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A CHEMICAL STUDY OF HEXAVALENT URANIUM COMPOUNDS IN SODIUM HYDROXIDE, SODIUM CARBONATE, AND SODIUM BICARBONATE SOLUTIONS

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ABSTRACT

Reactions of hexavalent uranium compounds in alkaline solutions have been studied. Titrations of U^{VI} solutions with base have been carried out and curves of pH vs. equivalents of base have been obtained. Back titrations with acid yield curves different from those obtained in the forward titration. Supersaturation is conspicuous. Sodium bicarbonate (0.05 M) and sodium carbonate (0.20 M) are sufficiently strong complexing agents to hold in solution at 90° at least 2 g/liter of U^{VI}.

The solubilities of U^{VI} in NaOH, Na_2CO_3, and $NaHCO_3$ solutions at room temperature were determined by shaking UO_3 with solutions of varying composition. The solubility of U^{VI} in 0.05 M NaOH is 3 mg/liter and in 12 M NaOH increases to 40 mg/liter. The solubility of U^{VI} in Na_2CO_3 increases slowly with increasing Na_2CO_3 concentration, from 2.3 g/liter at 0.05 M Na_2CO_3 to 3.7 g/liter at 0.40 M Na_2CO_3. The solubility of U^{VI} in $NaHCO_3$ solution is almost linear with increasing $NaHCO_3$ concentration; the concentration of U^{VI} (gram-atoms/liter) is approximately 0.45 the total $NaHCO_3$ concentration. The ion $UO_2(OH)CO_3^-$ has been postulated to explain this relationship.

A compound of the stoichiometric composition $Na_2U_2O_7$ has been prepared by igniting $NaUO_2Ac_3$ under special conditions. This compound proved to be very slightly soluble in Na_2CO_3 solution and is apparently not the same phase as that which is in equilibrium after UO_3 has been shaken with Na_2CO_3 solutions.

This report presents the results of a study of a portion of an important but neglected field in Project chemistry -- that of hexavalent uranium (U^{VI}) in aqueous solutions of pH greater than 2. The fact that pitchblende becomes soluble in water after being roasted with sodium carbonate has been known and utilized commercially for over a century[1][2], but the nature of the complexes is unknown and the compositions reported in published literature of the solids in equilibrium with the saturated liquids are quite inconsistent.

1. Preliminary Qualitative Observations

1.1 Visible Indications of Reactions. Solutions of U^{VI} salts of strong acids give yellow, dense, hydrated precipitates when made alkaline. The precipitate becomes colloidal around pH 7 or when washed but the sol is rapidly precipitated by electrolytes. If a complexing agent such as $CO_3^{=}$ or HCO_3^{-} is not present, the precipitate does not redissolve on adding an excess of base. The pH at which precipitation is first observed varies with rate of addition of base, concentration of uranium, agitation, and temperature; if the alkali is added slowly to a hot, dilute, well stirred solution, precipitation begins usually at pH 4.1.

A rise in pH deepens the color of a U^{VI} solution. This change was very pronounced at pH 3 for 0.02 M UNH solution, considerably below the pH of visible precipitation. It is therefore concluded that there is another dissolved component besides UO_2^{++} whose concentration is increased with increasing OH^- concentration until the point of precipitation.

The following hydrolysis reactions are possibilities:

$$UO_2^{++} + OH^- \rightleftharpoons UO_2OH^+$$

$$2UO_2^{++} + 2OH^- \rightleftharpoons U_2O_5^{++} + H_2O$$

Both of these reactions are considered by Best, Taub, and Longsworth[3]. As a result of their work, they concluded that the second reaction fits the data more satisfactorily. More detailed analysis of the soluble hydrolysis stages are presented by L. S. Goldring in Report MonC-106[12].

The solid that first separates on neutralization of a uranium solution is a yellow, slightly impure UO_3 hydrate which on standing incorporates an appreciable amount of cation -Na^+, NH_4^+, K^+- from the solution and becomes more orange in color.

1.2 Titration Curves of U^{VI} Solutions. In general pH curves of the neutralization of a cation solution give valuable indications of the ions involved and the mechanism of the neutralization reaction. In agreement with other experimenters(3)(4) it is found that in the case of U^{VI} a plot of pH vs. equivalents of base added is extremely difficult to interpret. The following facts are observed (as indicated in Figs. 1-3):

(1) No inflections of the curve occur at stoichiometric equivalence points.

(2) A back titration curve does not follow exactly the original curve because of initial supersaturation and slow dissolving of the precipitated solid upon back titration so that the solution is at less than saturation concentration.

(3) Addition of a small drop of base causes local precipitation. This solid disappears on stirring. However, once the pH gets high enough so that precipitation of a large amount of solid takes place, the pH is lowered by the precipitation process to a lower value than the pH at which small amounts of solid had previously redissolved. This behavior indicates that the solid which redissolves is different from that which finally precipitates.

(4) The pH decreases markedly after the first precipitation from the supersaturated solution occurs. For example, in the case shown graphically in Fig. II, the pH lowered from 6.1 to 4.5.

A major source of experimental difficulties was the Beckmann pH meter which gave erratic results in the frequently very hot, not air-conditioned room in which these experiments had to be conducted.

Fig. 1 presents the data obtained from the titration of 25 ml of 0.1617 M UNH with 0.1725 M NaOH and the back titration with 0.1005 M $HClO_4$. As the solution was neutralized it became darker in color; no solid precipitated until the pH reached 5.14, after 1.19 equivalents of base had been added. A large quantity of solid suddenly precipitated, lowering the pH rapidly until a minimum value was reached at 4.53. The remainder of the curve is similar to that of the neutralization of a

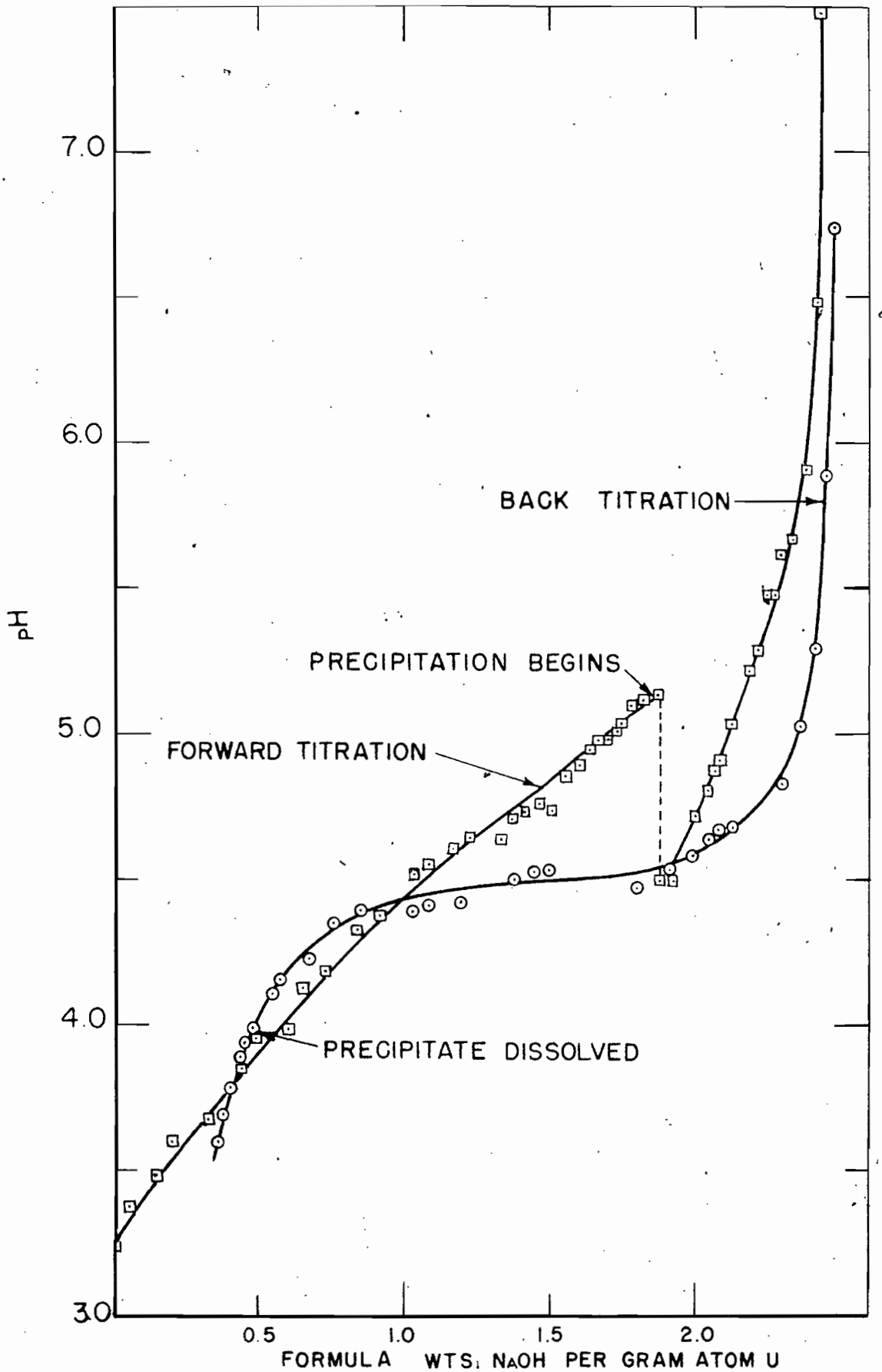

FIG. 1 TITRATION OF UNH SOLUTION (0.1725 M NaOH ADDED TO 0.1617 M UNH AND RESULTANT SOLUTION BACK TITRATED WITH 0.1005 M $HClO_4$)

weak acid. After approximately 2.45 equivalents of base were added, the pH had risen to 10.3. The graph of the titration indicates an asymptote at 2.48 equivalents of base. Since the original uranyl nitrate may be slightly deficient in nitric acid, the true asymptote is probably 2.50.

The value of 2.50 equivalents of base may possibly be explained by the following reaction:

$$UO_2^{++} \xrightarrow{2.5\ NaOH} \frac{1}{4}\ Na_2U_4O_{13} + \frac{1}{4}\ Na^+ + \frac{5}{4}\ H_2O$$

If we assume that further reaction with base is much slower than the above reaction, the apparent end point of a rapid titration of a uranyl solution would be at 2.50 equivalents of base and the empirical composition of the solid would be $Na_2U_4O_{13}$. This solid could consist of completely hydrated infinitele UO_3 chains -- O-U(OH)$_4$-O-U(OH)$_4$ -- with one Na^+ ion replacing one H^+ ion on alternate uranium atoms.

Figure 2 presents the data obtained from the titration of 25 ml of 0.040 M UNH with 1.988 M NaOH until the first precipitate appeared and a back titration with 7.217 M $HClO_4$ until the solid is redissolved. The acid and base used are so much more concentrated than the UNH that the volume of the solution is essentially constant throughout the titration. The back titration curve, as mentioned above, deviates appreciably from the forward curve.

Figure 3 presents the data obtained from the titration of 25 ml of 0.0202 M UNH with 1.988 NaOH and a back titration with 7.217 M $HClO_4$. The forward titration curve was continued to the point of turbidity; the back titration curve approximately followed the forward titration curve.

All three graphs represent metastable equilibria from which the stable equilibria data are not easily obtained.

1.3 Stability of Carbonate Solutions at 70° and 90°C. Preliminary experiments were carried out to determine roughly the effect of $CO_3^=$ and HCO_3^- on the solubility of U^{VI} in solutions of high pH. In one set of experiments loosely stoppered Erlenmeyers containing 2.0 g/liter of U^{VI} as UNH and Na_2CO_3 or $NaHCO_3$ solutions were kept in a water bath at 70 ± 1° for 43 days with daily shaking. Table I shows the experimental conditions and the observed results.

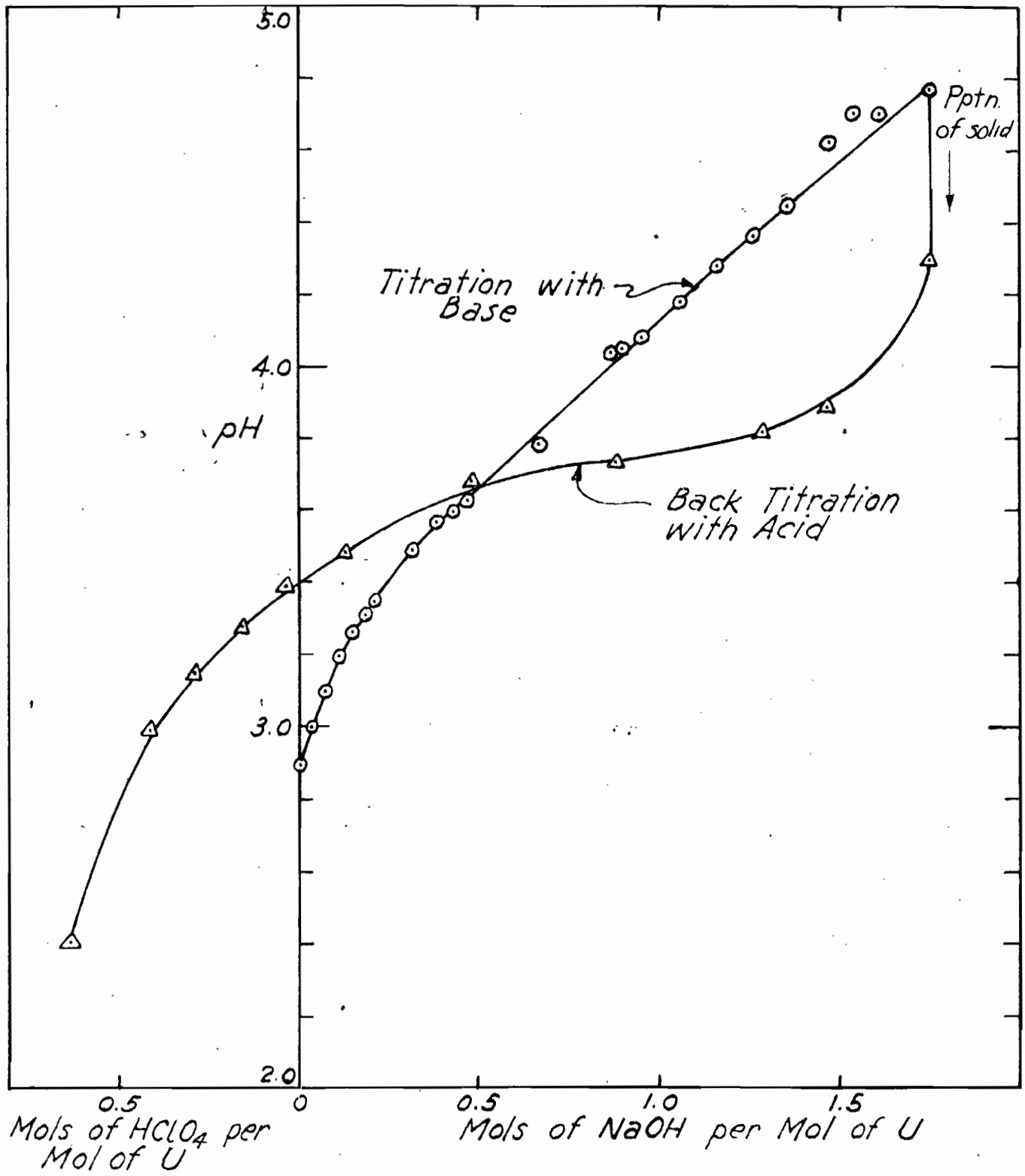

Fig. 2
Titration of UNH Solution (1.988 M NaOH added to 0.04040 M UNH and Resultant Solution Back Titrated with 7.217 M $HClO_4$)

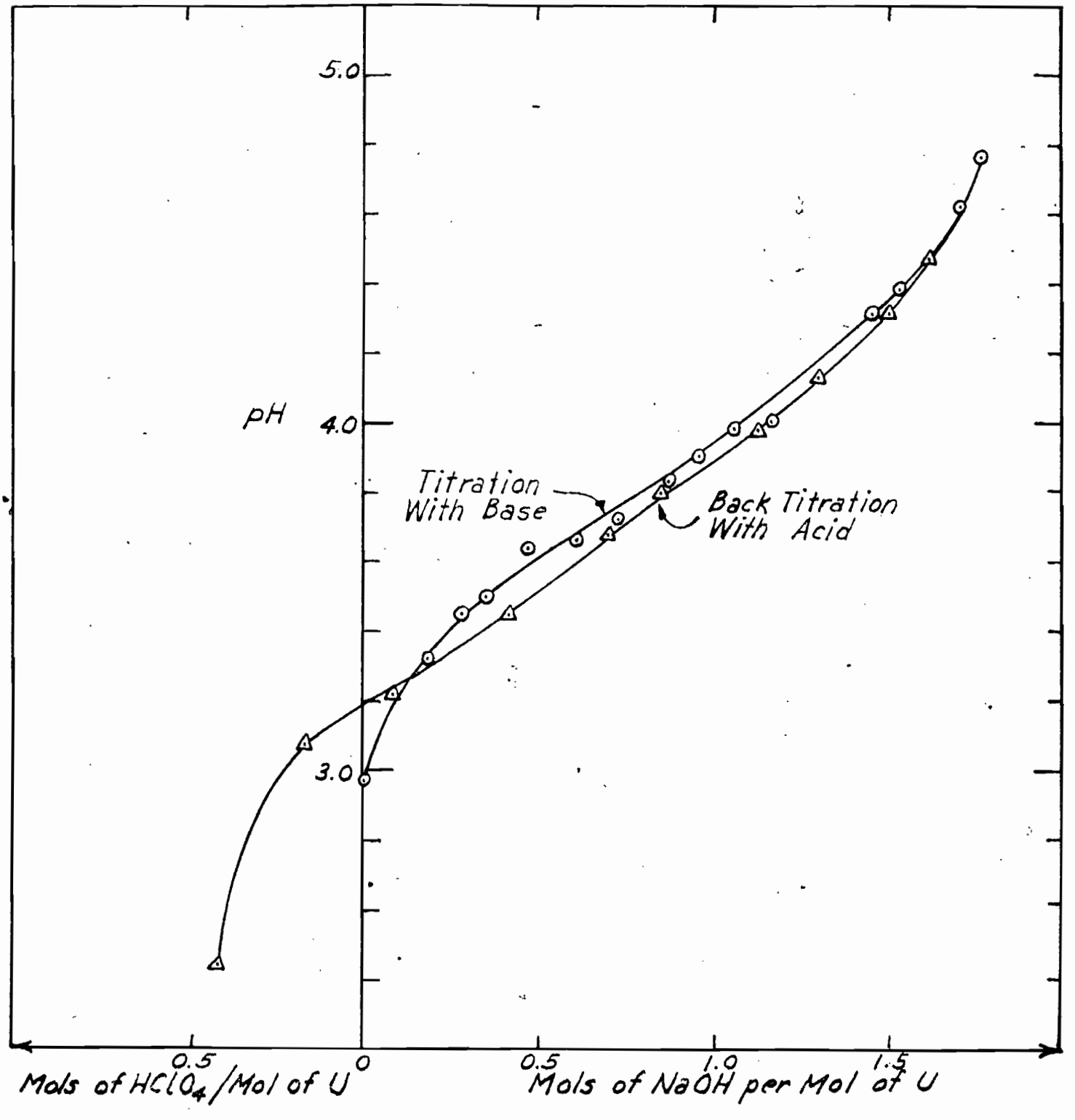

Fig. 3
Titration of UNH Solution. (1.988 M NaOH added to 0.0202 M UNH and Resultant Solution Back Titrated with 7.217 M $HClO_4$)

Table I.

Results of Preliminary Experiments on Solubility of U^{VI} in $NaHCO_3$ and Na_2CO_3 Solutions at 70°C

Initial $NaHCO_3$ (moles/l)	Final pH	Observations	Initial Na_2CO_3 (moles/l)	Final pH	Observations
0.040	6.5	no ppt.	0.080	11.2	Heavy yellow ppt. ~1/10 of total U^{VI}
0.100	6.9	no ppt.	0.100	11.2	no ppt.
0.140	7.0	no ppt.	0.139	11.3	no ppt.
0.200	7.3	no ppt.	0.199	11.3	no ppt.

In another set of experiments similar mixtures in bottles securely fastened with rubber stoppers were kept on a steam bath (solutions at ~90°) for 20 days with daily shaking. Table II shows the results of these experiments.

Table II.

Results of Preliminary Experiments on Solubility of U^{VI} in $NaHCO_3$ and Na_2CO_3 Solutions at 90°C

Initial $NaHCO_3$ (moles/l)	Final pH	Observations	Initial Na_2CO_3 (moles/l)	Final pH	Observations
0.040	6.1	no ppt.	0.080	11.1	Heavy yellow ppt ~1/3 of total U^{VI}
0.100	6.7	no ppt.	0.100	11.2	ppt. after several days
0.140	6.9	no ppt.	0.139	11.3	sl. ppt after several days
0.200	7.1	no ppt.	0.199	11.3	no ppt.

While the effect on the solubility of U^{VI} due to the presence of Na^+ and NO_3^- ions is unknown, these experiments indicate that in order to hold ~2 g/l of U^{VI} in solution at these temperatures, 0.2 M Na_2CO_3 or 0.05 M $NaHCO_3$ is necessary.

2. Preparation of Solids for Use as Initial Reactants

2.1 Preparation of UO_3. UO_3 seemed the most suitable compound of definite composition with which to begin phase studies. Following the method of C. A. Kraus*[6] UO_4 was precipitated from a warm 0.4 M solution of Mallinckrodt UNH by the addition of 3% H_2O_2. The precipitate was washed well and ignited at 300° for 3 hours to an orange solid. Kraus claimed that the solid prepared in this manner analyzed as 99.97% UO_3. This claim has been shown by R. Leininger[7] to be incorrect. Our product when dissolved in H_2SO_4 does not react with Ce^{IV}. This at first appeared to establish that no peroxide or U^{IV} was present. Gasometric analysis by R. Leininger showed that our oxide was actually $UO_{3.2}$, the exact composition varying slightly with each preparation. This did not affect this work since the oxide evolves the excess oxygen on contact with water and the resulting solid is a yellow, hydrated $UO_{3.00}$.

UO_3 prepared in this way is quite reactive** and was used in most of the present work. The disadvantage of using this compound is its reaction with aqueous solutions of NaOH, $NaHCO_3$, and Na_2CO_3, absorbing Na ion and liberating acid, thus lowering the pH of the solution.

2.2 Preparation of Sodium Diuranate, $Na_2U_2O_7$. A solid which would be closer to the equilibrium composition of the saturating solid would change the pH of the solution much less than does UO_3. A reactive sodium diuranate therefore might be a superior starting material for phase studies.

Sodium diuranate is mentioned extensively in the literature on uranium but there is a scarcity of analytical data to show that it is actually $Na_2U_2O_7$. Attempts to prepare $Na_2U_2O_7$ by precipitation from an aqueous solution have always produced solids of varying composition[8]. For this reason a different approach was investigated. Following a suggestion of Von Unruh[9] efforts were made to precipitate $Na_2U_2O_7$ with Na metal from a dried soln of uranyl nitrate in ether. In one experiment excess sodium was added to 2 dilute uranyl nitrate solns

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* cf. also Longsworth[3].

** Concentrated NaOH solution converts the yellow UO_3 immediately to an orange, sodium containing solid.

and the solid was washed with water to remove the sodium. The ignited solids analyzed 1.36% and 2.54% sodium. Sodium diuranate contains 7.24% Na. In another experiment a small amount of sodium was added to two concentrated solutions of UNH in ether and the solid was washed with ether to remove the excess UNH. These solids when ignited analyzed 8.90% and 9.22% sodium. It is clear that this method carried out as described does not produce the desired result.

Another non-aqueous preparation might be the ignition of a compound containing sodium and uranium in the same ratio as sodium diuranate-sodium uranyl acetate for example. By ignition of $NaUO_2Ac_3$ it was found possible to prepare a compound containing no acetate in which the mole ratio of Na to U was 1:1. The composition of this compound must therefore be expressed by the empirical formula $Na_2U_2O_7$.

Sodium uranyl acetate is best prepared[10] by precipitation of a UNH solution with a solution strong enough in $NaNO_3$ so that the filtrate will be 2.5 M in Na^+, 0.2 M in NaAc and 0.2 M in HAc. A large excess of sodium ion but not of acetate ion is required because in solution the salt exists largely as Na^+ and $UO_2Ac_3^-$ ions[11]. The precipitated salt must be washed with a solution similar to the mother liquor because a more dilute solution will wash sodium acetate selectively from the precipitate.

In the procedure developed in this laboratory, the conversion of $NaUO_2Ac_3$ to $Na_2U_2O_7$ takes place in two steps -- a short violent combustion and a long gradual ignition at 375°. The procedure is as follows. The dry double salt (~5 g) is wrapped in an eighty mesh platimum gauze and placed in a glass combustion tube under a slight stream of oxygen. On raising the temperature a slight darkening of the solid from the yellow color of $NaUO_2Ac_3$ to the orange of $Na_2U_2O_7$ is observed over the range 225°-250°C. The flow of oxygen is increased at this point to prevent reduction of the U^{VI}. At a temperature between 250° and 275° there is a burst of yellow flame followed by a red glow throughout the mass. In a few seconds the temperature of the solid rises to 1000° as measured by a thermocouple immersed in the solid. The temperature drops after about twenty seconds and at the end of a minute the temperature is down to 350°. Visible reaction is over and an orange solid remains.

The great initial rise in temperature is due to the heats of combustion of the mixture of gases evolved. These gases may be acetylene, ethylene, methane, carbon monoxide, and hydrogen. The hexavalent product in this case is in strong contrast to the reduced products of the heating of uranyl acetate.

The orange solid contains no reduced uranium, gives the cacodyl test for acetate and does not analyze as $Na_2U_2O_7$. After ignition for one week at 375° the solid is still unreduced but no longer gives a test for acetate and analyzes exactly for $Na_2U_2O_7$. Samples were taken at intervals in the week and their analyses show clearly that a slow reaction was taking place. These results are tabulated in Table III, and plotted in Fig. 4.

Table III.

Decomposition of $NaUO_2Ac_3$ at 375°

Time	% U	% Na	mol % U / mol % Na	fraction decomposed to $Na_2U_2O_7$
t = 0	50.2 (calc)	4.85 (calc)	(1)	0.000
t = 1m	55.7	5.50	0.99	0.30
16h	---	6.56	---	0.78
43h	---	6.94	---	0.91
71h	---	7.13	---	0.96
143h	final prod.			
	74.4	7.24	0.99	1.00
$Na_2U_2O_7$	75.0 (calc)	7.24 (calc)	(1)	1.00

The final product dissolves readily in acids, and is quite hygroscopic. Its rate of solution in the Na_2CO_3 solutions investigated (up to 0.05 M Na_2CO_3) is very low.

The overall equation for the decomposition reaction is:

$$2\ NaUO_2Ac_3 + 12O_2 \longrightarrow Na_2U_2O_7 + 12CO_2 + 9H_2O$$

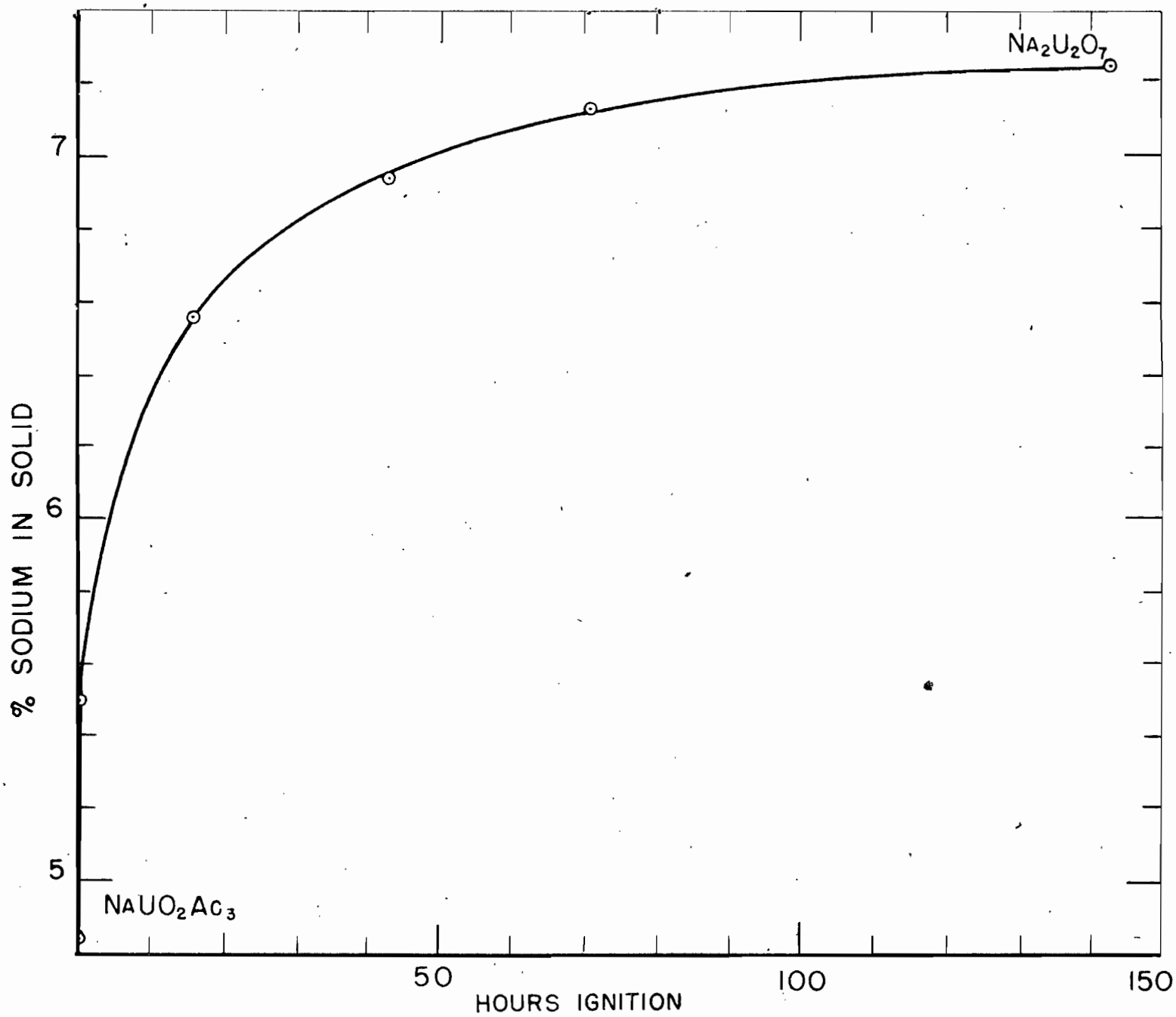

FIG.4 RATE OF DECOMPOSITION OF SODIUM URANYL ACETATE AT 375°

Calculations of the rate constants based on the Na analyses of intermediate products lead to values which make it impossible to decide between a first or second order mechanism for the rate determining step.

3. Solubility of U^{VI} in NaOH, Na_2CO_3, and $NaHCO_3$ Solutions

3.1 Analytical Methods.

3.1.1 Analysis of the Liquid Phases. Two to six weeks of constant shaking on a 1/6 H.P. International Bottle Shaker preceded the withdrawal of a sample of the solid and liquid for final analysis. In the case of the Na_2CO_3 solutions solubilities after six weeks differed by less than 5% from the solubilities after two days. These values in turn differed by ~ 25% from the solubilities after one day's shaking.

The bottles were shaken in the summer months in a room in which the temperature varied between 20 and 35°C. Prior to taking the final samples, all solutions were kept for several days in a room at 24 ± 1°C.

We conclude that if a constant temperature bath were used, the entire system might possibly come to equilibrium in a maximum of one week. Approaching equilibrium from the supersaturated side would test this conclusion. This could be accomplished by adding H_2O_2 which dissolves UO_3 easily but rapidly decomposes at pH > 7.

Variations in the solubility greater than the analytical error (~1%) may be due to temperature variations and the difficulty of separating the liquid and solid phases. Very fine suspensions tended to form in solutions of pH < 10, i.e., 0.06 M or less in $NaHCO_3$ and 0.03 M or less in Na_2CO_3. These suspended solids could neither be filtered nor centrifuged in an International Centrifuge running at 2000 R.P.M. Later it was found that a sharper separation of phases could be obtained by using a Sharples Supercentrifuge rotating at 50,000 R.P.M. One particular mixture, UO_3 and 0.05 M $NaHCO_3$ contained a suspended solid which made the liquid opalescent and almost opaque. This solid resisted all efforts at filtering or centrifuging, and had not settled after three months standing.

It was found that if samples taken from the very dilute U^{VI} solutions (gammas/ml) were not acidified immediately, adsorption of uranium on the surface of the glass container was sufficient to change the analysis by an appreciable fraction. Soft glass is a worse offender than Pyrex in this respect. These very dilute solutions were analyzed by the colorimetric thiocyanate complex method.

3.1.2 Analysis of the Solid Phases. The solid phases of the alkaline U^{VI} systems are in all cases yellow or orange-yellow, hydrous, and amorphous. Under the polarizing microscope they showed no anisotropy and appeared to consist of small particles of highly irregular shape.

Initially the assumption was made that the solids would not change in composition on moderate washing with water. The bulk of the solid was centrifuged from the bulk of the liquid, then washed carefully twice with 20 ml portions of water per gram of solid. The washing was followed by alcohol and ether rinses. The solid was put under vacuum to remove ether, weighed, dried at 110°C for 6-12 hours, weighed, dried at 350°C for 3 hours and reweighed. Heatings at 350°C were continued until constant weight was achieved. Loss in weight was assumed to be due to loss of water and the ignited solid was assumed to be free of water. These assumptions are not rigidly true unless care is taken to protect the solid from atmospheric moisture because at room temperature it is quite hygroscopic.

The solid was dissolved in dilute $HClO_4$ and aliquots were taken for sodium and uranium analysis. Sodium was determined by precipitating sodium uranyl acetate and uranium was determined by reducing with a Jones reductor and titrating with standard ceric sulfate. Because of the preliminary nature of the work analyses were performed rapidly with an error of 0.5-1.0%. No silica was present in the solids from the sodium hydroxide and sodium bicarbonate solutions; the silica residue was never greater than 0.1% of the weight of the ignited solids from the sodium carbonate solutions.

Contrary to expectation the solid phases in the systems being studied are rapidly decomposed by water. This lability is shown in the following experiment which was carried out after the bulk of the data on solid phases had been obtained.

Four 250 ml bottles containing 250 ml of 0.289 M Na_2CO_3 and 2.0 g of UO_3 were shaken for 36 days. One solid was analyzed by filtration and direct ignition without washing. The other three were washed with one, two, and three 20 ml portions of water, respectively, followed by alcohol and ether rinses, before ignition. Table IV shows the rapid change in composition of the solid.

TABLE IV.

Composition of a Washed Solid Phase from a 0.3 M Na_2CO_3 Mother Liquor

No. of times washed	0	1	2	3
Grams U^{VI}/liter of soln.	2.83	2.87	2.90	2.84
% H_2O (loss of weight from 25° to 350°)		9.05	9.08	9.14
% Na (dry weight)	8.76	7.09	6.58	5.90

These results indicate that analyses of washed solids do not give the composition of the solid in equilibrium with the solutions.

A promising method of determining the true composition of the solid phase is the Schreinemaker's wet residue method. Analysis of different wet solids and their saturated solutions enables the solid composition to be obtained graphically in three, as well as four, component systems. The water content of the equilibrium solid phase could be determined by tracer methods. If an active material which would not coprecipitate with the solid were added to the solution before centrifugation, the amount of occluded mother liquor could be calculated by analysis of the fraction of activity associated with the wet solid phase. An experiment with radioactive I^- in typical carbonate solutions indicated that this was not a suitable tracer because a high fraction of the activity was found in the solid phase together with only a small amount of occluded mother liquor.

3.2 Solubility of U^{VI} in NaOH Solutions. UO_3, prepared as described previously, was shaken at room temperature for 13 days with NaOH solutions of different concentrations in hard rubber bottles. The NaOH solutions had been prepared by diluting a freshly centrifuged concentrated C.P. NaOH solution with boiled distilled water.

Some of the solids were washed twice with water and others four times before ignition. The difference in analyses for the two cases is marked. Table V presents the analyses of the solid and liquid phases of the UO_3-Na_2O-H_2O system.

Table V.

Analyses of Liquid and Washed Solid Phases

Liquid Phase		Solid Phase						
Conc. NaOH (moles/l)	Mg. U^{VI}/l.	No. of washings	Wt. of Ignited Solid	% H_2O wet basis	% U dry basis	% Na dry basis	Na/U % ratio	%UO_3+ %Na_2O dry basis
0.0513	3.6	2	.5779	5.74	77.3	5.22	.70	100.2
0.103	9	2	1.2397	4.70	--	--	---	---
0.205	14	4	.3898	4.07	75.5	5.00	.69	98.8
0.308	16	2	.4134	4.09	75.5	5.52	.76	98.5
0.513	25	2	.6127	3.93	75.5	5.86	.80	99.0
1.03	34	4	.2817	4.31	76.4	5.12	.69	99.1
2.56	35	4	.3586	4.03	74.9	5.61	.78	97.9
5.13	34	2	.8641	3.28	74.6	8.20	1.09	101.0
11.2	53	0	.5760	assumed to be 0	64.9	16.5[a]	2.63	100.

a. Corrected for mother liquor occluded. Total loss in weight on ignition at 350° was assumed to be mother liquor. This gives a lower limit to the Na-U ratio since a slight over-correction was applied to the Na analysis.

The analyses of these solids were made prior to the discovery that the solid phase is radically altered by washing. However, the following qualitative conclusions may still be valid:

1) the concentration of Na^+ in the solid phase increases as the concentration of Na^+ increases in the liquid phase.

2) the smoothness with which the compositions vary indicates that no stoichiometric compounds are formed but rather homogeneous solid solutions of Na_2O in the UO_3 lattice exist over a wide range, and

3) H_2O tends to replace the Na_2O in the lattice. This is indicated by the fact that the H_2O content of the wet solid falls off with increasing Na^+ concentration of the solution.

3.3 Solubility of U^{VI} in Na_2CO_3 Solutions. Two grams of UO_3, prepared as described previously, and 200 ml of solutions of C.P. Na_2CO_3 of varying concentration were shaken in stoppered Erlenmeyers at room temperature (20-30°). Periodically samples were withdrawn for the determination of pH and U^{VI} concentration. The values of pH and U^{VI} concentration at different times of shaking are shown in Table VI. Fig. 5 is a graph of the variation of U^{VI} concentration with Na_2CO_3 concentration.

The variation in pH of the solutions can be explained by two reactions:

$$(1) \quad H_2O + \underline{2\ UO_3} + 2\ Na^+ + 2\ CO_3^= \rightleftharpoons Na_2U_2O_7 + 2\ HCO_3^-$$

$$(2) \quad H_2O + \underline{UO_3} + x\ CO_3^= \rightleftharpoons \underset{\text{(postulated)}}{UO_2(CO_3)_x^{\ 2-2x}} + 2\ OH^-$$

In the dilute solutions reaction (1) predominates and the pH decreases. In the more concentrated solutions (more than 1/3 of the uranium dissolved) reaction (2) predominates and the pH increases. Inaccuracies in the pH meter make possible only these qualitative conclusions.

Differences in solubility of solids shaken one week and those shaken six weeks were only 2-5% except in the dilute carbonate solutions which formed colloidal suspensions.

The solids were washed twice with water and then with alcohol and ether before ignition at 300° for 3 hours. Loss in weight was taken as the total water present. The ignited solid was dissolved in dilute $HClO_4$ and aliquots analyzed for Na and U^{VI}. Table VII presents the results of these analyses.

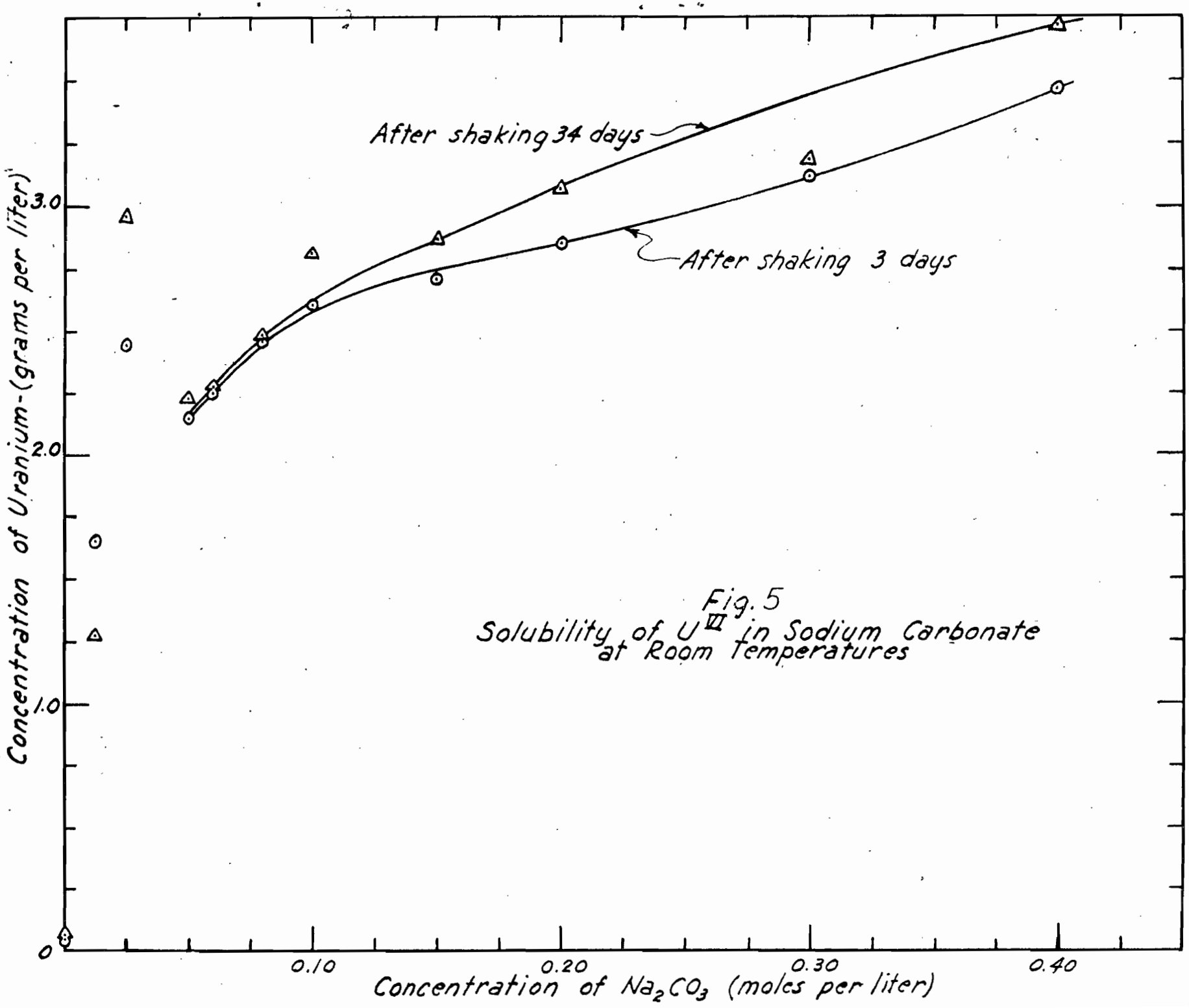

Fig. 5
Solubility of U^{VI} in Sodium Carbonate at Room Temperatures

Table VI.

Analyses of the Liquid Phase -- Initial System UO_3-Na_2CO_3-H_2O

Na_2CO_3 mols/l	0	0.0120	0.0260	0.0500	0.0600	0.0800	0.0880	0.100	0.150	0.200	0.300	0.400
pH t=0	---	10.99	11.09	11.20	11.22	11.22	11.22	11.24	11.22	11.20	11.23	11.24
1d	5.70	8.10	9.90	10.98	10.99	11.13	11.18	11.29	11.13	11.37	11.56	---
2d	6.53	8.12	9.72	10.74	10.87	11.06	11.08	11.05	---	---	---	---
6d	6.59	8.62	9.58	10.58	10.57	11.21	11.27	11.34	11.58	11.62	11.62	11.99
43d	7.85	7.77	8.84	11.20	10.82	10.95	10.96	10.98	11.26	11.46	11.46	11.73
123d [b] standing	6.40											
sol. g U^{VI}/l												
t=1d	0.077	0.283[a]	0.398[a]	1.59	1.81	1.83	2.05	2.25	---	---	---	---
2d	0.13	2.02[a]	2.17[a]	2.36	2.44	2.56	2.64	2.70	2.83	2.96	3.21	---
6d	0.055	1.65[a]	2.40[a]	2.15	2.25	2.46	2.57	2.61	2.71	2.85	3.12	3.46
43d	0.064	1.27[a]	2.92[a]	2.25	2.27	2.48	2.52	2.82	2.87	3.07	3.18	3.72
123d [b] standing	0.052											

a. Cloudy, colloidal suspensions leading to high results for U^{VI} content in solutions.

b. 43d shaking followed by 80d standing

Table VII

Analyses of the Washed Solid Phase -- Initial System UO_3-Na_2CO_3-H_2O

Na_2CO_3 mols/liter	Wt. of ignited solid sample UO_3	% H_2O wet basis	% U dry basis	% Na dry basis	mol % Na / mol % U	% UO_3 + % Na_2O
0.000	.5778	10.84	84.2	0	0	101.2
0.012	1.0552	---	78.8	2.39	3.18	96.8
0.050	1.3916	---	75.6	5.19	1.43	97.8
0.080	1.3855	4.84	72.9	5.50	1.28	95.0
0.100	1.4320	5.78	74.7	5.88	1.22	97.6
0.200	1.2367	---	68.7	5.90	1.13	90.4
0.400	1.2963	---	65.7	6.50	.98	87.5

The last two solids effervesced when acidified and the difference between their analyses and 100% is largely due to CO_2 content. It is again clear that these analyses are not representative of the original solids but the conclusions drawn from the analyses of the washed solids in contact with NaOH solutions are also applicable here.

In another series of experiments, $Na_2U_2O_7$, prepared as described previously, was used as the starting solid in order that the composition of the solid phase be changed as little as possible during the experiment. Two grams of $Na_2U_2O_7$ and 200 ml of solutions of C.P. Na_2CO_3 of varying concentration were shaken in glass stoppered Erlenmeyers at room temperature (20-30°) for 20 days. Table VIII presents the solubility of the $Na_2U_2O_7$ and the pH change of these solutions.

Table VIII

Solubility of $Na_2U_2O_7$ in Na_2CO_3 Solutions
Initial System $Na_2U_2O_7$-Na_2CO_3-H_2O

Na_2CO_3 mols/liter	U^{VI} conc. after 20 days shaking, mg/l	original pH	pH at t = 20 days
0.000	0.030	6.60	6.77
0.0116	0.033	10.89	9.73
0.0270	0.028	11.06	10.24
0.0401	0.033	11.06	10.45
0.0501	0.028	11.07	10.23

The appreciable change in pH of the solution, the very low solubility of the compound, and the fact that solubility is independent of Na_2CO_3 concentration cannot at present be reconciled with the data of Table VI for similar equilibrations of UO_3 in Na_2CO_3 solutions. It is possible that the $Na_2U_2O_7$ preparation had become inert by heating and that the concentrations represented by the data of Table VIII are very far from equilibrium.

3.4 Solubility of UO_3 in $NaHCO_3$ Solutions. Varying amounts of UO_3, prepared as described previously, were shaken in glass stoppered Erlenmeyers with C.P. $NaHCO_3$ solutions of varying concentrations at room temperature (20-30°). Periodically samples of the solution were withdrawn for determination of pH and U^{VI} concentration. Finally the flasks were placed in a room held at 24±1°C; after standing for 90 days with occasional shaking, final samples were taken. Table IX presents the values of pH and solubility as they varied with time. Fig. 6 shows graphically the variation of solubility of U with $NaHCO_3$ concentration.

The solubility of U^{VI} in $NaHCO_3$ is almost linear with HCO_3^- concentration. The uranium concentration (gram atoms/liter) is about 0.45 times the total $NaHCO_3$ concentration but at the same time the pH change of the solutions is relatively small, i.e., ~1 pH unit. The following equation is proposed to explain the observed facts:

$$\underline{UO_3} + HCO_3^- \rightleftharpoons UO_2OHCO_3^-$$

Other possible equations predict a non-linear relation of U^{VI} solubility to $NaHCO_3$ concentration or involve the production of OH^- or H^+ sufficient to have changed the pH to a greater extent than was observed.

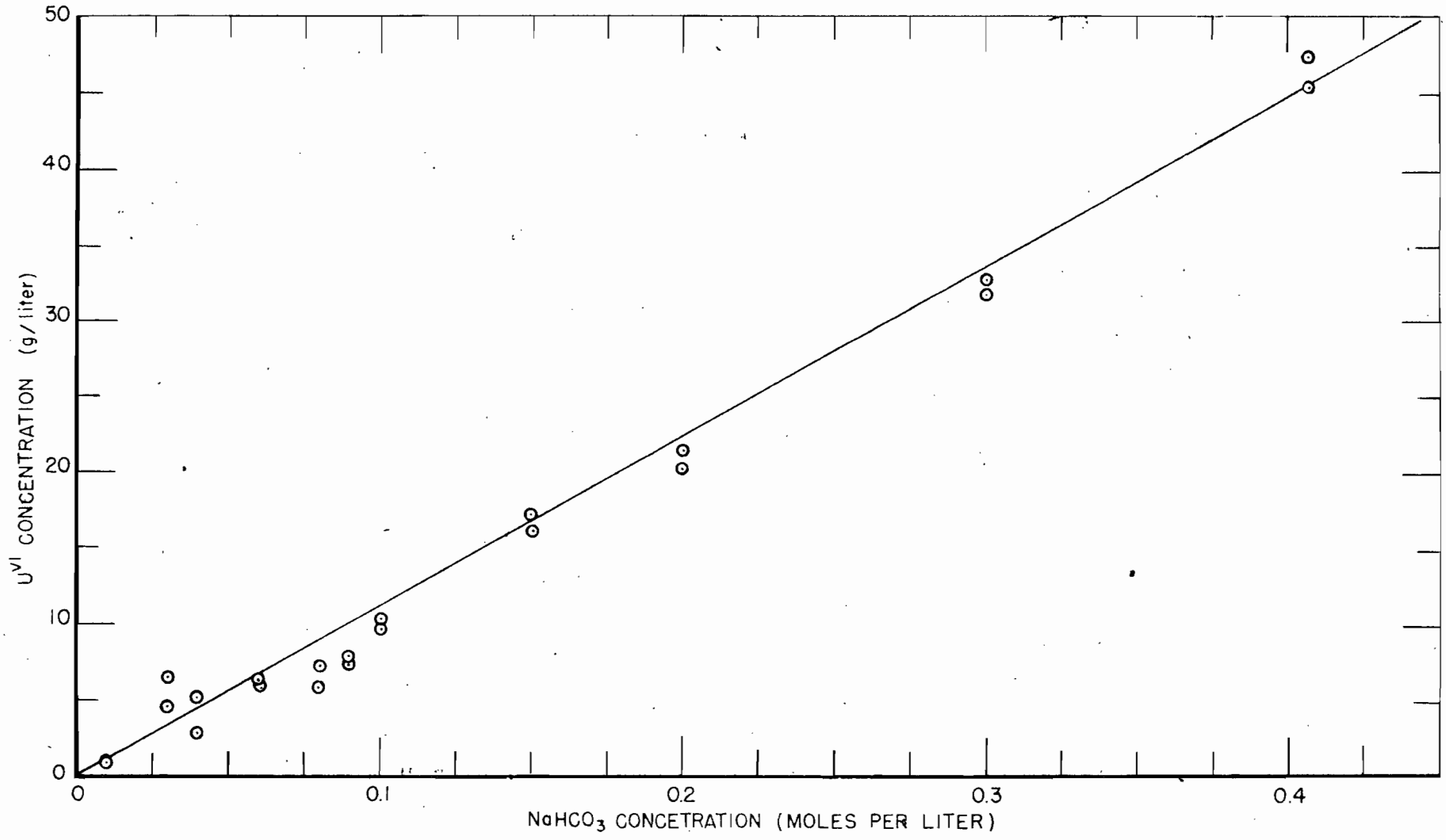

FIG. 6. SOLUBILITY OF U^{VI} IN SODIUM BICARBONATE AT ROOM TEMPERATURE

Table IX.

Solubility of U^{VI} in $NaHCO_3$ Solutions

$NaHCO_3$ conc. mols/liter	0.0100	0.0300	0.0400	0.0500	0.0600	0.0800	0.0900	0.100	0.150	0.200	0.300	0.407
grams solid UO_3	2	2	2	2	2	2	2	2	3	3	3	4
pH t ≅ 0	8.92	9.02	8.88	8.78	8.78	8.70	8.65	8.65	8.64	8.54	8.49	8.43
t ≅ 15d	-	-	-	-	8.07	8.24	8.13	7.73	7.53	7.46	7.75	7.54
t ≅ 31d	8.24	7.97	7.51	7.24	7.63	7.82	7.78	7.71	7.43	7.69	7.77	7.41
121d[a]												
U^{VI} concentration grams/liter												
at t ≅ 15	0.73	4.56	5.18	5.34	6.65	7.20	7.65	10.30	17.25	20.25	45.25	-
t ≅ 31	0.63	6.54	2.80	2.64	6.79	6.39	7.77	9.75	16.28	21.52	47.42	-
121d[a]												

a. 31d shaking followed by 90d standing.

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