

THE SOLUBILITY OF URANIUM(IV) HYDROXIDE IN SOLUTIONS OF SODIUM HYDROXIDE AND PERCHLORIC ACID AT 25° C.¹

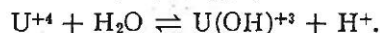
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ABSTRACT

The solubility of uranium(IV) hydroxide has been measured in sodium hydroxide, water, and perchloric acid solutions. A possible reaction in sodium hydroxide solutions is evaluated.

The purpose of this investigation was to measure the solubility of uranium(IV) hydroxide in dilute basic and dilute acidic media. Information pertaining to this subject is not available at this time in the literature except for the following:

Kraus and Nelson (3) investigated the hydrolytic behavior of uranium(IV) ions in excess perchloric acid (above 0.2 *M*) and in solutions of constant ionic strength ($\mu = 0.5$). They concluded that the simple ion U^{+4} exists in excess acid and is associated with eight water molecules, $U(H_2O)_8^{+4}$, and that the principal hydrolysis reaction is



$$pK = 1.44$$

where $pK = -\log [IV]_1$, and $[IV]_1 = [UOH^{+3}][H^+]/[U^{+4}]$.

Their results did not indicate an ion type such as UO^{++} .

They also found that uranium(IV) ions show a tendency to form rather stable polymeric solutions on hydrolysis, where the polymeric form has an approximate composition of $U(OH)_4$. When uranium(IV) hydroxide is dissolved in a non-complexing acid, such as perchloric, solutions containing polymeric products result. The difference in color between the simple solution and the polymeric form is very marked, being bright green for the former and almost black for the latter.

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 being boiled with nitrogen bubbling through it, and then stored under nitrogen.

Perchloric acid solutions.—Approximately 1 molar acid was prepared from 70% G. F. Smith purified perchloric acid with degassed conductivity water and stored under nitrogen. Standard acid solutions were also made with conductivity water and standardized against standard sodium hydroxide.

Sodium hydroxide solutions.—Approximately 1 molar solutions of base were prepared under nitrogen by dissolving Baker and Adamson reagent pellets in degassed conductivity water in a paraffined flask. Barium hydroxide was added to just precipitate any carbonate, and the solutions were stored under nitrogen. Standard base solutions were also prepared with conductivity water and standardized against potassium acid phthalate using phenolphthalein indicator.

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Uranium(IV) sulphate.—Crystalline uranium(IV) sulphate was prepared by the reduction of acid solutions of uranyl sulphate with Eastman Kodak sodium dithionite (1). The precipitated sulphur was filtered off and uranium(IV) hydroxide was precipitated with excess sodium hydroxide. The product was washed with distilled water until the absence of a sodium flame test, and then dissolved in Baker and Adamson A. C. S. standard sulphuric acid, and filtered. The sulphate solution was evaporated until crystals of $U(SO_4)_2 \cdot 4H_2O$ deposited. The crystals were filtered, dried, analyzed for uranium by 8-hydroxyquinoline precipitation, and ignited to U_3O_8 . Calculated % uranium is 47.4; found % uranium equals 47.6. Solutions of the sulphate were made by dissolving the crystals in degassed conductivity water and then stored under nitrogen.

Colorimetric reagents.—A standard uranium solution was prepared by dissolving stoichiometric $UO_3 \cdot H_2O$ (prepared from hydrolysis of uranyl acetate by boiling) 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(IV) hydroxide.—The hydroxide used in making samples for the acid series was precipitated from the sulphate solution with sodium hydroxide and washed with degassed conductivity water. Absence of a sodium flame test indicated completed washing.

Uranium(IV) hydroxide used in preparing basic samples was made by reacting sodium hydroxide with crystalline $U(SO_4)_2 \cdot 4H_2O$. In all other respects the treatment was the same as that just described. Such a preparation was necessary because the gelatinous hydroxide precipitated from solution was extremely sensitive to oxidation in alkaline medium. The dense hydroxide prepared from crystalline sulphate proved much more stable to oxidation and could be handled more easily. In order to eliminate any possibility of oxidation the system was kept under a nitrogen pressure of 4 to 5 lb. above that of the atmosphere.

Analysis showed that the solid phase was unchanged after equilibration with acid or base.

Equilibration.—Pairs of 100 ml. samples of the hydroxide in acid or base were collected in 125 ml. sample flasks under nitrogen. One of each pair was agitated in a 35° thermostat for 5 to 7 days, followed by agitation in a 25° thermostat for 5 to 7 days. The other member of each pair was directly agitated in the 25° thermostat for 5 to 7 days. After the agitation in the 25° C. thermostat, the samples were allowed to settle for 3 to 5 days.

Uranium analyses.—The uranium analyses was made with a Beckman Model B spectrophotometer using the $NaOH-Na_2CO_3-H_2O_2$ method described in *Analytical Chemistry of the Manhattan Project* (4).

THE DATA

The data are collected in Tables I and II. Owing to the polymeric nature of the acid solubility products no definite reactions or ionic species can be evaluated and proved to occur.

Assuming that the formula for solid uranium(IV) hydroxide can be represented by

TABLE I
SOLUBILITY OF URANIUM(IV) HYDROXIDE IN HClO₄ SOLUTIONS AT 25° C.*

Initial moles HClO ₄ / 1000 g. H ₂ O	Moles uranium/1000 g. H ₂ O at equilibrium
3.9 × 10 ⁻²	2.2 × 10 ⁻²
9.6	5.7
1.4 × 10 ⁻¹	6.7
1.9	9.5
2.9	1.5 × 10 ⁻¹
3.9	2.1

*Each set of values is actually the average of two experiments which agreed within 10% or less.

TABLE II
SOLUBILITY OF URANIUM(IV) HYDROXIDE IN NaOH SOLUTIONS AT 25° C.*

Moles NaOH/1000 g. H ₂ O at equilibrium	Moles uranium/1000 g. H ₂ O at equilibrium	K × 10 ⁴
0	3.0 × 10 ⁻⁶	—
0.080	6.3 × 10 ⁻⁶	—
0.144	2.7 × 10 ⁻⁵	1.9
0.215	4.1	1.9
0.266	4.5	1.7
0.484	7.0	1.4
0.632	5.9	—
		Average K = 1.7 × 10 ⁻⁴

*Each set of values is actually the average of two experiments which agreed within 10% or less.

U(OH)₄, we believe that the reaction in basic solution over the range studied (0.1 molal to 0.5 molal) can be written as follows:



Evidence for this reaction comes from (1) the fair constancy of the equilibrium constant, (2) the extremely low solubility of the oxide, and (3) the high equilibrium sodium hydroxide concentrations.

In calculating the equilibrium constant it was assumed

(1) that

$$\gamma_{\text{H}_3\text{UO}_4^-} / \gamma_{\text{OH}^-} = 1,$$

(2) that the dissolved uranium all occurred as H₃UO₄⁻. This latter assumption is not improbable since the solubility is very low.

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REFERENCES

1. ALOY AUBER, J. Bull. soc. chim. France, 1 (4), 569 (1907).
2. GARRETT, A. B. and HEIKS, R. E. J. Am. Chem. Soc. 63, 562 (1941).
3. KRAUS, K. A. and NELSON, F. AECD-1888, March 15, 1948 (date declassified).
4. RODDEN, C. J. Analytical chemistry of the Manhattan project, McGraw-Hill Book Company, Inc., New York, 1950. p. 93.