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FACTORS AFFECTING THE PRECIPITATION OF URANIUM PEROXIDE

ABSTRACT

This is a compilation of the data on uranium peroxide precipitations appearing in several reports. The solubility product is measured. The effect of many individual ions on the hydrogen peroxide decomposition rate and the complexing of uranium is demonstrated. Studies on plant and other highly contaminated solutions are not included.

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FACTORS AFFECTING THE PRECIPITATION OF URANIUM PEROXIDE

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(Authorship does not imply responsibility for the ideas or experimental data reported. For the source material consult the bibliography which appears at the end of the paper.)

INTRODUCTION

One of the most specific and useful reactions of uranium is the precipitation of uranium peroxide from acidic uranyl solutions by the addition of hydrogen peroxide. Under proper conditions this reaction is quantitative, and only a few of the less common elements are also precipitated. Thorium, zirconium, hafnium, and probably actinium and protoactinium are among those precipitated from acid solutions by hydrogen peroxide. Antimony, if present in high concentrations, is partially brought down, and the rare earths cause difficulty unless the pH is 1.0 or less.

Pure uranium peroxide, $\text{UO}_4 \cdot x\text{H}_2\text{O}$ is a light yellow crystalline solid with a density, when air dried, of about 2.5. At low temperatures it is surprisingly stable, but at 140°C it is decomposed to the trioxide. If precipitated under the proper conditions it can be separated from the solution phase using standard filtering or centrifuging equipment.

Although it has become fairly common practice to use the formula $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ the dihydrate appears to exist only when the compound is dried under special conditions. When air dried at room temperature the actual state of hydration is more than two water molecules per UO_4 . The use of the simple formula, UO_4 , in future discussion appears most practical.

The chief difficulties encountered in the precipitation of uranium peroxide are usually not due to the formation of other peroxide precipitates, but instead result from the fact that many electrolytes inhibit

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the uranium reaction. In the work described here the effects of the more important inhibitors were considered together with the other factors which are critical in determining the success of the precipitation.

In discussing the factors which influence the uranium peroxide precipitation it is important to distinguish between effects on the rate of precipitation and effects on the equilibrium state of the system. Any procedure or substance which prevents the reaction from becoming quantitative within a short time greatly limits its utility even if the equilibrium solubility remains unaffected. Since it often requires days or weeks to reach equilibrium, the rate of precipitation, particularly during the first hour or two, is the main consideration. However, in some of the experiments the precipitating systems were studied until the attainment of equilibrium, because this additional data is of help in understanding the phenomena which determine the initial precipitation rate.

DISCUSSION

Types of Interference

The reaction between uranyl ion and hydrogen peroxide can be represented formally by the equation:

Any uranium originally present in the plus 4 valence state will be oxidized to uranyl ion and also precipitated. Since hydrogen peroxide is consumed and hydrogen ion is liberated in the formation of uranium peroxide, completeness of precipitation is governed primarily by control of H_2O_2 and H^+ concentration. The range of H_2O_2 and H^+ concentrations over which the reaction is quantitative is greatly affected by many substances. On the basis of present knowledge one may say that the region of quantitative

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precipitation is probably larger for precipitations from pure uranyl nitrate solutions than for any other system.

Relative to the uranyl nitrate system then, one may speak of the interference of some other ion or ions as evidenced by a decrease in the $H_2O_2 - H^+$ region of quantitative precipitation. This point may be made in a slightly different way: At any given concentration of H_2O_2 and H^+ the reaction will be slower, or less quantitative, or both, in the presence of an interfering ion than in a pure system.

The interfering substances may be conveniently divided into three classes:

1. Anions which form weak salts or complex ions with uranyl ion. For example, sulfate, fluoride, oxalate, and many others.
2. (a) Substances, usually heavy metal cations, which catalytically decompose hydrogen peroxide. For example, ferric, cupric, and bromide ions.
(b) Substances which react with hydrogen peroxide.
3. Cations which do not decompose hydrogen peroxide but inhibit the precipitation, presumably due to the formation of soluble peruranates.

It is seen that the variety of interfering substances is large and that many of them are common. Therefore, the successful precipitation of uranium peroxide is, in general, a difficult operation requiring a thorough knowledge of the interfering substances and the means by which their effects can be minimized. Before discussing these interference effects in detail it is well to mention briefly some of the more important points regarding precipitation from pure uranyl nitrate systems.

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Pure Uranyl Nitrate Solutions

Maintenance of pH.--The precipitations of uranium peroxide, described in detail in the experimental section, were made from solutions over a wide pH range, and the starting pH was maintained constant during the precipitation by gradually adding ammonium hydroxide along with the hydrogen peroxide. With a pure uranyl nitrate solution either nitric acid or ammonium hydroxide is used to obtain the initial adjustment of the solution to the desired pH. While the uranium is precipitated by the hydrogen peroxide and the pH stabilized by the addition of ammonium hydroxide, a solution of ammonium nitrate is formed. Due to the unavoidable presence of high concentrations of ammonium and nitrate ions, precipitations from pure uranyl nitrate solutions, although exceedingly quantitative, were not used in computing the equilibrium constant for the reaction. The equilibrium state was approached from the opposite direction.

(2)

Equilibrium Constant.--The equilibrium constant for the reaction between uranyl ion and hydrogen peroxide may be expressed as:

$$K = \frac{(H^+)^2}{(UO_2^{++})(H_2O_2)} \quad 2$$

The data of Table 1 in the Experimental section gives an average value of 6.7×10^2 for K at 25-27°C. This figure was determined from "solid plus solution" experiments in which solid uranium peroxide was added to solutions of various HNO_3 and H_2O_2 concentrations which were then allowed to stand with occasional stirring until the attainment of equilibrium. The calculations were based on analytical values of U and H_2O_2 in solution and H^+ concentration as determined by a pH meter. In experiments 1A, 2A, and 3A no hydrogen peroxide was added to the solutions, so all the hydrogen peroxide present at equilibrium was formed from the dissolving uranium peroxide.

In Table 2 are several typical experiments showing the approach of solubility equilibrium from both sides. Although precipitation experiments

were not used in calculating K it can be seen from Table 2 that the effect of NH_4NO_3 on the value of K is very small.

The Solution pH.--The precipitation is quantitative over the pH range 1.0-3.5 even if the slurry is filtered with only a half hour of standing, provided that a fair excess of hydrogen peroxide is present. Over this range, as expected from Equation 2, the reaction is more quantitative with increasing pH. Due to the addition of ammonium hydroxide during the precipitation considerable uranium is held in solution as an ammonium peruranate complex when the pH is higher than 3.5.

(3)
Hydrogen Peroxide Concentration.--Ordinarily sufficient hydrogen peroxide is added to give an excess of about 0.3-0.5 M after the stoichiometric amount has been consumed. There is little point in adding more than this unless agents which decompose hydrogen peroxide are present. Once uranium peroxide has precipitated quantitatively at pH 2.0, a H_2O_2 concentration of 0.002 M is sufficient to prevent any significant dissolution. The much greater excess is used in practice simply to increase the reaction rate.

Original Uranium Concentration.--With solutions containing greater than 1% uranium the rate of precipitation shows little variation with U concentration. However, if the solution is less than 1% a serious delay is exhibited. Typical data over a range of concentrations are shown in Table 3. (2) Because of the heterogeneous nature of the system the results are only moderately reproducible. At pH = 1.0, H_2O_2 = .05 M, and uranium concentrations between 1 and 0.02%, the concentration of uranium, in the solution phase at any given time within the first 24 hours increases with increasing dilution. Although in a single experiment in Table 3 the delay (4) was not overcome by seeding, there is considerable evidence that rapid stirring of the slurries increases the precipitation rate, indicating that the

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delay is due to slow crystal growth.

Interfering Substances

Since ammonium and nitrate ions exert so little influence on the uranium peroxide precipitate, ammonium salts were used in studying anion effects and nitrate salts in the study of cation effects. For the same reason, uranyl ion was introduced as the nitrate, and nitric acid and ammonium hydroxide were used for pH adjustment.

The behaviour of the uranium peroxide reaction in the presence of added electrolytes can, in general, be adequately explained by examining the chemical relationships between the ions in the system. For example, ammonium sulfate seriously inhibits the precipitation because of the strong association between sulfate and uranyl ions. Magnesium sulfate, on the other hand, causes little trouble due to the fact that it is a very weak salt, capable of yielding only a small effective concentration of sulfate ion.

Interfering Anions.---The magnitude of the interference exhibited by any anion is dependent upon the weakness of the salt and the stability of the complexes which it forms with uranyl ion. An excellent way of overcoming the effect of an anion is to add a cation which is capable of complexing it even more strongly than uranyl ion. The sulfate effect, as noted above, is lessened by the presence of magnesium ion, and fluoride is rendered almost harmless by the addition of an equi-molar amount of aluminum nitrate.

An exact comparison of the "inhibiting strengths" of the anions for which data are available is difficult because of the different experimental situations in which they have been studied. However, they may be roughly classified in the following order of increasing strength (based on equal molar concentrations of the anion): nitrate, acetate, chloride, malonate, sulfate, and fluoride.

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(2.5)

Nitrate.--Moderate amounts of nitrate do not effect the precipitation. High concentrations of NH_4NO_3 delay the reaction somewhat but do not greatly influence the equilibrium solubility, see Table 2.

(5.6)

Acetate.--Acetate has only a minor effect on the precipitation. Concentrations up to 2.0 M of NH_4Ac do not significantly raise the equilibrium solubility at pH 2.0. Concentrations between 0.5 and 2.0 M delay the reaction slightly.

(6)

Chlorides.--Chloride ion is a much more serious offender. At pH 2.0, 1 M NH_4Cl causes significant delay; 2.0 M chloride makes the reaction altogether unquantitative even after standing 24 hours. Data for several typical experiments are shown in Table 4.

(4.7)

Malonate.--Because of the use of malonic acid in one method to be discussed for controlling hydrogen peroxide decomposition, it is important to know what effect, if any, it has on the precipitation. At a pH of 1.5, uranium peroxide can be precipitated quantitatively from solutions containing less malonic acid than approximately 0.7 moles per liter. However, at higher pH (2.5 and 3.0) serious delay is encountered at malonic acid concentrations of about 0.2M, unless the malonic acid is consumed by complexing impurities such as iron. It has not been established whether malonic acid significantly increases the equilibrium solubility. Polarographic measurements have indicated that uranyl malonate is a weak electrolyte, and since malonic acid is a weak dibasic acid it is reasonable that the uranium remaining in solution should increase with pH, at least over some pH range.

Sulfate.--When sulfate ion is present in the precipitating system there are three observable effects: (1) the precipitation is delayed, (2) the equilibrium UO_4 solubility is raised, and (3) the physical properties of the precipitate (such as filterability and sedimentation rate) are improved. So great is the improvement in filtration rate that

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it is often desirable to add a small amount of sulfate to save time, but the success of this technique depends in part upon the extent to which sulfate renders the precipitation incomplete.

Since the rate of and completeness of precipitation vary greatly with relatively small variations in sulfate concentration, it is important to know under what conditions the formation of uranium peroxide is quantitative. This point is well illustrated by the experiments in Table 5. (8) It is seen that the "sulfate effect" is a major one; for this reason it has been investigated over a fairly wide range of sulfate (0.05 to 2.0 M), hydrogen ion (pH 1.0 to 3.0), and hydrogen peroxide (0.1 to 1.0 M) concentrations. Precipitations from solutions containing less than 1% uranium were not studied since the delay in precipitation due to the low concentration would have been added to that caused by the sulfate.

In order to approach equilibrium from both sides the solubility of uranium peroxide was investigated as a function of time by using both the "solid plus solution" and precipitation experiments. Observations on both types of experiments were made over a long enough period of time so that equilibrium was reached in most cases. At each of five pH values, 1.0, 1.5, 2.0, 2.5, and 3.0, ten precipitation and ten solid plus solution (8) experiments were carried out according to the following pattern:

a. Variation of Sulfate

Exp.	NH_4NO_3 added ³ M	H_2O_2 M	$(\text{NH}_4)_2\text{SO}_4$ M
1	0	0.1	0.05
2	0	0.1	0.1
3	0	0.1	0.2
4	0	0.1	0.5
5	0	0.1	1.0
6	0	0.1	2.0

b. Addition of NH_4NO_3

Exp.	$\frac{\text{NH}_4\text{NO}_3}{\text{added}}$ M	$\frac{\text{H}_2\text{O}_2}{\text{M}}$	$\frac{(\text{NH}_4)_2\text{SO}_4}{\text{M}}$
7	1.0	0.1	0.2

c. Variation of Sulfate and H_2O_2

8	0.0	0.5	0.2
9	0.0	1.0	0.2
10	0.0	1.0	1.0

Although solid NH_4NO_3 was added in only one experiment of each series, some NH_4NO_3 was present in each of the precipitation experiments due to neutralization of the $\text{UO}_2(\text{NO}_3)_2$ solution used as a source of uranium. However, the effects of such concentrations is negligible compared to that of sulfate.

Each analysis for uranium in solution was accompanied by a determination of H_2O_2 and H^+ concentration at the same time. This was necessary since H_2O_2 solutions, especially if high in nitrate and sulfate, are not very stable, and since H^+ is liberated in the slow precipitation of uranium peroxide. Sulfate was determined once or twice during the course of each experiment. No attempt was made to thermostat the mixtures, but room temperature did not vary more than a few degrees during the period of the investigation. Each slurry was stirred occasionally by hand. In the precipitation experiments NH_4OH was added at frequent intervals to bring the H^+ concentration back to its original value. In the solid plus solution experiment this was unnecessary since there was no significant pH change as the UO_4 dissolved in the solutions.

A number of analyses were performed on UO_4 obtained from 2 M sulfate solutions to determine whether or not sulfate was an important constituent of the solid phase. The highest percentage of sulfate found

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on the dry cakes was about 0.5.

A few observations made during the precipitation experiments are of interest. When equivalent H_2O_2 is added to a solution high in U and sulfate the color of the solution becomes deep orange and in some cases nearly red. By choosing a sufficiently high concentration of sulfate, no precipitate will appear for a considerable time after adding the H_2O_2 , but the pH will nevertheless decrease in some cases. Thus when equivalent H_2O_2 was added to a solution the pH dropped from 1.5 to 0.9 and no visible precipitate formed for 15 minutes. On standing the UO_4 precipitates and solutions gradually revert to the yellow color of U^{+6} salts. It is interesting to note that a similar red color and slowness of precipitation can also be observed in solutions concentrated in U and NH_4NO_3 (e.g. 10% U and 10 M NH_4NO_3). Unfortunately, these phenomena have not been studied in any detail.

(8)

Sulfate-Treatment of Experimental Results.---The data obtained from the pH 1.0 experiments are presented in Tables 6 and 7. For brevity, data at the other pH values, which were recorded in exactly the same manner, are not included. By looking at the original tables it is very difficult to get a good overall picture of the sulfate interference or to study the magnitude of the interferences as a function of the variables (i.e. sulfate concentration, pH, H_2O_2 concentration, and time). In the original paper the treatment below was undertaken to facilitate interpretation of the data, and also to put the data in a form more convenient for quick reference.

Inspection of the results in Tables 6 and 7, and of data obtained at the other pH values, shows that in general there was significant

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decomposition of hydrogen peroxide over the long periods studied and that the rate of decomposition varied considerably between experiments (increasing with increase in pH, nitrate, and sulfate concentration). This not only makes it difficult to judge whether or not a precipitated system has reached equilibrium, but also to tell if the equilibrium concentration of uranium is the same as that obtained from the corresponding solid plus solution experiment. Fortunately this difficulty in interpretation was resolved quite simply. If it is assumed that the equilibrium solubility of uranium peroxide in sulfate solutions varies inversely with H_2O_2 concentration, then reasonable agreement between the product of $(H_2O_2)(U)$ exists at equilibrium in solutions which have the same concentrations of SO_4^{2-} and H^+ but not necessarily the same H_2O_2 concentration.

This assumption was utilized to determine the approach to equilibrium as follows. The quantity called p was calculated for each time of measurement in each experiment where

$$p = (H_2O_2)(U).$$

The concentrations (H_2O_2) and (U) were expressed in moles/l and mg/l respectively. For convenience $\log p$ values were used in graphical treatment.

Plots of $\log p$ vs time were made for each pair of corresponding precipitation and solid plus solution experiments. In general, $\log p$ fell from a high initial value and reached a constant value, approximately an equilibrium value, in the neighborhood of thirty days for a precipitation experiment; correspondingly, $\log p$ rose from a slightly low value and leveled off in about ten days to about the same value for the corresponding solid plus solution experiment. Schematic diagrams with straight

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lines were used since too few points were obtained to permit the drawing of smooth curves. Two typical diagram pairs are shown in Figure 1.

In most cases log p rose slightly after thirty days, probably due to the increase in sulfate concentration by evaporation of the solutions on long standing. Agreement between the two types of experiments with respect to log p value was not satisfactory in all cases; however, the discrepancies appear to be random and are believed due to experimental error. Equilibrium values of log p estimated by inspection of all diagram pairs are recorded along with the three hour values from precipitation experiments in Table 8. Due to uncertainties caused by increase in sulfate concentration, the equilibrium values are recorded to only one or two significant figures in most cases.

A test of the original assumption, that at equilibrium U concentration is inversely proportional to H_2O_2 concentration, is presented schematically in Figure 2. If this assumption is valid, then log p should be independent of H_2O_2 concentration at constant sulfate and hydrogen ion concentrations. The agreement between this hypothesis and experiment is fairly good. Figure 2 shows that the equilibrium solubility increases with a power of H^+ concentration slightly greater than one rather than according to the square as with pure uranyl nitrate solution.

(8)

Sulfate-Prediction of Minimum Uranium Concentration in Effluents.--

In Figure 3 the equilibrium values of log p from Table 8 are plotted against observed sulfate concentration at a series of constant pH values. The values at zero sulfate were computed using 6.7×10^2 as the equilibrium constant for uranium peroxide. This graph is useful in predicting the minimum concentration of uranium in the effluent from a peroxide precipitation in the presence of sulfate. A similar graph of the 3 hour log p values obtained from the precipitation experiments showed a very irregular structure. The equilibrium U concentration increases linearly

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TYPICAL LOG p - TIME DATA

FIGURE: (8)

● PRECIPITATION; ■ SOLID PLUS SOLUTIONS

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EQUILIBRIUM LOG p VALUES AT VARIOUS H_2O_2 CONCENTRATIONS FOR SEVERAL $SO_4^{=}$ AND pH PAIRS

FIGURE 2 (8)

○ PRECIPITATION ; □ SOLID PLUS SOLUTION

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FIG. 3 (8)

○ PRECIPITATIONS
 ■ SOLID PLUS SOLUTIONS

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REGIONS OF QUANTITATIVE UO_4 FORMATION
FOR THE SYSTEM $UO_2(NO_3)_2 \cdot (NH_4)_2SO_4 \cdot H_2O_2$

FIGURE: 4 (8)

1) 1.0 M H_2O_2 , EQUILIBRIUM
2) 0.1 M H_2O_2 , EQUILIBRIUM

3) 1.0 M H_2O_2 , 3 HOURS
4) 0.1 M H_2O_2 , 3 HOURS

SYSTEMS BELOW CURVES CORRESPOND TO
 U CONC. ≤ 10 mg/l

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with sulfate for low sulfate (less than about 0.5 M) and greater than that for high sulfate. In the neighborhood of 1.0 M sulfate the solubility is roughly proportional to the square of the sulfate concentration.

(8)

Sulfate-Regions of Quantitative Precipitation.--A quantitative SO_4 -pH region is defined here as one in which at a constant H_2O_2 concentration the U in solution is 10 mg/l or less. The limits of such regions at equilibrium are easily read from Figure 3. Quantitative regions for 1.0 and 0.1 M H_2O_2 , both at equilibrium and 3 hours after precipitation are shown in Figure 4. The very much greater areas of these regions at equilibrium indicate clearly the important effect that sulfate has on the rate of precipitation of uranium peroxide. The 3 hour regions should not be considered as exact since their geometry doubtless depends somewhat upon original uranium concentration and such factors as agitation and rate of H_2O_2 addition which were not standardized. Much smaller 3 hour regions would be expected if the study had utilized solutions with original uranium concentrations less than 1%.

Sulfate-Summary.--The most important facts concerning the sulfate effect may be summarized as follows:

1. Sulfate both delays the precipitation and increases the equilibrium solubility of uranium peroxide. These effects are large enough to make the reaction non-quantitative over a wide range of conditions.
2. As with solutions containing no sulfate, the solubility varies inversely with H_2O_2 concentrations.
3. The precipitation rate is decreased if 1 M NH_4NO_3 is added to the system, however the equilibrium solubility is not greatly altered.
4. The equilibrium solubility increases with a power of hydrogen ion slightly greater than one rather than according to the square of H^+

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concentration as is the case in pure uranyl nitrate systems.

5. The equilibrium uranium concentration increases linearly with sulfate for low sulfate (less than about 0.5 M) and greater than that for high sulfate. In the neighborhood of 1.0 M sulfate the solubility is roughly proportional to the square of the sulfate concentration.

(9-14)

Fluoride.--The effect of fluoride ion is even greater than that of sulfate. Data for several precipitations from dilute fluoride solutions are shown in Table 9. It is seen that 0.06 M fluoride is sufficient to make the precipitation useless as a quantitative method, even after long standing.

In an attempt to gain a more complete picture of the fluoride interference the interaction between fluoride and uranyl ions has been studied conductimetrically. Conductivity measurements are often used in determining the end point of reactions in which one of the products is weakly dissociated, for example in titrating the salt of a weak acid with a strong acid. The investigation reported here represents an effort to study more loosely associated species by similar methods.

Very dilute solutions of $\text{UO}_2(\text{NO}_3)_2$ were titrated with KF solution (much more concentrated so as to make the volume increase negligible) and the specific conductivity was plotted against the molar ratio of fluoride to uranium. The data thus obtained is very consistent but not easily interpreted. About all that can be stated with certainty is that the added fluoride is tied up by the uranyl ion with varying degrees of effectiveness until a molar F/U ratio of about 5 is reached, after which the conductance increases as a straight line function of the molar ratio. The neutral molecule, UO_2F_2 , appears to be the dominant association form in the system.

(11-14)

By the use of aluminum ion as a complexing agent, the effect of fluoride is largely overcome, even in fairly concentrated fluoride solutions. In a system where the bulk of fluoride is tied up by aluminum the precipitation is about equally quantitative over the pH range 1.5 to 3.5 rather than becoming more quantitative with increasing pH as might be expected. (12) This fact can be accounted for by the weakness of HF as an acid; in other words H^+ itself is a fairly effective fluoride complexing agent.

Interfering Cations.---Some cations affect the precipitation of uranium peroxide by forming soluble peruranate, particularly at high pH. The precipitation is also materially influenced by those which catalyze the decomposition of H_2O_2 . However, since the precipitate, once formed, is prevented from redissolving by very little hydrogen peroxide, any catalyst which fails to effect fairly complete decomposition within the first hour or two does not interfere in work where the precipitate is removed quickly.

By far the most important catalyst in acid solution is ferric ion. Cupric ion is also of importance. However, its principal effect probably arises from its promoter action with respect to ferric catalysis. Previous workers have established the fact that small concentrations of copper increase the rate of decomposition due to iron many fold. (15,16)

In this section we will consider the interference of only a few of the common cations.

(4,5,7,17-21)

Iron.---The rate of decomposition of hydrogen peroxide by iron in an acid solution at constant temperature is proportional to the concentrations of hydrogen peroxide and ferric ion (not to total iron) and inversely proportional to hydrogen ion concentration. These proportionalities are not

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exact, especially during the latter part of the reaction when the rate falls off considerably. The decomposition rate is greatly lessened by lowering the temperature.

Three methods have been used with success for minimizing the iron effect: (1) preliminary precipitation of the iron, (2) the addition of a complexing agent to reduce ferric ion activity, and (3) precipitation of the uranium peroxide at a reduced temperature. The last two methods will be considered here.

Under carefully controlled conditions either (2) or (3) is suitable for the quantitative recovery of uranium from iron solutions. Since the two methods are based on essentially independent phenomena, a combination of these techniques permits the precipitation of uranium peroxide in the presence of greater iron concentrations than can be handled by either method alone.

(4,7,17)

Iron-Complexing Method.--A wide variety of substances, most of them organic acids, have been tried as complexing agents for iron. To be useful the complexing agent must reduce the ferric ion activity without inhibiting the uranium peroxide precipitation.

(4)

The reagent which has been found most successful is malonic acid. Oxalic, acetic and lactic acids give satisfactory reductions in decomposition rate if considerably more acid is used. The usefulness of malonic acid can be seen by examining Tables 10 and 11. Table 10 shows the effect of 0.05% iron on hydrogen peroxide decomposition and the concentration of uranium in the effluent when no complexing agent is present. Table 11 presents data on precipitations in the presence of various iron concentrations up to 0.75% where twice as many moles of malonic acid as

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iron are in the system. A large number of experiments have demonstrated that the optimum conditions for the precipitation are a molar malonic acid to iron ratio of 2, at a pH of 2.0-2.5, and that 0.7% iron can be handled. (5,17,19-21)

Iron-Cold Precipitation Method.--Solutions of moderate iron concentration can be precipitated quite well at reduced temperatures without the use of complexing agents. Data is shown in Table 12⁽⁵⁾ for precipitations at 2°C and pH 2.0 in the presence of varying amounts of iron. Under the conditions of these experiments 0.7% iron does not noticeably interfere. The advantage of precipitation in the cold may be seen easily by reference to Table 13⁽²¹⁾ where the hydrogen peroxide remaining in the system at various times is shown for two runs which are identical except for temperature.

When using reduced temperatures the precipitate formed is often difficult to filter or centrifuge. One method of obviating this difficulty is to add the hydrogen peroxide at room temperature, thereby forming a filterable precipitate, and then quickly cooling the system to avoid decomposition. Another procedure is to precipitate in the cold with use of suitable flocculating agents.

In considering Tables 10, 11, 12, and 13, it should be remembered that they represent the ideal case in which iron is the only impurity. The presence of other interfering constituents, especially substances which promote ferric ion catalysis, would render the results somewhat less favorable.

(6)
Cobalt, Manganese, and Cerium.--Cobaltous, manganous, and cerous ions form insoluble peroxides in alkaline solution which are powerful

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catalysts for the decomposition of hydrogen peroxide. When uranium peroxide is precipitated in the usual way by concurrent addition of ammonium hydroxide and hydrogen peroxide, peroxides of these metals form in the regions of the solution where there is a temporary excess of NH_3 . The peroxides so formed redissolve very slowly, hence the hydrogen concentration in such a system rapidly reduced to a low value. This complication can easily be overcome by simply precipitating uranium peroxide without the addition of alkali. Although the pH decreases, sufficient hydrogen peroxide can be added to make the precipitation quantitative.

(5,6)

Alkaline Earth and Alkali Metals.--The influence of the alkali metals and the alkaline earth metals is considered to result from the formation of soluble peruranates. The alkaline earth metals decrease the rate of precipitation to a significant extent, except magnesium which has no effect. The delay increases with increasing atomic number of the element. The same rule may also be applicable to the alkali metals, since potassium causes important delay while sodium and lithium have little effect,

(6)

Table 13.

Miscellaneous Cations--Zn, Cd, Ni, Al, and Cr. (5,6)--Zinc, cadmium, and nickelous ions in moderate concentration do not appear to interfere with the precipitation. If zinc or cadmium is added as the chloride the resulting delay is much less than that caused by the same molarity of ammonium chloride. The chlorides of these metals are weak electrolytes, and the chief action of the metal in this case is to decrease the chloride effect. One molar aluminum nitrate had only a minor influence on the precipitation, and this may have been due to iron impurities in the salts used. Chromium, in low concentrations, and copper have no significant effect.

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EXPERIMENTAL

Before precipitating a solution it was adjusted to the desired pH with ammonium hydroxide or nitric acid. While the solution was mechanically stirred, the stoichiometric amount of 50% hydrogen peroxide was added slowly together with sufficient ammonium hydroxide to prevent an increase in acidity. The desired excess of hydrogen peroxide was then added rapidly, and a final careful adjustment of pH made. The solution was allowed to stand with occasional stirring, except in the experiments shown in Tables 12 and 13 in which cases the mechanical stirring was maintained.

After standing for the desired length of time the slurry or a portion of it was filtered through a fine sintered glass plate in order to analyze the filtrate. Sometimes a series of small batches were precipitated with an entire batch being filtered to obtain a sample of filtrate. More frequently a large amount was precipitated, and small samples of the slurry removed from time to time for analysis.

When it was intended to study the effect of a reaction condition or a substance on the equilibrium solubility of uranium peroxide, equilibrium was approached from both sides. This was done by making precipitation experiments as outlined above, and "solid plus solution" experiments in which solid uranium peroxide was added to solutions of hydrogen peroxide and the desired impurity adjusted to the proper pH.

In experiment G, Table 3, solid uranium peroxide was added in order to observe whether the delay in precipitation exhibited by solutions dilute in uranium solid could be reduced by seeding.

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In Table 9 the fluoride molarities shown are analytical values determined at the indicated time. Except for slight increases due to evaporation the concentrations remained constant throughout each experiment.

Table 11 shows the small amount of iron precipitated along with the uranium peroxide, since precipitates formed at a pH in the region of 3 would contain most of the iron if malonic acid were not present. Before the iron analyses were made, the precipitates were washed with about 20 ml of water per gram of uranium peroxide.

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(2)*

Table 1

Equilibrium Constant of Uranium Peroxide

(Solid Plus Solution Experiment - Temperature 25-27°C)

Exp.	Time Days	Solution Composition				$K \times 10^3$
		pH	H^+ M	H_2O_2 M	Uranium M	
1A	35	1.60	2.61×10^{-2}	8.7×10^{-4}	8.87×10^{-4}	1.22
2A	41	1.04	9.12×10^{-2}	3.19×10^{-3}	3.41×10^{-3}	1.31
3A	41	2.16	6.92×10^{-3}	2.30×10^{-4}	2.40×10^{-4}	1.16
4A	41	2.00	1.00×10^{-2}	8.38×10^{-5}	2.8×10^{-5}	2.3
5A	41	0.98	1.05×10^{-2}	9.26×10^{-2}	1.86×10^{-4}	1.66
6A	41	1.03	9.33×10^{-2}	5.51×10^{-1}	2.68×10^{-4}	1.7
Average of K^*						1.6×10^{-3}
K^*						6.7×10^2

*Data compiled from CD-4021 as being the most reliable for forming an average.

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(2)*

Table 1

Equilibrium Constant of Uranium Peroxide

(Solid Plus Solution Experiment - Temperature 25-27°C)

Exp.	Time Days	Solution Composition				$K' \times 10^3$
		pH	H^+ M	H_2O_2 M	Uranium M	
1A	35	1.60	2.61×10^{-2}	6.7×10^{-4}	6.87×10^{-4}	1.22
2A	41	1.04	9.12×10^{-2}	3.19×10^{-3}	5.41×10^{-3}	1.31
3A	41	2.16	6.92×10^{-3}	2.30×10^{-4}	2.40×10^{-4}	1.15
4A	41	2.00	1.00×10^{-2}	8.38×10^{-5}	2.8×10^{-5}	2.3
5A	41	0.98	1.05×10^{-2}	9.26×10^{-2}	1.86×10^{-4}	1.56
6A	41	1.03	9.33×10^{-2}	6.61×10^{-1}	2.68×10^{-4}	1.7
Average of $K' =$						1.5×10^{-3}
$K =$						6.7×10^2

*Data compiled from CD-4021 as being the most reliable for forming an average.

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Table 2⁽³⁾Equilibrium Constant of Uranium Peroxide

(Typical Data - Temperature 25-27°C)

A. Solid Plus Solution Experiments

Exp.	Time	pH	Solution Composition		Uranium M	K [*] x 10 ³
			H ⁺ M	H ₂ O ₂ M		
1A	12 days	1.45	3.55x10 ⁻²	8.6x10 ⁻⁴	8.42x10 ⁻⁴	0.575
	23 days	1.58	2.63x10 ⁻²	8.2x10 ⁻⁴	7.75x10 ⁻⁴	0.922
	35 days	1.60	2.51x10 ⁻²	8.7x10 ⁻⁴	8.87x10 ⁻⁴	1.22
2A	7 days	1.00	1.00x10 ⁻¹	3.31x10 ⁻³	2.62x10 ⁻³	0.87
	16 days	0.97	1.07x10 ⁻¹	3.60x10 ⁻³	3.45x10 ⁻³	1.08
	30 days	1.04	9.12x10 ⁻²	3.37x10 ⁻³	3.42x10 ⁻³	1.39
	41 days	1.05	9.12x10 ⁻²	3.19x10 ⁻³	3.41x10 ⁻³	1.31
2'A*	10 days	1.00	1.00x10 ⁻¹	3.51x10 ⁻³	3.16x10 ⁻³	0.99
	16 days	1.03	9.33x10 ⁻²	3.34x10 ⁻³	3.37x10 ⁻³	1.29
	30 days	1.00	1.00x10 ⁻¹	3.44x10 ⁻³	3.40x10 ⁻³	1.17
	41 days	1.05	8.91x10 ⁻²	3.18x10 ⁻³	3.66x10 ⁻³	1.47

B. Precipitations From 1% UO₂(NO₃)₂ Solutions

1B	1 hour	1.00	1.00x10 ⁻¹	4.74x10 ⁻¹	1.89x10 ⁻⁴	8.95
	4 hours	1.00	1.00x10 ⁻¹	4.76x10 ⁻¹	1.64x10 ⁻⁴	7.81
	2 days	1.03	9.33x10 ⁻²	4.75x10 ⁻¹	7.18x10 ⁻⁵	3.92
	10 days	0.95	1.12x10 ⁻¹	4.73x10 ⁻¹	2.35x10 ⁻⁵	0.87
	21 days	0.97	1.08x10 ⁻¹	4.67x10 ⁻¹	3.57x10 ⁻⁵	1.40
1'B**	1 hour	0.94	1.15x10 ⁻¹	4.76x10 ⁻¹	1.15x10 ⁻³	41.4
	4 hours	0.94	1.15x10 ⁻¹	4.68x10 ⁻¹	2.28x10 ⁻⁴	8.1
	2 days	0.87	1.35x10 ⁻¹	3.87x10 ⁻¹	3.84x10 ⁻⁵	0.81
	10 days	1.00	1.00x10 ⁻¹	2.15x10 ⁻¹	4.29x10 ⁻⁵	0.92
	21 days	1.03	9.84x10 ⁻²	9.42x10 ⁻²	1.06x10 ⁻⁴	1.14

*1.0 M NH₄NO₃ added**10 M NH₄NO₃ added

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(2)
Table 3

Effect of Uranyl Nitrate Concentration

<u>Experiment</u>	<u>Original Uranium Concentration %</u>	<u>Time After Precipitation</u>	<u>pH</u>	<u>H₂O₂</u>	<u>Uranium mg/l</u>
1	10.0	1 hour	1.15	.274	14.7
		4 hours	1.15	.274	10.1
		5 days	1.25	.274	4.2
2	5.0	1 hour	1.15	.493	15.5
		5 days	1.20	.470	4.5
		16 days	1.23	.498	6.8
3	1.0	1 hour	1.08	.478	39.4
		4 hours	1.08	.473	35.0
		5 days	1.12	.463	7.8
		16 days	1.07	.477	5.8
4	0.50	1 hour	1.00	.494	44.5
		4 hours	1.00	.495	41.1
		24 hours	1.00	.492	21.9
5	.10	1 hour	1.00	.493	97.2
		4 hours	1.04	.492	76.1
		24 hours	1.03	.487	31.9
6*	0.02	1 hour	1.00	.488	271
		4 hours	1.04	.488	270
		29 hours	1.00	.484	72.1
		47 hours	1.04	.483	42.3
		96 hours	1.00	.485	26.1

*At six hours solid UO₃ added

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Table 4Effect of Chloride on the Precipitation of Uranium Peroxide(Orig. $\text{UO}_2(\text{NO}_3)_2$ conc. = 2%. pH = 2.0.)

<u>Experiment</u>	<u>NH_4Cl Added M</u>	<u>Time After Precipitation Hours</u>	<u>pH</u>	<u>H_2O_2 Mx10²</u>	<u>Uranium mg/l</u>
1	0.05	1	2.00	5.98	4.9
		3	2.00	6.00	5.5
		24	2.04	6.02	5.2
2	1.0	1	2.00	5.77	42.0
		3	2.00	5.71	34.0
		24	1.94	5.45	17.5
3	2.0	1	2.00	6.71	1.58×10^3
		3	2.00	6.18	8.02×10^2
		24	1.96	5.45	2.14×10^2

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Table 6Effect of Sulfate

<u>pH</u>	<u>Orig. $\text{UO}_2(\text{NO}_3)_2$ Concentration %</u>	<u>Excess H_2O_2 M</u>	<u>$(\text{NH}_4)_2\text{SO}_4$ Concentration M</u>	<u>Uranium in Solution After 3 hours mg/l</u>
3.0	5	0.1	0.04	1.2
3.0	5	0.1	0.45	2.3×10^2
3.0	5	0.1	1.66	2.0×10^4

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Table 6

The Effect of Sulfate

(Precipitation Experiments at pH = 1.0)

Exp.	Orig:		Observed SO_4^{--} concn. M		3 Hours			15 Days		
	U	NH_4NO_3								
	Conc. %	Conc. M	9 days	70 days	pH	H_2O_2 M	U mg/l	pH	H_2O_2 M	U mg/l
1	2.0	0.17	0.0496	--	1.00	0.0936	2.24×10^2	1.00	.0910	8.15×10^2
2	2.0	0.17	0.102	--	1.00	0.0970	4.46×10^2	1.00	.0933	1.75×10^2
3	5.0	0.48	0.189	--	1.00	0.108	5.53×10^2	1.00	.0929	2.32×10^2
4	7.5	0.63	0.450	0.547	1.00	0.137	5.93×10^3	1.00	.0977	9.57×10^2
5	10.0	0.84	0.876	1.03	1.00	0.276	3.60×10^4	1.00	.118	5.14×10^3
6	10.0	0.84	1.60	1.76	1.00	1.00	5.52×10^4	1.00	.734	5.34×10^3
7	5.0	1.42	0.180	0.203	1.00	0.105	2.99×10^3	1.00	.0804	4.56×10^2
8	5.0	0.42	0.186	--	1.00	0.449	--	1.00	.424	5.84×10^2
9	5.0	0.42	0.177	--	1.00	0.840	1.15×10^2	1.00	.801	1.96×10^2
10	10.0	0.84	0.709	--	1.00	0.691	1.45×10^4	1.00	.606	9.23×10^2

Exp.	22 Days			34 Days			47 Days			61 Days		
	pH	H_2O_2 M	U mg/l	pH	H_2O_2 M	U mg/l	pH	H_2O_2 M	U mg/l	pH	H_2O_2 M	U mg/l
1	1.00	.0897	9.16×10^2	0.96	.0863	1.06×10^2	--	--	--	--	--	--
2	1.00	.0943	1.94×10^2	0.96	.102	2.36×10^2	--	--	--	--	--	--
3	1.00	.0876	2.80×10^2	1.10	.0603	3.61×10^2	--	--	--	--	--	--
4	1.00	.0937	1.19×10^3	0.96	.0827	1.35×10^3	0.95	.0663	2.29×10^3	1.05	.0488	3.31×10^3
5	1.00	.112	4.91×10^3	0.98	.101	4.54×10^3	0.93	.0943	6.63×10^3	1.03	.0772	7.45×10^3
6	1.00	.697	4.93×10^3	1.05	.640	3.95×10^3	0.96	.597	4.32×10^3	1.04	.520	6.48×10^3
7	1.00	.0765	4.78×10^2	0.94	.0698	4.14×10^2	0.84	.0606	6.96×10^2	0.93	.0455	1.13×10^3
8	1.00	.413	6.64×10^2	1.04	.413	7.58×10^2	--	--	--	--	--	--
9	1.15	.782	1.95×10^3	1.22	.748	2.13×10^3	--	--	--	--	--	--
10	--	--	--	1.06	.542	6.82×10^2	1.00	.486	8.80×10^2	--	.405	1.21×10^3

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Table 7

The Effect of Sulfate

(Solid Plus Solution Experiments at pH = 1.0)

Exp.	NH ₄ NC ₃ Conc. M	Observed SO ₄ Conc. M		20 Days			30 Days		
		12 days	72 days	pH	H ₂ O ₂		pH	H ₂ O ₂	
					M	mg/l		M	mg/l
1	--	0.0616	--	1.00	.1095	9.23x10 ²	0.96	.0732	1.20x10 ²
2	--	0.101	--	1.00	.0772	1.52x10 ²	1.00	.0706	2.00x10 ²
3	--	0.200	0.224	1.00	.0766	3.40x10 ²	1.00	.0707	4.31x10 ²
4	--	0.476	0.558	0.95	.0778	1.57x10 ³	1.00	.0708	1.76x10 ³
5	--	0.909	0.978	0.89	.0885	5.69x10 ³	0.93	.0807	6.93x10 ³
6	--	1.75	1.86	1.00	.0906	9.95x10 ³	1.04	.0926	1.33x10 ⁴
7	1.0	0.195	--	1.00	.0655	2.46x10 ²	1.00	.0540	4.96x10 ²
8	--	0.197	--	1.00	.398	5.80x10	1.03	.379	8.72x10
9	--	0.186	--	1.00	.786	2.99x10 ²	1.03	.750	3.97x10 ²
10	--	.968	1.25	1.00	.742	4.69x10 ²	1.02	.696	7.98x10 ²

Exp.	39 Days			52 Days			52 Days		
	pH	H ₂ O ₂		pH	H ₂ O ₂		pH	H ₂ O ₂	
		M	mg/l		M	mg/l		M	mg/l
1	0.97	.0667	1.38x10 ²	--	--	--	--	--	--
2	1.02	.0638	2.40x10 ²	--	--	--	--	--	--
3	1.03	.0628	5.06x10 ²	0.96	.0681	7.60x10 ²	1.03	.0486	1.11x10 ³
4	1.00	.0618	1.87x10 ³	0.94	.0550	2.68x10 ³	1.02	.0455	3.32x10 ³
5	0.94	.0716	6.25x10 ³	0.87	.0637	7.18x10 ³	0.94	.0542	5.03x10 ³
6	1.04	.0845	1.40x10 ⁴	1.00	.0832	1.79x10 ⁴	1.07	.0703	3.15x10 ⁴
7	1.00	.0450	7.00x10 ²	0.96	.0321	1.13x10 ³	--	--	--
8	1.01	.358	1.04x10 ³	--	--	--	--	--	--
9	1.00	.758	4.08x10	--	--	--	--	--	--
10	0.96	.630	9.80x10 ²	0.96	.571	1.44x10 ³	1.00	.646	2.17x10 ³

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Table 8

The Effect of Sulfate

Equilibrium and 3-Hour Values of Log p for all Pairs

Type of Exper.	Approx. Conc. M H ₂ O ₂	SO ₄	Log p at pH 1.0 3 Hrs.	Equil.	Log p at pH 1.5 3 Hrs.	Equil.	Log p at pH 2.0 3 Hrs.	Equil.	Log p at pH 2.5 3 Hrs.	Equil.	Log p at pH 3.0 3 Hrs.	Equil.
P 1	0.1	0.05	1.32	0.88	0.900	0.15	0.449	-0.075	-0.234	-1.2	-1.000	---
S 1	0.1	0.05		0.95		0.20		-0.3		-1.1		-1.5
P 2	0.1	0.1	1.636	1.2	1.44	0.53	1.01	-0.07	0.124	---	0.695	-1.5
S 2	0.1	0.1		1.2		0.55		0.0		-0.85		-1.0
P 3	0.1	0.2	1.776	1.4	1.70	0.95	1.92	0.2	0.155	-0.7	1.30	0.8
S 3	0.1	0.2		1.5		0.90		0.35		-0.45		-0.7
P 4	0.1	0.5	2.913	2.0	3.38	1.4	2.98	0.90	2.339	0.0	2.06	0.03
S 4	0.1	0.5		2.1		1.7		0.90		0.20		-0.10
P 5	0.1	1.0	4.029	2.7	4.06	2.0	3.74	1.45	3.27	0.48	3.51	---
S 5	0.1	1.0		2.7		2.1		1.37		0.80	2.36	0.8
P 6	0.1	2.0	4.741	3.4	4.54	2.8	3.94	2.15	3.88	1.28	2.36	0.3
S 6	0.1	2.0		3.2		2.5		2.35		1.35		---
P 7	0.1	0.2	2.497	3.4	2.49	0.6	2.96	0.05	1.91	-0.8		
S 7	0.1	0.2		3.2		0.8		0.05		-0.2		
P 8	0.5	0.2	---	1.4	2.05	0.90	1.63	0.5	-0.536	-0.4		
S 8	0.5	0.2		1.5		0.95		0.3		-0.3		
P 9	1.0	0.2	1.985	1.2	2.28	0.7	1.19	0.3	0.328	-0.4		
S 9	1.0	0.2		1.5		0.9		0.3		---		
P 10	1.0	1.0	4.000	2.6	3.83	2.0	3.30	1.2	3.23	0.5		
S 10	1.0	1.0		2.7		2.2		1.5		0.75		

*p = (U)(H₂O₂) where the concentrations (U) and (H₂O₂) are expressed in mg/l and moles /l respectively

**p = precipitations

S = solid plus solution

1,2 etc. refer to pages B-9

Table 9⁽⁹⁾Fluoride Interference in Precipitation of Uranium Peroxide

(pH = 2. Orig. U Conc. = 2%)

Experiment	Time	Solution Composition		
		H_2O_2 M	Fluoride* M	Uranium mg/l
1	1 hour	0.143		749
	4 hours	0.145		722
	24 hours	0.141		546
	7 days	0.114	0.0675	964
	16 days	0.111		1500
2	1 hour	0.167		5140
	4 hours	0.166	0.084	2910
	24 hours	0.160		2560
	7 days	0.152	0.091	1970
	16 days	0.122		1650
3	1 hour	0.170		6600
	4 hours	0.165	0.202	7970
	24 hours	0.160		7430
	7 days	0.159	0.206	7500
	16 days	0.143		7290

*Analytical values determined at time indicated.

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Table 10Interference Due to .05% Iron(Orig. U Conc. = 5%. $\text{Fe}(\text{NO}_3)_3 = .009 \text{ M}$. $\text{pH} = 2.0$. Orig. Excess $\text{H}_2\text{O}_2 = 0.3 \text{ M}$)

Time Min.	Temp. °C	Solution Composition	
		H_2O_2 M	GRABER mg/l
0	25	0.256	—
10	27	0.199	5.4
20	28	0.127	5.6
30	28	0.086	6.8
40	28	0.044	0.2
50	28	0.045	11
60	27	0.039	11
90	28	0.016	19
120	26	0.007	35
180	26	0.002	80

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Table 11

Precipitation of Uranium Peroxide in
the Presence of Iron and Malonic Acid

(Orig. U Conc. = 3%. Initial Excess H_2O_2 = 0.3 M. Temp. = 25°/30°)

a. pH = 2.0

Exp.	Ferric Iron Concentration		Malonic Acid Conc. M	Filtrate at 3 hrs. mg U/l	H_2O_2 Concentration, M			Fe on Calc %	% Total Fe Fpt'd
	%	M			1 hr.	3 hrs.	24 hrs.		
1	0.03	0.0033	0.011	<1.2	0.27	0.25	0.15	0.037	3.8
2	0.10	0.010	0.034	1.9	0.27	0.23	0.07	0.045	1.4
3	0.15	0.027	0.054	1.2	0.25	0.21	0.01	0.050	1.0
4	0.20	0.036	0.072	<1	0.24	0.20	0.03	0.064	0.96
5	0.30	0.054	0.11	2.2	0.27	0.17	0.01	0.074	0.74
6	0.75	0.15	0.27	50	0.25	0.15	0.02	0.125	0.51

b. pH = 2.5

1A	0.03	0.0033	0.011	1.1	0.32	0.29	0.10	0.045	4.6
2A	0.10	0.010	0.036	<1.2	0.24	0.23	0.06	0.075	2.3
3A	0.15	0.027	0.054	<1.0	0.26	0.23	0.06	0.097	1.9
4A	0.20	0.036	0.072	<1.0	0.27	0.25	0.02	0.14	2.1
5A	0.30	0.054	0.11	1.2	0.23	0.24	0.01	0.16	1.6
6A	0.75	0.15	0.27	1.4	0.26	0.17	0.01	0.27	1.1

c. pH = 3.0

1B	0.03	0.0033	0.011	1.2	0.29	0.24	0.06	0.058	5.9
2B	0.10	0.010	0.036	1.4	0.29	0.23	0.01	0.19	6.7
3B	0.15	0.027	0.054	<1	0.25	0.23	0.02	0.18	3.8
4B	0.20	0.036	0.072	6.5	0.23	0.22	0.01	0.23	5.5
5B	0.30	0.054	0.11	5.1	0.25	0.19	0.01	0.42	4.2
6B	0.75	0.15	0.27	260	0.15	0.12	0.04	2.5	10.4

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Table 12

The Precipitation of Uranium Peroxide
At 2°C in the Presence of Iron

(pH = 2.0. Orig. H_2O_2 Excess = 0.25 N)

a. Original U Conc. = 0.15%

Fe(NO ₃) ₃ Added %	Ferrio Iron Concentration		Filtrate at 1/2 Hr. mg/l
	M	%	
0.2	0.006	0.05	4
0.4	0.017	0.09	1.5
0.8	0.033	0.19	1.8
1.6	0.07	0.31	2
3.2	0.13	0.74	10
6.4	0.25	1.48	59
12.8	0.53	2.96	334

b. Original U Conc. = 1.0%

0.2	0.006	0.05	2
0.4	0.017	0.09	2
0.8	0.033	0.19	4
1.6	0.07	0.37	3
3.2	0.13	0.74	4.5
6.4	0.25	1.48	54
12.8	0.53	2.96	90

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Table 13

Effect of Temperature on the rate
of Decomposition of H_2O_2 by Iron

(Orig. U Conc. = 0.15%. Fe = 0.1%. pH = 2.0%)

Time After Precipitation Min.	H_2O_2 Molarity in Filtrate	
	Ppt'n #1 20°C	Ppt'n #2 24-25°C
0	0.48	0.48
5	0.396	0.229
10	0.389	0.110
20	0.374	0.054
30	0.353	0.015
60	0.304	

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Table 14

**Precipitations in the Presence of Alkali
and Alkaline Earth Metals**

(Orig. $\text{H}_2\text{O}_2(\text{NO}_3)_2 = 2.0\text{M}$. pH = 2.0. Orig. known $\text{H}_2\text{O}_2 = 0.1\text{M}$)

Metal Salt Added	Conc. Added Metal Salt	Solution Composition					
		1 Hour		4 Hours		24 Hours	
		$\frac{\text{H}_2\text{O}_2}{\text{M}}$	$\frac{\text{M}}{\text{mg/l}}$	$\frac{\text{H}_2\text{O}_2}{\text{M}}$	$\frac{\text{M}}{\text{mg/l}}$	$\frac{\text{H}_2\text{O}_2}{\text{M}}$	$\frac{\text{M}}{\text{mg/l}}$
None	None	0.115	2.6	0.115	2.6	0.115	1.6
LiNO_3	1.0	0.0886	4.4	0.0886	2.3	0.0886	1.7
NaNO_3	1.0	0.0838	4.1	0.0819	6.4	0.0766	2.2
KNO_3	1.0	0.0858	145	0.088	102	0.0917	63.6
$\text{Hg}(\text{NO}_3)_2^*$	1.0	0.0822	4.5	0.0810	2.2	0.0800	2.0
$\text{Ca}(\text{NO}_3)_2$	1.0	0.0847	99.2	0.0840	6.6	0.0810	1.7
$\text{Sr}(\text{NO}_3)_2$	1.0	0.0894	228	0.0897	25	0.0912	16
$\text{Ba}(\text{NO}_3)_2$	0.2	---	1060	0.0979	1000	0.0998	465

* (25)

143.38

SUMMARY

Factors affecting the precipitation of uranic peroxide are described. Initially the data on pure uranyl nitrate solutions is presented. The equilibrium constant for the reaction

is shown to be 4.7×10^3 . A delay in precipitation is found to occur in dilute uranic solutions in the presence of high concentrations of excess hydrogen peroxide. There is some evidence that this may be due to slow formation of crystals.

The precipitation is adversely affected by a number of ions. The anions tested are listed in order of increasing interference: nitrate, acetate, chloride, malonate, sulfate, and fluoride. It is shown that the interference from malonate is reduced or eliminated when ferric iron is present, and that fluoride interference can be overcome by complexing with aluminum. The reduction of the reaction rate, and increased equilibrium solubility caused by sulfate is demonstrated.

Ferric ion due to its ability to catalyze the decomposition of hydrogen peroxide is a most harmful cation. Two methods of overcoming its effect are demonstrated, complexing with malonic acid, or reducing its activity by lowering the temperature of precipitation. By such methods solutions with an iron concentration of 0.7% can be successfully precipitated.

The peroxide of cobalt, manganese and cerium are shown to be precipitated by local basic concentrations due to the addition of ammonium hydroxide during the precipitation. These dissolve very slowly and cause the hydrogen peroxide to decompose at a rapid rate.

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The alkali and alkaline earth metals are shown to become more active inhibitors as the atomic number increases within each group. The formation of soluble peroxides is proposed as the cause of the interference by such metal ions. With magnesium no effect was detected, the effects of lithium and sodium were small, and the inhibition due to potassium was considerable.

Zinc, cadmium, nickel, aluminum, chromium and copper are shown to have little effect on the precipitation. Copper, however, can act as a promoter of the catalytic iron effect.

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