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DISSOLUTION OF URANIUM TETRAFLUORIDE

Five new dissolution processes for uranium tetrafluoride are discussed - the $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$ method, the $\text{H}_2\text{SO}_4 - (\text{NH}_4)_2\text{S}_2\text{O}_8$ method, the AlCl_3 method, the NaAlCl_4 method, and the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ method. It is concluded that NaAlCl_4 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are preferable to the other agents, especially with regard to rate of dissolution and ease of manipulation.

V. F. Calkins

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DISSOLUTION OF URANIUM TETRAFLUORIDE

By V. P. Calkins

Considerable interest has always been attached to the development of a simple and rapid method for the dissolution of uranium tetrafluoride. Like calcium fluoride and other difficultly soluble inorganic fluorides, uranium tetrafluoride resists ordinary dissolution reagents such as nitric and hydrochloric acids. The tetrafluoride is soluble in ferric chloride solution and in concentrated phosphoric acid, but these substances are serious contaminants in themselves. Although the tetrafluoride is soluble in ammonium oxalate, this method involves large volumes of solution. Again, the tetrafluoride can be burned cautiously to the more soluble U_3O_8 , but in this case there is danger of losing uranium by the vaporization of uranyl fluoride and uranium hexafluoride, formed by the disproportionation of the tetrafluoride in the presence of oxygen; this is especially true when samples larger than analytical size are ignited to the oxide.

However, none of these methods proved too satisfactory and certainly none of them could be classified as a simple and rapid dissolution process for uranium tetrafluoride. Upon this basis five new dissolution processes for the tetrafluoride were developed -- the $NH_4OH-H_2O_2$ method⁽¹⁾, the $H_2SO_4-(NH_4)_2S_2O_8$ method⁽¹⁾, the $AlCl_3$ method^(2,3,4), the $NaAlCl_4$ method^(2,3,4), and the $Al(NO_3)_3 \cdot 9H_2O$ method^(2,5).

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DISCUSSION

Since uranium tetrafluoride is itself difficultly soluble in most solvents, the general theory involving a successful dissolution process for this material is based upon the reaction of the tetrafluoride with some substance or substances to form a reaction product which is readily soluble in ordinary solvents. The dissolution processes described below serve to illustrate this point.

NH₄OH-H₂O₂ Method⁽¹⁾

The ammonium hydroxide-hydrogen peroxide dissolution method is based on the oxidation of the tetrafluoride by the peroxide with the subsequent formation of ammonium diuranate, the latter being readily dissolved.

This method consists of placing finely ground uranium tetrafluoride in 1:1 ammonium hydroxide solution, 30 percent hydrogen peroxide (aqueous solution) being added dropwise to the solution at such a rate that the exothermic reaction just maintains the solution at the boiling point. During the addition the flask is covered due to a slight amount of spraying. Additional ammonia and peroxide are usually added after the initial reaction subsides, and the solution is boiled about one hour to effect more complete solution after which the solution is acidified cautiously with concentrated nitric acid and boiled at least another hour to destroy peroxide. A hundred-gram portion of the tetrafluoride requires approximately 100 ml of 1:1 ammonium hydroxide, 75 ml of 30 percent hydrogen peroxide and 300 ml of nitric acid, the time for

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dissolution of the 100-gram batch being between 3 to 4 hours. Typical results obtained with this method and with other dissolution processes are recorded in Table 1 for ready comparison of the merits of the various methods employed.

H₂SO₄-(NH₄)₂S₂O₈ Method⁽¹⁾

The chemistry of the concentrated sulfuric acid-ammonium persulfate method does not seem to be fully understood though it appears likely that a water soluble complex such as UF₂SO₄ or H₂U(SO₄)₂F₂ may be formed⁽¹⁾.

This method consists of digesting the tetrafluoride (100 gm) with approximately 300 ml of concentrated sulfuric acid for at least 15 minutes after the appearance of dense fumes of SO₃. After the solution is cooled and cautiously diluted with 2.5 liters of water and boiled for 1/2 hour, several 5-gm portions of ammonium persulfate are added cautiously to oxidize the uranium to the hexavalent state. Excess SO₂ is then removed by boiling for 15 minutes. After the cooled solution is treated with ammonium hydroxide and filtered to remove fluoride, the uranium is brought into solution by dissolving the cake off the filter with nitric acid. The time involved in the use of this method for the same weight of residue is approximately the same as for the NH₄OH-H₂O₂ method, that is from three to four hours.

AlCl₃ Method^(2,3,4)

The use of aluminum chloride was based entirely upon theoretical considerations of the molecular structure of the compound⁽²⁾. From its various properties, aluminum chloride appears to be capable of

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acting as either a polar or non-polar substance, its action probably depending upon the circumstances involved, that is, in any one case with any single substance its action is apparently definitive. Furthermore AlCl_3 appears to exist in a monomer and dimer form in equilibrium with each other. Uranium tetrafluoride can react with the monomeric chloride, perhaps by having one of its fluorine atoms share two of its electrons with the aluminum atom. This linkage permits monomeric AlCl_3 to achieve an octet form, and after successive complexation in this manner, metathesis occurs, uranium tetrachloride being formed. The uranium can then be easily solubilized by dissolution of the resulting tetrachloride in a slightly acidified aqueous solution.

With this method approximately 15 to 40 grams of anhydrous AlCl_3 and 1 to 27 grams of UF_4 are placed in a 50 ml Carius tube, the tube then being chilled while the system is being evacuated. After the tube is sealed off and allowed to come to room temperature, it is heated in an oil bath to 215° to 230°C until the AlCl_3 melts. The tube is then broken and the melt is dissolved in water, the resulting solution being acidified slightly to dissolve the uranous hydroxide. As a consequence of these various experiments it was established that the molar reaction ratio of AlCl_3 to UF_4 is approximately 2-3 to 1. The values recorded for AlCl_3 and UF_4 in Table 1 are based upon this ratio.

NaAlCl_4 Method^(2,3,4)

The theory underlying the NaAlCl_4 dissolution method is essentially the same as that just described for AlCl_3 . However, since AlCl_3 sublimes

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at atmospheric pressure, it is necessary to use a bomb container in order to melt the chloride. This apparent disadvantage can be circumvented by heating a 1:1 molar ratio of NaCl and anhydrous AlCl_3 , the resulting NaAlCl_4 compound having a liquid range from approximately 180° to over 600°C .

The usual procedure for these experiments consists of mixing 66.5 grams of anhydrous AlCl_3 with 29 grams of NaCl and melting the mixture. To this mixture 10 to 20 grams excess of AlCl_3 are added to offset the gradual loss of AlCl_3 as the molten liquid is heated to high temperatures. While the mixture is maintained at approximately 250° to 300°C , 25 grams of test material are added, and within 5 to 15 minutes after the addition of the test material, the molten mass is poured gradually into a cold pot of water, the solution then being made slightly acid. Under these conditions it is found that not only does UF_4 dissolve rapidly but UO_2 , UO_3 and U_3O_8 can also be brought into solution very readily.

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Method ^(2,5)

In an ionic medium such as molten $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or an approximately saturated aqueous solution of the nitrate, the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ decomposes to form nitric acid which tends to oxidize the UF_4 to UO_2F_2 . Although the oxidation of UF_4 by nitric acid is ordinarily a very time-consuming reaction, the $\text{Al}(\text{H}_2\text{O})_6^{+++}$ probably present could react with the fluoride ion of the UO_2F_2 , thus shifting the equilibrium of the nitric acid-tetrafluoride reaction to the right and hence to completion.

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Table 1

Comparison of Dissolution Methods for UF₄

<u>UF₄</u> <u>g</u>	<u>Method</u>	<u>Reference</u>	<u>Solvents Used</u>	<u>Solution Time</u>	<u>Remarks</u>
100	NH ₄ OH-H ₂ O ₂	(1)	100 ml of 1:1 NH ₄ OH 75 ml of 30% H ₂ O ₂ 300 ml of conc. HNO ₃	3 to 4 hr.	Reaction requires careful regulation. Very time consuming.
100	H ₂ SO ₄ -(NH ₄) ₂ S ₂ O ₈	(1)	300 ml of 36N H ₂ SO ₄	3 to 4 hr.	Same as for above method.
100	AlCl ₃	(3)	100 grams AlCl ₃	15 min.	Bomb container needed.
100	NaAlCl ₄	(3)	100 grams AlCl ₃ 44 grams NaCl	15 min.	Smooth reaction. Very rapid.
200	Al(NO ₃) ₃ ·9H ₂ O	(5)	600 grams Al(NO ₃) ₃ ·9H ₂ O 500 ml H ₂ O	1 to 2 hr.	Ingress of UF ₄ must be controlled.

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In using this method the tetrafluoride is added to an approximately saturated aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the mixture heated. After a short warming period the mixture begins to bubble vigorously, copious fumes of nitrogen oxides being evolved. With this method, 200 grams of uranium tetrafluoride dissolve within 1 to 2 hours in a solution of 600 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500 ml of water. However, a shorter dissolution time is obtained when the tetrafluoride is added fairly gradually to a boiling solution of the nitrate. Similar results are obtained when a molten solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is used.

EXPERIMENTAL

The results recorded in Table 1 were obtained by using the individual dissolution methods for uranium tetrafluoride as already described. The numbers tabulated in the reference column refer to the individual reports from which the corresponding dissolution values for that particular method were taken. However, the values recorded for the $\text{AlCl}_3\text{-UF}_4$ and the $\text{NaAlCl}_4\text{-UF}_4$ systems are based upon a molar reaction ratio of AlCl_3 to UF_4 of approximately 2-3 to 1.

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SUMMARY

Of the various dissolution mediums for solubilizing uranium tetrafluoride, both NaAlCl_4 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ seem to be far more preferable than the other agents especially in regard to rate of dissolution and ease of manipulation. However, whereas the tetrafluoride is rendered soluble practically immediately upon reaction with molten NaAlCl_4 , dissolution of the tetrafluoride in either molten or aqueous $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ requires a relatively long period of time. The NaAlCl_4 method is based upon the conversion of insoluble UF_4 to soluble UCl_4 and the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ process is based upon the conversion of the insoluble tetrafluoride to the soluble uranyl fluoride.

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