analytical concentration of HCl subtract 0.075 pH units from each of the above values.

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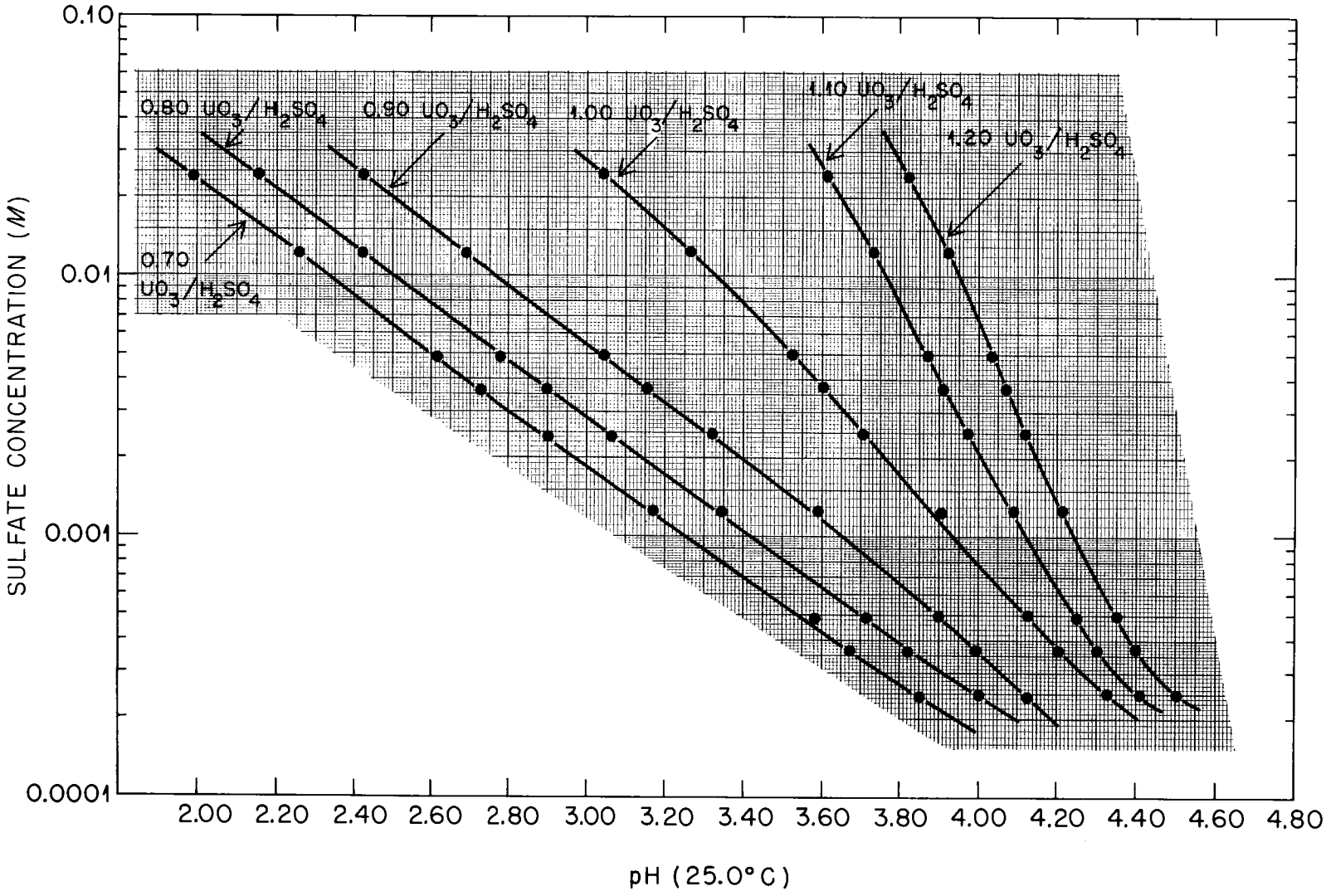

Fig. 3. The pH at 25.0°C of UO_3-H_2SO_4-H_2O Mixtures; H_2SO_4 Concentration vs pH.

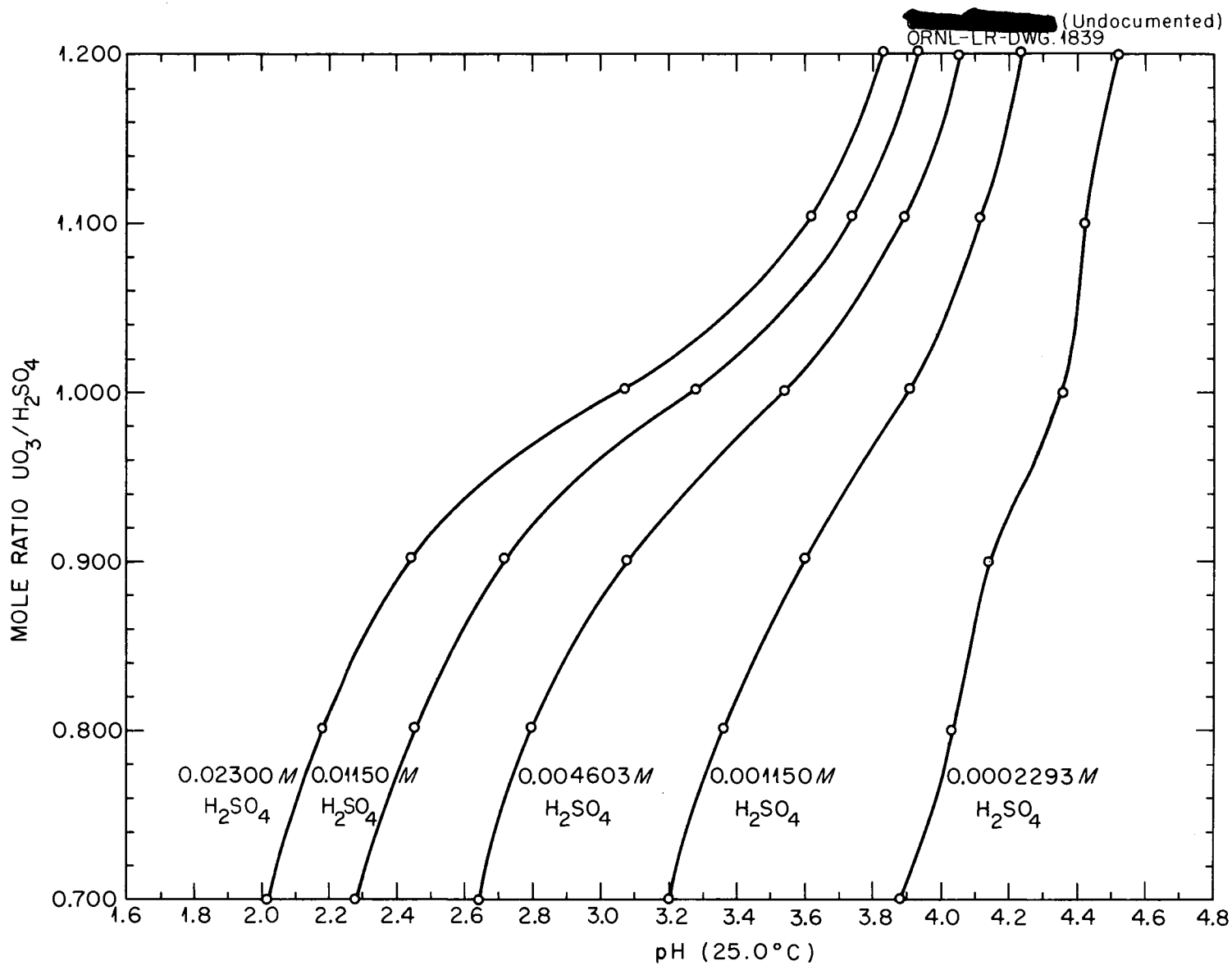

Fig. 4. The pH at 25.0°C of UO_3-H_2SO_4-H_2O Mixtures; Mole Ratio vs pH.

Table 2. Solubility of UO_3 in H_2SO_4-H_2O Solutions

	Molarity 25°C H_2SO_4	Molarity 25°C UO_3	UO_3/H_2SO_4 Molar Ratio	pH 25.0°C	Molality H_2SO_4	Molality UO_3
150°C						
	1.000	1.318	1.318	3.111		
	0.1000	0.1205	1.205	3.627	0.1008	0.1215
	0.02300	0.02686	1.168	3.784	0.02309	0.02697
	0.01150	0.01318	1.146	3.843	0.01154	0.01322
	0.001150	0.001230	1.070	4.053	0.001154	0.001235
175°C						
	1.000	1.300	1.300	3.081		
	0.1000	0.1174	1.174	3.565	0.1008	0.1183
	0.02300	0.02578	1.121	3.676	0.02309	0.02588
	0.01150	0.01255	1.091	3.699	0.01154	0.01259
	0.004603	0.004792	1.041	3.700	0.004618	0.004807
	0.0002293	0.0002080	0.907	4.153	0.0002301	0.0002087
200°C						
	1.000	1.285	1.285	3.053		
	0.1000	0.1151	1.151	3.503	0.1008	0.1160
	0.02300	0.02498	1.086	3.543	0.02309	0.02507
	0.01150	0.01194	1.038	3.484	0.01154	0.01198
	0.004603	0.004465	0.970	3.368	0.004618	0.004479
	0.001150	0.001015	0.883	3.560	0.001154	0.001019
	0.0002293	0.0001704	0.743	3.953	0.0002301	0.0001710
225°C						
	1.000	1.268	1.268	3.019		
	0.1000	0.1132	1.132	3.443	0.1008	0.1141
	0.02300	0.02392	1.040	3.302	0.02309	0.02401
	0.01150	0.01138	0.990	3.191	0.01154	0.01142
	0.004603	0.004193	0.911	3.103	0.004618	0.004207
	0.001150	0.0009016	0.784	3.331	0.001154	0.0009047
	0.0002293	0.0001497	0.653	3.793	0.0002301	0.0001502
250°C						
	1.000	1.243	1.243	2.967		
	0.1000	0.1114	1.114	3.372	0.1008	0.1123
	0.02300	0.02318	1.008	3.095	0.02309	0.02327
	0.01150	0.01080	0.939	2.868	0.01154	0.01084
	0.004603	0.003903	0.848	2.908	0.004618	0.003916
	0.001150	0.0008314	0.723	3.224	0.001154	0.0008343

Table 2. Solubility of UO_3 in H_2SO_4-H_2O Solutions

	Molarity 25°C H_2SO_4	Molarity 25°C UO_3	UO_3/H_2SO_4 Molar Ratio	pH 25.0°C	Molality H_2SO_4	Molality UO_3
270°C						
	0.1000	0.1105	1.105	3.330	0.1008	0.1114
	0.02300	0.02256	0.981	2.895	0.02309	0.02265
	0.01150	0.01037	0.902	2.709	0.01154	0.01041
	0.004603	0.003710	0.806	2.813	0.004618	0.003722
	0.001150	0.0007590	0.660	3.137	0.001154	0.0007616
290°C						
	0.1000	0.1098	1.098	3.293	0.1008	0.1107
	0.02300	0.02213	0.962	2.762	0.02309	0.02212
	0.01150	0.01008	0.877	2.622	0.01154	0.01012
	0.004603	0.003599	0.782	2.765	0.004618	0.003611
	0.001150	0.0007164	0.623	3.088	0.001154	0.0007189

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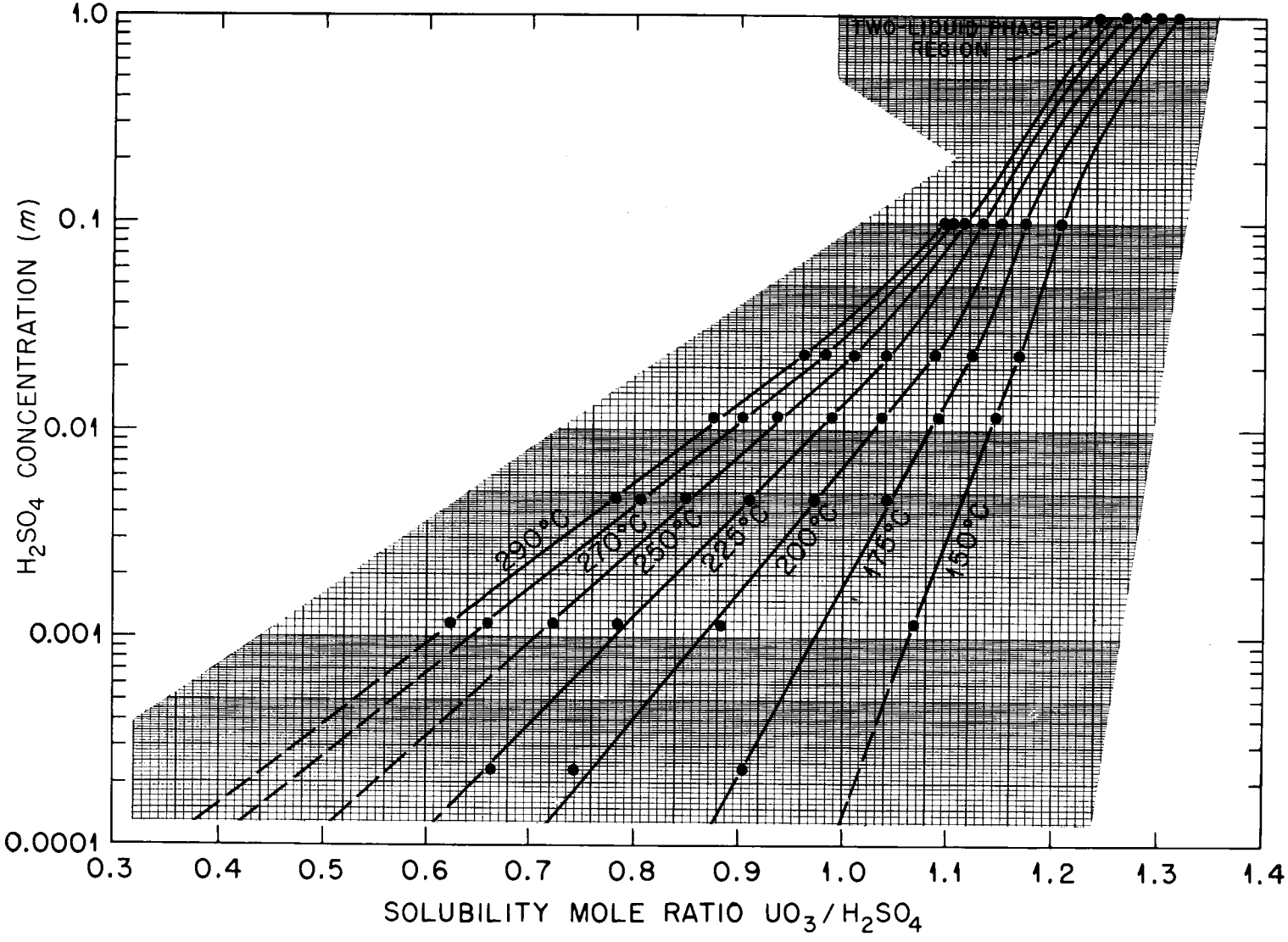

Fig. 5. The Solubility of UO_3 in H_2SO_4-H_2O Mixtures from 150° to 290°C; H_2SO_4 Concentration vs Mole Ratio.

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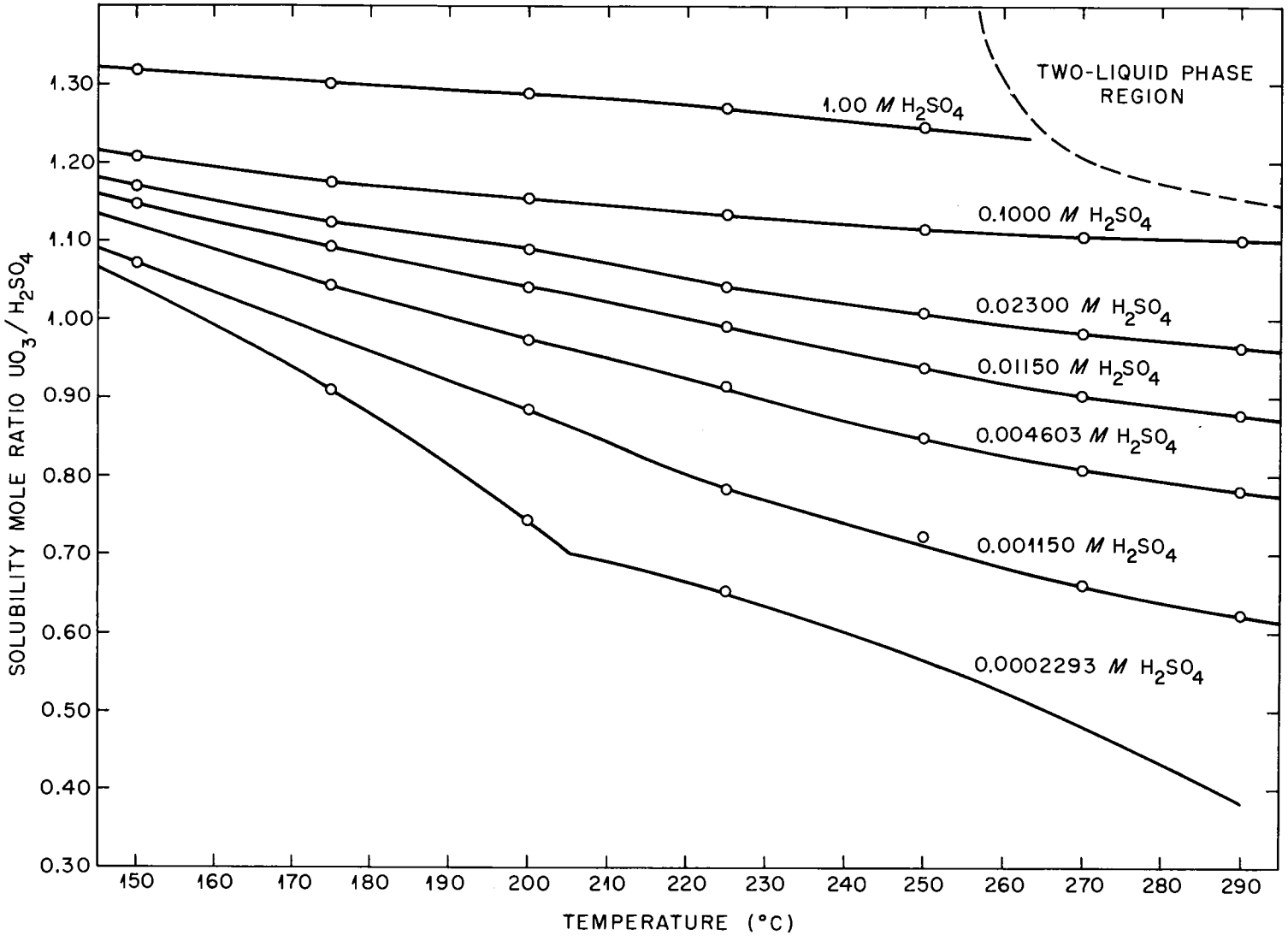

Fig. 6. The Solubility of UO_3 in H_2SO_4-H_2O Mixtures from 150° to 290°C, Mole Ratio vs Temperature.

as a function of H_2SO_4 concentration as evidenced by the linear relationships shown on the log H_2SO_4 vs. solubility mole ratio, UO_3/H_2SO_4, plot (Fig. 5). The straight line portions of Fig. 5 can be represented by the equation,

$$\log H_2SO_4 = k\ UO_3/H_2SO_4 + C.$$

If the slopes, k, are plotted against $1/T^oA$, a break in the resultant curve occurs at 205°C. The break presumably represents a transition from α $UO_3 \cdot H_2O$ to β $UO_3 \cdot H_2O$. By means of x-ray diffraction J. O. Blomeke, of this Laboratory, previously has observed a transition of α $UO_3 \cdot H_2O$ to β $UO_3 \cdot H_2O$ occurring at approximately 200°C for solids[8]. The above findings are in

(8) J. O. Blomeke, "Crystallography of $UO_3 \cdot H_2O$," Homogeneous Reactor Project Quarterly Report, ORNL-1554, p. 112. (March 31, 1953).

agreement both with Blomeke's observation and also with E. V. Jone and C. H. Secoy's investigation[9].

(9) C. H. Secoy et al., "The System UO_3-NiO-SO_3-H_2O," Homogeneous Reactor Project Quarterly Report, ORNL-1658, p. 87 (1953).

A similar break as mentioned above also appears at 205° on plots of C vs $1/T^oA$. Approximate linear relationships are observed on both sides of 205° for both k and C plots. Two

empirical equations have been derived to express the solubility data and are believed accurate to $\pm$ 1% in mole ratio in the respective temperature and concentration ranges with the exception of 290°C at which temperature the particular equation is in error by -0.01 at -0.03 ratio units. Both equations are given as follows and are applicable from approximately 0.05 to 10^{-4} molal H_2SO_4:

Equation 1 (for use between 150° and 205°C.)

$$\log H_2SO_4 = \left(\frac{4150}{t^{\circ}C} - 14.42\right)\frac{UO_3}{H_2SO_4} - \frac{5230}{t^{\circ}C} + 17.74$$

Equation 2 (for use between 205° and 290°C.)

$$\log H_2SO_4 = \left(\frac{1400}{t^{\circ}C} - 1.096\right)\frac{UO_3}{H_2SO_4} - \frac{1880}{t^{\circ}C} + 1.324$$

where UO_3 and H_2SO_4 are expressed in molalities. The equations also are applicable to concentrations of sulfate as high as one molal but approach a maximum deviation of $\pm$8% at 290°C and at the highest concentration.

One Application to Homogeneous Reactor Fuels

The pH's at 25° of solution mixtures saturated with uranium trioxide at the elevated temperatures are given in Table 2 and are shown in Fig. 7 as a series of isotherms. These isotherms indicate a reasonable minimum acidity which must be maintained at a particular concentration of sulfate in order to prevent hydrolytic precipitation of uranium trioxide. This relationship should

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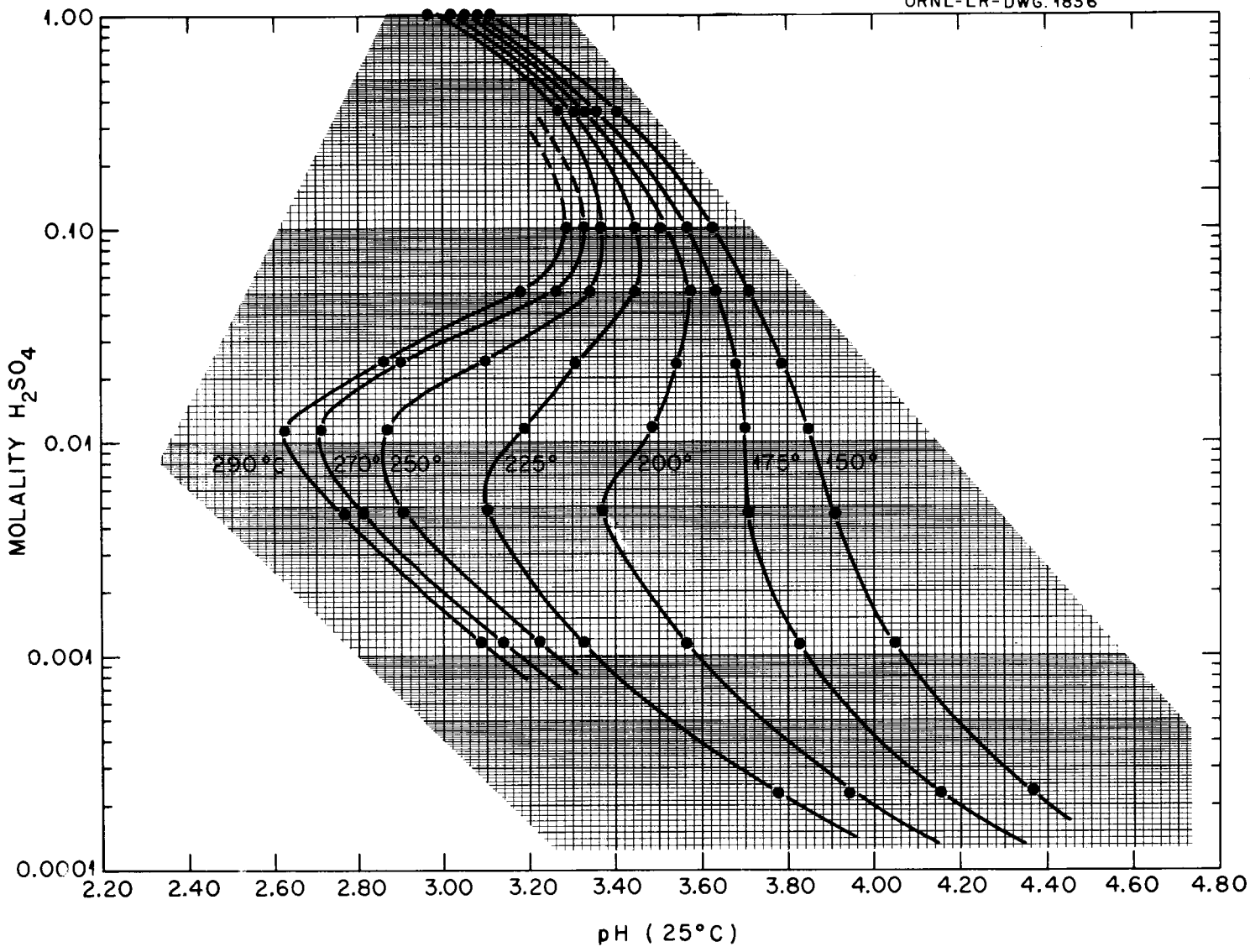

Fig. 7. The pH at 25°C of H_2SO_4-H_2O Solutions Saturated at Various Temperatures with UO_3.

approach ideality as the sulfate concentration approaches infinite dilution. The deviations expected at finite concentrations would be attributed to the changes in activity coefficients of the solutions components and to the extent of complexing with sulfate and/or uranyl ion by impurities and fission products. However, the data should indicate within several tenths of a pH unit the true 25° pH at which precipitation of UO_3 hydrate at the elevated temperature would occur.

Acknowledgement

It is a pleasure to acknowledge the able suggestions of R. W. Holmberg and K. A. Kraus on determination of pH using a vibrating reed electrometer and the reliable services of D. A. Weber in setting up the electronic parts of the pH apparatus. It also is a pleasure to acknowledge the help of D. M. Richardson in pressure testing the solubility bomb.