temperature. X-Ray analysis of the product from a typical calorimetric run showed that the solid consisted of 25% α-phase and 75% β-phase. Attempts to prepare the pure α-phase resulted in a product containing only 50% alpha even when the reaction chamber was maintained at −80°.

If there were an appreciable heat of transition between alpha and beta then the results reported here would differ from the heat of formation of the beta form by about 25% of the heat of transition. However, the recent work of Bigeleisen and Kant[9] on the exchange equilibria of HD with UH_3 indicates that the difference in the heat of formation of UH_3 and UD_3 is -641 ± 50 cal./mole, which is in excellent agreement with the measured value of -669 ± 45, from Table I. Since they made no attempt to dissipate the heat during the preparation of their hydride samples, their uranium hydride would be practically pure β-form. We conclude that the heat of transition of alpha to beta is small and that the heats reported here represent the heats of formation of beta UH_3 within the precision given.

Acknowledgment.—We wish to thank Dr. D. W. Osborne for assistance with the calorimetric techniques and Dr. Stanley Siegel for the X-ray analysis of our samples. We also wish to thank Dr. J. Bigeleisen for helpful discussions. This work was performed under the auspices of the U.S. Atomic Energy Commission.

LEMONT, ILLINOIS

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[9] J. Bigeleisen and A. Kant, THIS JOURNAL, **76**, 5957 (1954).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

The Solubility of Uranium Trioxide, $UO_3 \cdot H_2O$, in Solutions of Sodium Hydroxide and Perchloric Acid at 25°[1]

BY K. H. GAYER AND H. LEIDER

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The solubility of uranium trioxide has been studied in perchloric acid and in sodium hydroxide solutions at 25°. The oxide reacts predominantly as a basic oxide, the chief reaction being $UO_3 \cdot H_2O + 2H^+ = UO_2^{++} + 2H_2O$ in concentrated acid. K_6 for this reaction is 1.1×10^6, and $\Delta F^0 = -8100$ cal./mole. $K_{sp} = K_6 K_w^2 = 1.1 \times 10^{-22}$ for the reaction $UO_3 \cdot H_2O = UO_2^{++} + 2OH^-$. The presence in dilute solutions of polymerized ions is indicated.

The purpose of this investigation was to obtain information regarding the reactions of uranium trioxide with respect to acid and base, to determine the possible ionic species involved in such reactions, and to evaluate free energies and equilibrium constants for such reactions.

$UO_3 \cdot H_2O$ is treated here as amphoteric oxide, but the results of this work indicate that it reacts more as a base than as an acid.

Procedure

The general procedure is similar to that described by Garrett and Heiks.[2] An all-glass apparatus was used.

Water.—Conductivity water was prepared in a Barnstead conductivity still, degassed by boiling with nitrogen bubbling through it, and then stored under nitrogen.

Perchloric Acid Solutions.—Approximately one molar acid solutions were prepared from 70% G. F. Smith purified perchloric acid with degassed conductivity water, and then stored under nitrogen. Standard acid solutions were also prepared with conductivity water and standardized against standard sodium hydroxide solution.

Sodium Hydroxide Solutions.—Approximately one molar solutions of base were prepared under nitrogen by dissolving Baker and Adamson reagent pellets with degassed conductivity water in a paraffined flask. Barium hydroxide solution was added in amount just sufficient to precipitate any carbonate. The solutions were then stored under nitrogen. Standard base solutions were also prepared with conductivity water and standardized against potassium acid phthalate using phenolphthalein indicator.

Uranyl Acetate Solutions.—Baker and Adamson uranyl acetate reagent grade was dissolved in degassed conductivity water and stored under nitrogen.

Colorimetric Reagents.—A standard uranium solution was prepared by dissolving stoichiometric $UO_3 \cdot H_2O$ (prepared by hydrolysis of the uranyl acetate) in perchloric acid. Aliquot portions of this solution were used to prepare the color standards. A 10% sodium hydroxide solution was prepared from Baker and Adamson reagent pellets and distilled water. A 20% sodium carbonate solution was prepared with Baker and Adamson anhydrous reagent and distilled water. Baker and Adamson 30% hydrogen peroxide was used in preparing colorimetric solutions.

Uranium Trioxide.—Pure $UO_3 \cdot H_2O$ was prepared by hydrolysis of uranyl acetate solution by prolonged boiling, followed by fifteen to twenty 500-ml. washings with distilled water and five 500-ml. washings with conductivity water. A small amount of sodium chloride was then added to the precipitate, and the washing with conductivity water continued. A negative sodium flame test indicated complete washing. Weighed samples of $UO_3 \cdot H_2O$ prepared in the manner described and dried over drierite were ignited to U_3O_8, and the uranium content was found to be 78.2, 78.2 and 78.3%; calcd., 78.3%. Also, the solid phase from some acid samples was washed, dried and ignited. On drying over drierite for 24 hours, the uranium content was 77.5, 77.8 and 78.1%. The solid phase from basic samples contained associated sodium.[3]

Equilibration.—Pairs of 100-ml. samples of the oxide in acid or base were collected in 125-ml. florence flasks under nitrogen at each concentration. One of each pair was agitated in a 35° thermostat for at least seven days, and then allowed to settle in the 25° thermostat for three to five days before analysis. The other member of each pair was immediately agitated for at least seven days in the 25° thermostat and allowed to settle for three to five days.

Determination of *p*H ($-\log a_{H^+}$).—The flask necks were broken while enclosed in a rubber membrane and samples were taken using a Beckman 290-78 hypodermic type glass electrode. Measurements were made with a Beckman Model G meter which was calibrated at *p*H 4 with 0.05 *M* potassium acid phthalate buffer, at *p*H 7 with Beckman 3581 buffer, and at *p*H 10 with boric acid-sodium hydroxide buffer.

Uranium Analysis.—The uranium analysis was made with a Beckman Model B spectrophotometer using the

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[1] From a dissertation submitted by Mr. Herman Leider in partial fulfillment of the requirements for the Doctor of Philosophy degree at Wayne University.

[2] A. B. Garrett and R. E. Heiks, THIS JOURNAL, **63**, 562 (1941).

[3] C. A. Wamser, J. Belle, E. Bernsohn and B. Williamson, *ibid.*, **74** 1020 (1952).

TABLE I

SOLUBILITY OF $UO_3 \cdot H_2O$ IN NaOH SOLUTIONS AT 25°

Initial moles NaOH/1000 g. H_2O	Gram atoms uranium/1000 g. $\times 10^5$	$K_3 \times 10^4$	$K_4 \times 10^4$
0.0	3.95	...	...
.0045	4.75	105	...
.0076	6.22	82	...
.0090	3.95	44	...
.0199	7.90	40	...
.0203	4.45	22	...
.0390	7.09	18	...
.0453	6.30	14	..
.0777	10.0	13.0	102
.1114	4.20	3.8	19.5
.5545	19.7	3.6	3.0
.6093	9.5	1.6	1.2
.6106	13.1	2.2	1.6
.6816	13.5	2.0	1.4
.7668	14.7	1.9	1.2
		Av. K_3 = 2.5×10^{-4}	Av. K_4 = 1.7×10^{-4}

TABLE II

Solubility of $UO_3 \cdot H_2O$ IN $HClO_4$ SOLUTIONS AT 25°

Initial moles $HClO_4$/1000 g. H_2O[a]	Moles uranium/ 1000 g. H_2O
0	3.95×10^{-5}
2.02×10^{-2}	1.84×10^{-2}
4.06×10^{-2}	4.20×10^{-2}
1.01×10^{-1}	9.46×10^{-2}
1.42×10^{-1}	1.13×10^{-1}
2.02×10^{-1}	1.85×10^{-1}
4.06×10^{-1}	2.90×10^{-1}
6.08×10^{-1}	3.60×10^{-1}
8.12×10^{-1}	4.88×10^{-1}
10.1×10^{-1}	6.52×10^{-1}

[a] Calculated as UO_2^{++}.

TABLE III

SOLUBILITY OF $UO_3 \cdot H_2O$ IN $HClO_4$ SOLUTIONS AT 25°

a_{H^+}	Moles uranium/ 1000 g. H_2O[a]	$K_5 \times 10^{-2}$	$K_6 \times 10^{-6}$
6.02×10^{-6}	3.99×10^{-4}	0.7	11
6.31×10^{-6}	5.67×10^{-4}	0.9	14
6.45×10^{-6}	3.78×10^{-4}	0.6	9.1
8.91×10^{-6}	8.23×10^{-4}	0.9	10
9.77×10^{-6}	6.17×10^{-4}	0.6	6.6
1.17×10^{-5}	1.22×10^{-3}	1.0	8.9
1.20×10^{-5}	8.27×10^{-4}	0.7	5.7
1.35×10^{-5}	1.26×10^{-3}	0.9	6.9
1.55×10^{-5}	5.64×10^{-4}	0.4	2.4
1.59×10^{-5}	8.44×10^{-4}	0.5	3.3
1.74×10^{-5}	1.17×10^{-3}	0.7	3.9
2.09×10^{-5}	1.47×10^{-3}	0.7	3.4
2.14×10^{-5}	1.15×10^{-3}	0.5	2.5
3.24×10^{-5}	2.36×10^{-3}	0.7	2.2
4.17×10^{-5}	3.70×10^{-3}	0.9	2.0
4.27×10^{-5}	4.41×10^{-3}	1.0	2.4
5.37×10^{-5}	6.88×10^{-3}	1.3	2.1
5.50×10^{-5}	3.67×10^{-3}	0.7	1.1
6.31×10^{-6}	4.62×10^{-3}	0.7	1.2
6.31×10^{-5}	5.36×10^{-3}	0.9	1.1
6.61×10^{-5}	6.78×10^{-3}	1.0	1.4
7.41×10^{-5}	5.25×10^{-3}	0.7	0.9
7.59×10^{-5}	7.73×10^{-3}	1.0	1.2
7.76×10^{-5}	7.73×10^{-3}	1.0	1.1
8.91×10^{-5}	7.67×10^{-3}	0.9	0.9

[a] Calculated as UO_2^{++}.

$NaOH-Na_2CO_3-H_2O_2$ method to produce the color, as described in "Analytical Chemistry of the Manhattan Project."[4]

The Data

The data are presented in Tables I, II and III and are represented graphically in Fig. 1, which shows the change in solubility of $UO_3 \cdot H_2O$ in going from sodium hydroxide solutions to perchloric acid solutions. The acid solubility curve does not seem to indicate a simple stoichiometry. The uranium concentration shown in Table III, calculated as UO_2^{++}, shows discontinuity. This may be explained if the ions present over the *p*H range studied exist as various polymerized species in different concentration ranges. Above values of $a_{H^+} = 5.5 \times 10^{-5}$, it appears that the uranium ions are predominately UO_2^{+2}.

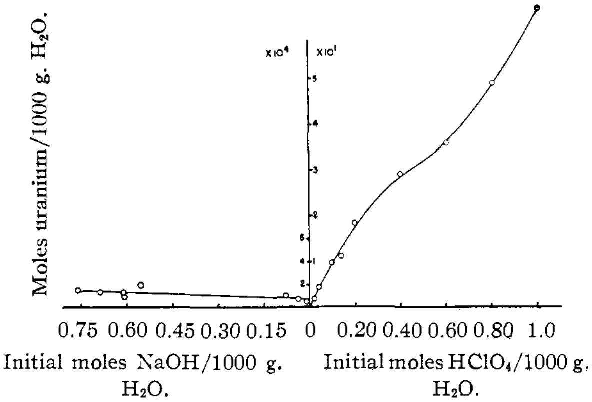

Fig. 1.—Solubility curve for $UO_3 \cdot H_2O$ at 25°.

The data in Tables II and III were obtained from different experiments. To facilitate obtaining data for construction of the solubility curve (Table II), samples of dried $UO_3 \cdot H_2O$ were put into a sample flask, aliquot portions of standard perchloric acid were added, and the final liquid volume was brought to a known value by addition of conductivity water. All other samples were prepared in the apparatus.

The constant for the reaction

$$H_2UO_4 \rightleftarrows UO_2^{++} + 2OH^-$$

is given by Latimer[5] as 2×10^{-23}. Our data give a value of 1.1×10^{-22} for the reaction

$$UO_3 \cdot H_2O \rightleftarrows UO_2^{++} + 2OH^-$$

By combining K_5 and K_6, the hydrolysis constant, K_h, for the reaction

$$UO_2^{++} + H_2O \rightleftarrows UO_2(OH)^+ + OH^-$$

can be calculated

$$K_h = \frac{K_5}{K_6} = 7.3 \times 10^{-5}$$

This value is in agreement with that reported by MacInnes and Longsworth as 6.0×10^{-5}.[6] However, they add that the hydrolysis process is not satisfactorily explained on the basis of this reaction.

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(4) C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 93.

(5) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 303.

(6) D. A. MacInnes and L. C. Longsworth, USAEC Report MDDC-911 (1943).

Sutton[7] has evaluated constants for the following hydrolysis reactions

$$2UO_2^{++} + H_2O \rightleftarrows U_2O_5^{++} + 2H^+ \quad K_I = 1.1 \times 10^{-6}$$

$$U_2O_5^{++}UO_2^{++} + H_2O \leftrightarrows U_3O_8^{++} + 2H^+ \quad K_{II} = 5 \times 10^{-9}$$

$$U_3O_8^{++} + H_2O \leftrightarrows U_3O_8(OH)^+ + H \quad K_{III} = 1 \times 10^{-12}$$

General Equilibria.—The possible equilibria of $UO_3 \cdot H_2O$ in acid, base and water solution may be represented by equations 1 to 8

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2^{++} + 2OH^- \qquad (1)$$

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2(OH)^+ + OH^- \qquad (2)$$

$$UO_3 \cdot H_2O(s) + OH^- \leftrightarrows HUO_4^- + H_2O \qquad (3)$$

$$UO_3 \cdot H_2O(s) + 2OH^- \leftrightarrows UO_4^{=} + 2H_2O \qquad (4)$$

$$UO_3 \cdot H_2O(s) + H^+ \leftrightarrows UO_2(OH)^+ + H_2O \qquad (5)$$

$$UO_3 \cdot H_2O(s) + 2H^+ \leftrightarrows UO_2^{++} + 2H_2O \qquad (6)$$

$$UO_3 \cdot H_2O(s) \leftrightarrows HUO_4^- + H^+ \qquad (7)$$

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_4^{=} + 2H^+ \qquad (8)$$

Apparently, the reaction $UO_3 \cdot H_2O(s) \leftrightarrows UO_3 \cdot H_2O(aq)$ is not important since the solubility curve extrapolates directly to the water solubility value.

Equilibria in Basic Solutions.—The values of K_3 and K_4 in Table I indicate that in solutions above 0.1 molar sodium hydroxide the important reactions of $UO_3 \cdot H_2O$ are (3) and (4) and that these reactions occur to the same order of magnitude. In the more dilute range of sodium hydroxide solutions, reactions appear to be complex. K_3 for the following reaction was calculated

$$UO_3 \cdot H_2O(s) + OH^- \leftrightarrows HUO_4^- + H_2O \qquad (3)$$

$$K_3 = \frac{M_{HUO_4} - \gamma_{HUO_4^-}}{M_{OH^-}\gamma_{OH^-}} = 2.5 \times 10^{-4}$$

$$\Delta F^0 = 4900 \text{ cal./mole}$$

and K_4 for the reaction

$$UO_3 \cdot H_2O(s) + 2OH^- \leftrightarrows UO_4^{=} + 2H_2O \qquad (4)$$

$$K_4 = \frac{M_{UO_4^=}\gamma_{UO_4^=}}{M^2_{OH^-}\gamma^2_{OH^-}} = \frac{M_{UO_4^=}}{M^2_{OH^-}}\gamma^2_{NaOH} = 1.7 \times 10^{-4}$$

$$\Delta F^0 = 2800 \text{ cal. mole}$$

It is assumed in these calculations that (1) $\gamma_{HUO_4^-}/\gamma_{OH^-} = 1$ and (2), $\gamma_{UO_4^=}/\gamma^2_{OH^-} = \gamma^3_{Na_2UO_4}/\gamma^4_{NaOH} = \gamma^6_{NaOH}/\gamma^4_{NaOH} = \gamma^2_{NaOH}$, from the Debye–Huckel theory. The values of γ_{NaOH} are given by Robinson and Stokes.[8]

Using K_3 and the ionization constant for water, K_w, K_7 for the following reaction was calculated

$$UO_3 \cdot H_2O(s) \rightleftarrows HUO_4^- + H^+ \qquad (7)$$

$$K_7 = K_3K_w = 2.5 \times 10^{-18}$$

$$\Delta F^0 = 24{,}000 \text{ cal./mole}$$

Likewise, K_8 for the reaction using K_4 and K_w

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_4^{=} + 2H^+ \qquad (8)$$

$$K_8 = K_4K_w^2 = 1.7 \times 10^{-32}$$

$$\Delta F^0 = 42{,}000 \text{ cal./mole}$$

Equilibrium in Acid Solutions.—The data in Table III indicate that the principal reaction of $UO_3 \cdot H_2O$ in acid solution is given by equation 6. The constancy of K_5 indicates that the monovalent ionic species is an unpolymerized form of the type $UO_2(OH)^+$. For the reactions

$$UO_3 \cdot H_2O(s) + 2H^+ \leftrightarrows UO_2^{++} + 2H_2O \qquad (6)$$

$$K_6 = \frac{M_{UO_2^{++}}\gamma_{UO_2^{++}}}{M^2_{H^+}\gamma^2_{H^+}} = 1.1 \times 10^6$$

$$\Delta F^0 = -8100 \text{ cal./mole}$$

The assumption was made that $\gamma_{UO_2^{++}} = \gamma^2_{H^+}$, where $\gamma^2_{H^+}$ was calculated from the Debye–Hückel equation.

For the reaction

$$UO_3 \cdot H_2O + H^+ \leftrightarrows UO_2(OH)^+ + H_2O \qquad (5)$$

$$K_5 = \frac{M_{UO_2(OH)^+}\gamma_{UO_2(OH)^+}}{M_{H^+}\gamma_{H^+}} = 0.8 \times 10^2$$

$$\Delta F^0 = -2600 \text{ cal./mole}$$

The assumption has been made that $\gamma_{UO_2(OH)^+}/\gamma_{H^+} = 1$.

Using K_5 and K_w, K_2 is evaluated for the reaction

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2(OH)^+ + OH^- \qquad (2)$$

$$K_2 = K_5K_w = 8 \times 10^{-13}$$

$$\Delta F^0 = 17{,}000 \text{ cal./mole}$$

Similarly, for the reaction

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2^{++} + 2OH^- \qquad (1)$$

$$K_1 = K_6K^2_w = 1.1 \times 10^{-22}$$

$$\Delta F^0 = 29{,}000 \text{ cal./mole}$$

Water Solubility.—It was possible to determine the water solubility of $UO_3 \cdot H_2O$ directly due to the dense crystalline form of the oxide. The values for the solubility from samples approaching equilibrium from above and below saturation coincided at 3.95×10^{-5} mole/liter.

Summary.—The solubility studies in $UO_3 \cdot H_2O$ indicate that it reacts as a basic material. The principal reaction in concentrated acid is: $UO_3 \cdot H_2O + 2H^+ \rightleftarrows UO_2^{++} + 2H_2O$. The constants and free energies for the possible equilibria are

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2^{++} + 2OH^- \qquad (1)$$

$$K_1 = K_6K_w^2 = 1.1 \times 10^{-22};\ \Delta F^0 = 29{,}000$$

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_2(OH)^+ + OH^- \qquad (2)$$

$$K_2 = K_5K_w = 8 \times 10^{-13};\ \Delta F^0 = 17{,}000$$

$$UO_3 \cdot H_2O(s) + OH^- \leftrightarrows HUO_4^- + H_2O \qquad (3)$$

$$K_3 = 2.5 \times 10^{-4};\ \Delta F^0 = 4900$$

$$UO_3 \cdot H_2O(s) + 20H^- \leftrightarrows UO_4^{=} + H_2O \qquad (4)$$

$$K_4 = 1.7 \times 10^{-4};\ \Delta F^0 = 5100$$

$$UO_3 \cdot H_2O(s) + H^+ \leftrightarrows UO_2(OH)^+ + H_2O \qquad (5)$$

$$K_5 = 0.8 \times 10^2;\ \Delta F^0 = -2600$$

$$UO_2 \cdot H_2O(s) + 2H^+ \leftrightarrows UO_2^{++} + 2H_2O \qquad (6)$$

$$K_6 = 1.1 \times 10^6;\ \Delta F^0 = -8100$$

$$UO_3 \cdot H_2O(s) \leftrightarrows HUO_4^- + H^+ \qquad (7)$$

$$K_7 = K_3K_w\, 2.5 \times 10^{-18};\ \Delta F^0 = 24{,}000$$

$$UO_3 \cdot H_2O(s) \leftrightarrows UO_4^{=} + 2H^+ \qquad (8)$$

$$K_8 = K_4K_w^2 = 1.7 \times 10^{-32};\ \Delta F^0 = 42{,}000$$

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DETROIT, MICHIGAN

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[7] J. Sutton, *J. Chem. Soc.*, S273 (1949).

[8] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).